

**Transient Spectroscopic Studies of Charge
Carrier Dynamics in Organic Solar Cells**

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Doctor of Philosophy

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To my parents

致我的父母

Declaration

I hereby declare that the contents of this thesis are of my own work, except where specific reference is made to the contribution of work by others. This thesis has not been submitted in whole or in part for consideration for any other degree or qualification at this, or any other university.

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Yifan Dong
October 2020

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Abstract

Organic solar cells (OSCs) are one of the promising third-generation lightweight and flexible photovoltaics. Since the 1990s, the development of OSCs can be described in three phases. In the first phase, the ‘bulk heterojunction’ concept was established. From the 2000s, the second phase focused on pairing different polymers with fullerene derivatives, following the observation of ultrafast electron transfer from polymer donors to fullerene acceptors. Most recently, in the third phase, the development of non-fullerene acceptors has led to a surge in the efficiency. While the material design has been driving such developments, photophysical understandings of the mechanisms are still lagging yet are crucial towards the evolution of OSCs. This thesis describes an experimental investigation into the functional mechanisms of charge generation, separation, and recombination processes in non-fullerene based OSCs by steady-state and transient spectroscopies.

Chapter 3 and 4 investigate the carrier dynamics in polymer:non-fullerene bulk heterojunction OSCs with small driving forces for charge separation, probing their particular photophysics. Specifically, Chapter 3 shows that charge-transfer state recombination becomes more severe in a low-offset system. This analysis has been extended to six other systems in Chapter 4, suggesting that the lifetime of charge-transfer states becomes shorter as their energetics are suppressed.

Chapter 5 and Chapter 6 focus on the carrier dynamics in homojunction OSCs employing small molecules. While bulk heterojunction OSCs are currently leading the efficiency, homojunction OSCs are still attractive due to their enhanced device stability and high photovoltages. Chapter 5 shows that the molecular electrostatics arising from different molecular orientations drives charge separation in a sexithiophene pristine film, leading to efficient charge photogeneration in devices. In contrast, Chapter 6 attributes the origin for charge generation in naphthalocyanine based devices to the built-in field, meaning no sign of charge generation is observed in pristine films. Finally, the impact of these two charge generation pathways on the carrier dynamics in planar heterojunction OSCs employing the aforementioned two materials is investigated.

Overall, this thesis examines the impacts of the driving force, molecular electrostatics and electric field on charge generation, separation, and recombination processes in both heterojunction and homojunction OSCs. The unique findings within this thesis have unlocked greater understandings of the fundamental mechanisms of charge generation in OSCs and it is hoped that this will aid in the design of future material systems.

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List of Publications

1. **Y. Dong**, H. Cha, H. L. Bristow, J. Lee, A. Kumar, P. S. Tuladhar, I. McCulloch, A. A. Bakulin, J. R. Durrant, Correlating Charge-transfer State Lifetimes with Material Energetics in Polymer:non-Fullerene Acceptor Organic Solar Cells (under preparation).
2. H. Cha, J. Wu, T. Du, **Y. Dong**, W. Xu, C.-T. Lin and J. R. Durrant, A Comparison of Charge Carrier Dynamics in Organic and Perovskite Photovoltaics (under preparation).
3. A. A. Mohapatra, **Y. Dong**, P. Boregowda, A. Mohanty, A. Sadhanala, A. Sadhanala, A. Narayan, C. McNeill, J. R. Durrant, S. Patil, X. Jiao and P. C. Parambil, Rational Design of Donor Acceptor Based Semiconducting Copolymers with High Dielectric Constants (under review).
4. V. C. Nikolis, **Y. Dong**, J. Kublitski, J. Benduhn, X. Zheng, C. Huang, A. C. Yüzer, M. Ince, D. Spoltore, J. R. Durrant, A. A. Bakulin and K. Vandewal, Field Effect versus Driving Force: Charge Generation in Small-Molecule Organic Solar Cells. *Adv. Energy Mater.*, 2020, 2002124.
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Nomenclature

Physical constants

ϵ_0	Permittivity of vacuum	$8.85 \times 10^{-12} \text{ Fm}^{-1}$
$\hbar$	Reduced Planck's constant	$1.05 \times 10^{-34} \text{ Js}$
c	Speed of light in a vacuum	$3.00 \times 10^8 \text{ ms}^{-1}$
h	Planck's constant	$6.63 \times 10^{-34} \text{ Js}$
k_B	Boltzmann constant	$1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
q	Elementary charge	$1.60 \times 10^{-19} \text{ C}$

Chemical Names

α -NPD	2,2'-Dimethyl-N,N'-di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine
α -6T	alpha-sexithiophene
Alq ₃	Tris(8-hydroxyquinoline) aluminum(III)
BF-DPB	N,N'-diphenyl-N,N'-bis(9,9-dimethyl- fluorene-2-yl)-benzidine
BPAPF	9,9-bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H—fluorene
BPhen	Bathophenanthroline
C545T	10-(2-Benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1) benzopyrroprano (6,7-8-I,j)quinolizin-11-one
CB	Chlorobenzene
CF	Chloroform
CuI	Copper (I) iodide
DBP	Tetraphenyldibenzoperiflanthene
DBzA	9,10-Bis[4-(6-Methylbenzothiazol-2-yl)phenyl]anthracene

DCB	Dichlorobenzene
DIO	1,8-diiodooctane
FBR	(5Z,5'Z)-5,5-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis[2,1,3-benzothiadiazole-7,4-diyl(Z)methylylidene]bis(3-ethyl-2-thioxo-1,3-thiazolidin-4-one
IDIC	2,7-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-4,4,9,9-tetrahexyl-sindaceno[1,2-b:5,6-b']dithiophene
IDT	Indacenodithiophene
IT-4F	3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone)) - 5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene
ITIC	3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)) -5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene
ITO	Indium tin oxide
MoO ₃	Molybdenum trioxide
PBDB-T-SF	Poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PBDB-T	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)- benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PC ₇₀ BM	[6,6]-Phenyl-C71-butyric acid methyl ester
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PffBT4T-2OD	poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)- alt-(3,3''-di(2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)]
PM6	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo [1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PTQ10	Poly[(thiophene)-alt-(6,7-difluoro-2-(2-hexyldecyloxy)quinoxaline)]
Rubrene	5,6,11,12-Tetraphenyltetracene
SubNc	Chloroboron subnaphthalocyanine

SubPc	Chloroboron subphthalocyanine
TBPc	2,5,8,11-Tetra-tert-butylperylene
TPBA	9,9',10,10'-Tetraphenyl-2,2' bianthracene
TPBI	2,2',2-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
Y6	2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno [2,3'':4',5']thieno [2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene)) bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile
ZnO	Zinc oxide

Acronyms / Abbreviations

τ	Decay lifetime
J_{SC}	Short-circuit current density
l_D	Exciton diffusion length
V_{OC}	Open-circuit voltage
A	Electron accepting materials
AO	Atomic orbital
CT	Charge transfer
D	Electron donating materials
EA	Electroabsorption
EEA	Exciton-exciton annihilation
EQE	External quantum efficiency
ES	Excited state
ET	Electron transfer
FF	Fill factor
FRET	Föster resonance energy transfer
GIWAXS	Grazing-incidence wide-angle X-ray scattering
GR	Geminate recombination

GSB	Ground state bleach
GS	Ground state
HOMO	Highest occupied molecular orbital
IR	Infrared
LUMO	Lowest unoccupied molecular orbital
MO	Molecular orbital
NFA	Non-fullerene acceptor
NGR	Non-geminate recombination
NIR	Near-infrared
OD	Optical density
OLED	Organic light-emitting diode
OSC	Organic solar cell
PIA	Photoinduced absorption
PL	Photoluminescence
PPP _c	Pump push photocurrent
PV	Photovoltaics
SE	Stimulated emission
TA	Transient absorption
TCSPC	Time-correlated single photon counting
TRES	Time-resolved emission spectra
UV-vis	Ultraviolet-visible

Chapter 1

Introduction

1.1 Motivation

Our generation is facing the biggest environmental crisis ever experienced by mankind. With increasingly acidic oceans bleaching coral reefs and endangering wildlife, shrinking of sea ice, more extreme weather conditions causing disruption and increasing energy demand; these unprecedented changes are all happening right now primarily because of global warming and they are largely irreversible. In our ecosystem, everything is connected to everything else and eventually, the whole ecosystem may collapse if mankind doesn't take sufficient action.

Many indications suggest that the global warming is closely related to human activity. The greenhouse gas level remained relatively low and constant before 1900. However, as a result of the Industrial Revolution, the combustion of fossil fuels became the main energy source and it has resulted in a dramatic increase in the emission of greenhouse gases, such as carbon dioxide. Since 1900, the carbon dioxide level has risen by 40%, with half of this increase happening since 1970.¹ Greenhouse gases can absorb the heat emitted from the Earth's surface; an increase in their concentration results in more heat absorbed and radiated back to the Earth's surface, hence driving global warming. As a result, the global average surface temperature has risen by 1 °C since 1900 as shown in Figure 1.1.² The continued emission of greenhouse gases will further increase the surface temperature and result in irreversible environmental damage.

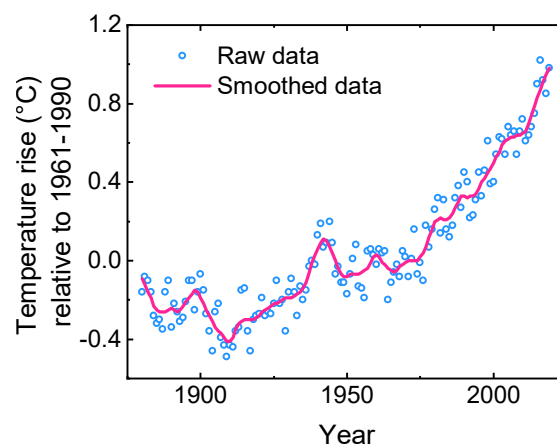


Figure 1.1 Global average surface temperature rise from 1850 to 2019 relative to the averaged temperature from 1961-1990. Data source: the US National Aeronautics and Space Administration Goddard Institute for Space Studies.

To tackle this climate crisis, representatives from 196 countries gathered together and formed The Intergovernmental Panel on Climate Change (IPCC). In 2015, IPCC reached the 'Paris

Agreement' where the goal was set to limit global warming to within 2 °C.³ Reaching this goal requires us to make rapid efforts to change the way we are currently living in many aspects. Among these, energy is the biggest sector, which contributes at least two-thirds of the total carbon dioxide emissions, therefore the transitions from fossil fuel derived energy sources to low-emission energy sources, such as renewable energy including solar, wind, and hydro, needs to be accelerated.⁴⁻⁶

The most abundant renewable energy source is the Sun. Utilising sunlight to generate electricity can be achieved with photovoltaics (PV), which in many areas provides the cheapest source of electricity among all the renewable energy sources. PV currently has the second-largest renewable power generation capacity and is projected to become the largest source of globally installed power generation capacity by 2040 (It should, however, be noted the average power generated by PV is 10-25% of its capacity).⁷ Harvesting energy from the Sun and converting it into electricity can help to accelerate the transitions into low carbon emissions. In 2019, solar generation grew by around 340 MWh and provided more than 40% of the total renewable energy growth.⁸ Together with other low-carbon sources, half of the total electricity supply will be generated by renewables by 2040 according to World Energy Outlook.⁴ Without a doubt, PV technology is playing and will continue to play a vital role in realising this transition, as its market share and capacity to continue to rise.⁹

1.2 Overview of Photovoltaics

1.2.1 Photovoltaic technology

The first commercially viable PV device was invented in the 1950s in the Bell laboratories, where crystalline silicon was employed to convert solar energy to electricity, laying the foundation for the first generation of PV devices. Currently, silicon still dominates the PV market due to its high efficiency, low cost and robust stability. Second-generation PV, based on thin-film technologies, were developed to overcome the then drawbacks of silicon PV including high manufacturing costs and high energy consumption during fabrication. Commonly used materials for the second-generation PV include copper indium gallium diselenide (CIGS) and cadmium

telluride (CdTe) which are well known for their strong, direct band gap absorption.¹⁰ Second-generation PV based on CIGS and CdTe have already been successfully commercialised and installed for various applications.¹¹ Although CdTe PV shows a low carbon footprint and a short energy payback time, the rarity of tellurium has pushed researchers to seek for other alternatives using Earth-abundant materials. In addition, potential health risks arising from the toxicity of cadmium in second-generation PV has raised some concerns.¹² Emerging PV technologies such as dye-sensitised solar cells were first reported in 1988 by incorporating organometallic dyes to absorb the sunlight.¹³ More recently, the increase in the power conversion efficiencies of both organic solar cells (OSCs) and perovskite solar cells has attracted a high level of research interest.¹⁴ Section 1.4 will discuss in detail the development of OSCs over the last decades.

1.2.2 Photovoltaic device characterisation

When a PV device is under operation, the absorption of photons excites the electrons to higher energy levels and the built-in potential difference in the device pulls the electrons and holes to an external circuit. The photovoltaic device performance is characterised by current-voltage curves measured both under dark and illumination where the standard test condition for solar cells is the Air mass 1.5G spectrum, with an incident power density of 100 mW cm^{-2} and at a temperature of 25°C . Figure 1.2 presents the typical current-voltage curves under dark and illumination as well as the relevant parameters. The operational regime of a photovoltaic device is between the short circuit (bias voltage is 0 V) and the open circuit (net current is 0 A). In the dark, it behaves like a diode, showing a larger current under forward bias than reverse bias. Under illumination, the amount of photocurrent generated at the short circuit is dependent on the intensity and the energy of the incident light. External quantum efficiency (EQE) describes the ratio of the number of charge carriers collected by the device and the number of incident photons for given energy or wavelength. It thus strongly depends on the extinction coefficient of the absorbing materials, as well as the charge separation, recombination and transport processes. For an operational PV device, the power output density (orange line, Figure 1.2) reaches a maximum at the maximum power point (MPP) where the bias is V_m with a current density of J_m . The fill factor (FF) measures the ‘squareness’ of the current-voltage curve, where a higher

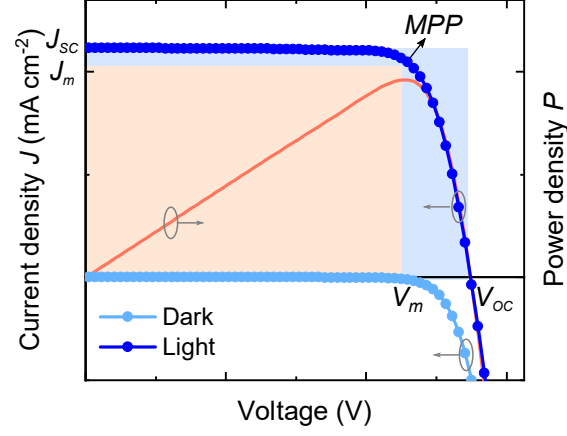


Figure 1.2 Typical current-voltage characteristics for a solar cell device. MPP is the maximum power point, V_m and J_m indicate the corresponding voltage and current density at the MPP, V_{OC} is the open-circuit voltage and J_{SC} is the short-circuit current density.

FF indicates a more ‘square’ curve. FF is defined as:

$$FF = \frac{J_m \times V_m}{J_{SC} \times V_{OC}} \quad (1.1)$$

The power conversion efficiency (PCE) is defined as the power density output at the operating point against the incident power density, P_i ¹⁵:

$$PCE = \frac{J_m \times V_m}{P_i} = \frac{J_{SC} \times V_{OC} \times FF}{P_i} \quad (1.2)$$

Overall, the main parameters extracted from the current-voltage characteristics are V_{OC} , J_{SC} , FF and PCE, which are used to compare different PV device performance.

1.3 Fundamentals of organic semiconductors

Conductive polymers were first discovered at the end of 1970s by Heeger, MacDiarmid and Shirakawa.¹⁶ This crucial finding opened up the field of organic semiconductors and forms the basis of organic electronics including organic light-emitting diodes, organic field-effect transistors and organic solar cells. Organic semiconductors mostly consist of carbon and hydrogen atoms along with heteroatoms such as nitrogen, oxygen, and sulfur. Organic semiconductors can be small molecules or polymers and can exist in the form of molecular crystals or amorphous films.

The semiconducting properties of these organic molecules share the same origin, despite wide variations in their photophysical properties¹⁷. This section reviews the basic building blocks that dictate the electronic structure of organic semiconductors, from atomic orbitals to molecular orbitals and electronic states.

1.3.1 Electronic structures

From atomic orbitals to molecular orbitals

To understand the electronic structure of organic semiconductors, it is useful to first consider the concepts of atomic orbitals (AOs). An AO is essentially a one-electron wavefunction (Ψ), which describes the region of space where the electron can be found with a high probability. In the carbon atom, AOs consist of s and p orbitals, representing different electron density distributions around its nucleus as illustrated in Figure 1.3. The ground state (GS) electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$, consisting of six electrons in total. In the outer shell, two electrons reside in the $2s$ orbital with anti-parallel spins according to the Pauli exclusion principle, while the other two unpaired electrons reside in the $2p_x$ and $2p_y$ orbitals, respectively. When the carbon atom comes to bind with other atoms, one of the electrons in the $2s$ orbital can be promoted to the empty $2p_z$ orbital, bringing the $2s$ and $2p$ orbitals into degeneracy. As a result, the $2s$ and three $2p$ orbitals can now hybridise in different ways to form new hybrid orbitals. Simply put, the $2s$ orbital can mix with either one, two or three p orbitals, giving two sp , three sp^2 or four sp^3 hybrid orbitals, respectively. Different hybridisation leads to different distributions of hybrid orbitals and thus governs the coordination geometry, which forms the basis of valence bond (VB) theory. The original VB theory is useful to understand the coordination chemistry, however, it does not help one to rationalise the electronic transitions occurring between energy levels. To understand these spectroscopic properties in organic semiconductors, it is prudent to talk about the molecular orbital (MO) theory instead.

When it comes to small molecules, the overlap between AOs on adjacent atoms forms MOs. As mentioned above, each AO is an electron wavefunction. The sign of the wavefunction can be $+$ or $-$, implying that two AOs can thus overlap either constructively or destructively depending

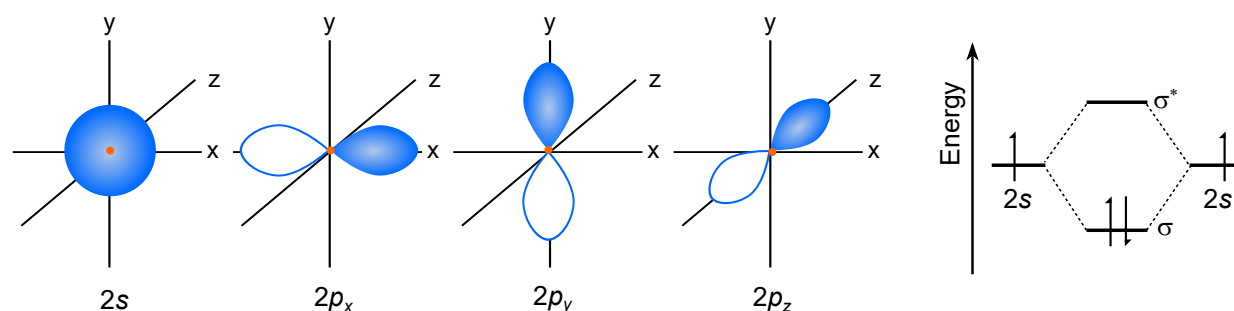


Figure 1.3 Left: Atomic $2s$ and $2p$ orbitals in the carbon atom. Right: formation of bonding σ and anti-bonding σ^* molecular orbitals from two $2s$ atomic orbitals.

on whether the signs are the same or opposite. As a result, constructive interference leads to bonding orbitals whereas destructive interference leads to anti-bonding orbitals. The overlapping geometry of the AOs determines the electron density distribution in the newly formed MOs. When two AOs overlap in a head-to-head fashion, the electron density is centred along the axis joining the two atoms and σ (or σ^*) orbital is formed. When two AOs overlap in a lateral way, the electron density is distributed above and below the axis joining the two atoms and this type of bonding orbital is referred to as a π (or π^*) orbital. Figure 1.3 shows an example of the bonding and anti-bonding MOs formed as a result of the overlap between two $2s$ orbitals, where the bonding MO is stabilised in energy.

From molecular orbitals to electronic states

MO theory not only serves to explain the bonding in small molecules but can also be extended to large molecules of infinite size including crystalline solids. As previously shown, the number of MOs is the same as the contributing AOs. When extending this approach to bigger molecules, the increase in the number of MOs thus reduces the average gap between adjacent MOs until it eventually becomes negligible and forms a continuum in energy. The electrons will occupy the lowest energy MO to stabilise the overall energy of the molecule. Following this pattern, the MOs are filled up to the highest occupied molecular orbital (HOMO) and the unfilled MOs start with the lowest unoccupied molecular orbital (LUMO). The ground state configuration of a molecule thus refers to when it has the lowest possible energy. When the energy gap between the HOMO and LUMO falls within 3 eV, the molecule is described as a semiconductor. In organic semiconductors, the HOMO to LUMO transition mostly corresponds to the π - π^* transitions,

which governs the basic electronic processes and enables the favourable energy levels for solar energy conversion applications.

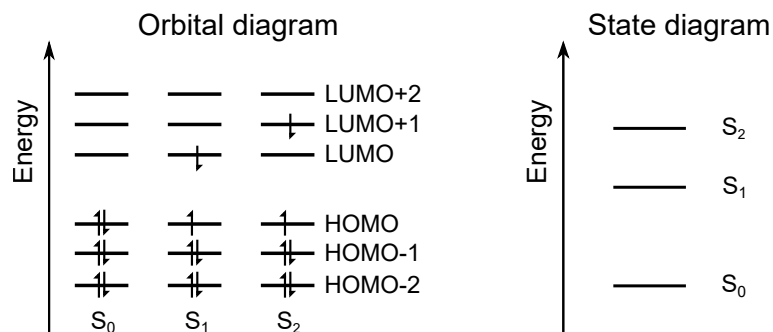


Figure 1.4 Schematic illustration for singlet exciton states including the ground state, S_0 , and the excited-states, S_1 and S_2 in an orbital diagram showing the dominant configuration as well as a state diagram showing molecular electronic states. HOMO and LUMO represent the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively.

Figure 1.4 shows the electronic states of a molecule represented in an orbital diagram and the corresponding state diagram. The ground state, i.e. S_0 , is depicted when all electrons stay pairwise and fill all the lowest energy MOs, leaving the molecule at its lowest energy. While the first excited-state, S_1 , can be described approximately by having one electron in the HOMO and one electron in the LUMO in the absence of electron-electron interactions.

1.3.2 Excitons and polarons

Excited-state generation by photoexcitation or injection of electrons/holes governs the basic operation of organic electronics. Understanding the nature of excited states is thus crucial to maximising the application/commercialisation potential. This section covers the fundamentals of electronically excited states in organic semiconductors. Specifically, sufficient energy can populate excited-states in organic semiconductors including excitons and polarons.

Frenkel excitons

Light absorption in organic semiconductors creates molecular excited-states, termed Frenkel excitons, where the electron and hole are tightly bound with Coulombic binding energy (also known as exciton binding energy), E_b , as a result of the low dielectric constants ($\epsilon_r \simeq 3$ -4) in organic semiconductors.¹⁸ This binding energy (typically on the order of several hundreds of

meV¹⁹) stabilises the Frenkel excitons and results in their localisation and can be represented by the Coulomb electrostatic potential between the electron and hole:

$$E_b = \frac{q^2}{4\pi\epsilon_0\epsilon_r r} \quad (1.3)$$

where q is the elementary charge, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant and r is the distance between the electron and hole.

Frenkel excitons are observed in all the materials studied in this thesis following light absorption, and their kinetics are mostly investigated with transient absorption spectroscopy (see further discussions in Section 2.4). To understand the exciton binding energy of organic semiconductors, one must first consider the difference between the electrical band gap and optical band gap. The electrical gap (also known as the transport gap) is defined as the energy difference between the ionisation potential (IP) and electron affinity (EA) (i.e. $E_{el} = IP - EA$) of the molecule and can be obtained experimentally from a combination of ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES), for example.^{20–23} That is, IP and EA represent the transport energy levels of polarons. As a result of the polaron formation in organic semiconductors, as discussed below, E_{el} can deviate from the energy spacing between HOMO and LUMO bands.^{24,25} In contrast, the optical gap (E_g) corresponds to the energy of the lowest accessible electronic transition via photon absorption, and is often determined from the intersection point between the reduced absorption and photoluminescence spectra, depicting the singlet exciton energy in most cases.²⁶ The exciton binding energy is understood as the enthalpy difference between a free electron-hole pair (mobile along the band) and an exciton as:

$$E_b = E_{el} - E_g \quad (1.4)$$

that is, the energy of the singlet exciton state is reduced by the Coulombic binding energy compared to the electrical gap determined by the IP-EA difference.²⁷ The exciton binding energy needs to be taken into account when drawing the orbital diagrams involving HOMO and LUMO energies for OSCs, whereas the use of a state diagram generally avoids this problem.²⁸

Due to the charge-neutral nature of Frenkel excitons, their diffusion in OSCs is mostly facilitated by non-radiative Förster resonance energy transfer.²⁹ Details on exciton diffusion will be further discussed in Section 1.5.1. Finally, depending on the spin alignment, Frenkel excitons can be in either a singlet (with anti-parallel spins) or a triplet (with parallel spins) state. Following the selection rule, only singlet excitons are generated under photoexcitation, while triplet excitons can be formed from intersystem crossing from singlet excitons or recombination of free charges (see further discussions in Section 1.3.3).

Charge-transfer excitons

The previous section features the fundamentals of Frenkel excitons, which are often observed in materials with small dielectric constants such as organic semiconductors. For materials with relatively large dielectric constants (e.g. $\epsilon_r > 10$), the distance between the electron and the hole within the photogenerated bound state is usually much larger than the lattice spacing. This type of bound state is termed a ‘Wannier-Mott exciton’, which are more often observed in inorganic semiconductors. An intermediate case between Frenkel and Wannier-Mott excitons, namely charge-transfer (CT) excitons, can also be observed in organic semiconductors. CT excitons are states with the electron and the hole occupying different molecules, causing its wavefunction to spread across a few lattice sites. In D:A OSCs, for example, charge transfer across the D:A interface can form localised CT states with a binding energy between the constituent electron and hole, and these localised states can be considered a type of intermolecular CT excitons.^{30–32} However, in addition to naming those CT states as CT excitons,^{33–36} many other names can be found in literature when it comes to describe the CT states, including geminate pairs,^{37,38} interfacial charge pairs,³⁹ polaron pairs,^{40,41} bound polaron pairs,⁴² and intermolecular radical pairs etc. For clarity, these intermolecular CT excitons formed across the D:A junction are thereafter referred to as CT states unless otherwise specified. Such CT states can be coupled to the ground state by a CT optical transition.⁴³ In the case of OSCs, this is supported by the evidence of absorption from the ground state to these states and CT emission from decay of these states to the ground state.^{43–46} Nevertheless, the weak coupling between D and A in

most OSCs results in a weak CT transition and high sensitivity experimental approaches are therefore often essential to probe these CT state optical transitions.³⁰

Polarons

The fundamental charged states in organic semiconductors are often referred to as polarons.⁴⁷ A polaron can be understood as a charge plus the distortion of the charge's surroundings while it is moving in a dielectric medium, which is often observed in soft materials like organic semiconductors as a result of the strong electron-phonon coupling. That is, adding or removing an electron in disordered organic materials can lead to a deformation of the electron density of the surrounding materials and may result in a change in molecular configurations including bond lengths and bond angles to minimise the overall energy. Therefore, in order for charges to move through the material, this deformation energy needs to be overcome, and in most cases, thermal energy is sufficient to assist the transport of polarons through the materials via a hopping model.^{48,49}

1.3.3 Fate of excited states

An organic molecule will find itself in an excited state with excess energy following the absorption of a photon with energy larger than its band gap.⁵⁰ It will relax to the GS when the excess energy is dissipated via non-radiative (emission of phonons) and radiative (emission of photons) processes. Radiative decay processes include fluorescence and phosphorescence depending on the change in spin multiplicity, while in non-radiative decay, the excess energy is mostly transferred to the lattice vibrations. The electronic transitions involved are illustrated by a simple energy diagram, the Jablonski Diagram (Figure 1.5).⁵¹ The thicker lines at the bottom represent the ground vibrational state within each electronic state, including S_0 for the GS, S_1 and T_1 for the lowest singlet and triplet excited states, namely excitons in organic semiconductors, respectively. For simplicity, Figure 1.5 only shows the excitation into the first singlet excited state S_1 , although higher electronic states (S_n) can also be populated following photon absorption.

An excited molecule can be both electronically and vibrationally excited. Following excitation, the first event to happen is the ultrafast vibrational relaxation (< 100 fs) within the first electronically singlet excited state manifold (S_1), depicted as R_1 . This occurs as a result of the vibration (conformational reorganisation) on the molecule and the transfer of its vibrational energy to lower energy intramolecular modes. From the ground vibrational state of S_1 , there are several non-radiative decay pathways. It can undergo internal conversion, depicted as IC , to a vibrationally excited state within S_0 , followed by vibrational relaxation, R_2 , to the GS. It can also undergo intersystem crossing, ISC_{T_1} , to the vibrationally excited state within the first electronic triplet excited state, leaving a molecule in the ground vibrational state of T_1 after the vibrational relaxation (R_4). From there, intersystem crossing (ISC_{S_0}) to S_0 is also possible. These processes are all non-radiative, represented by squiggly arrows in Figure 1.5. Coming back to radiative decay pathways, two straight arrows (labelled as F and P) illustrate two types of radiative decay, fluorescence and phosphorescence. Fluorescence originates from the ground vibrational state of S_1 to S_0 , without any change in the spin multiplicity, while phosphorescence occurs from the ground vibrational state of T_1 to S_0 , with a change in the spin multiplicity from 1 to 0. Since phosphorescence is a spin-forbidden process, it usually occurs with a relatively slow rate on the order of μ s–s.

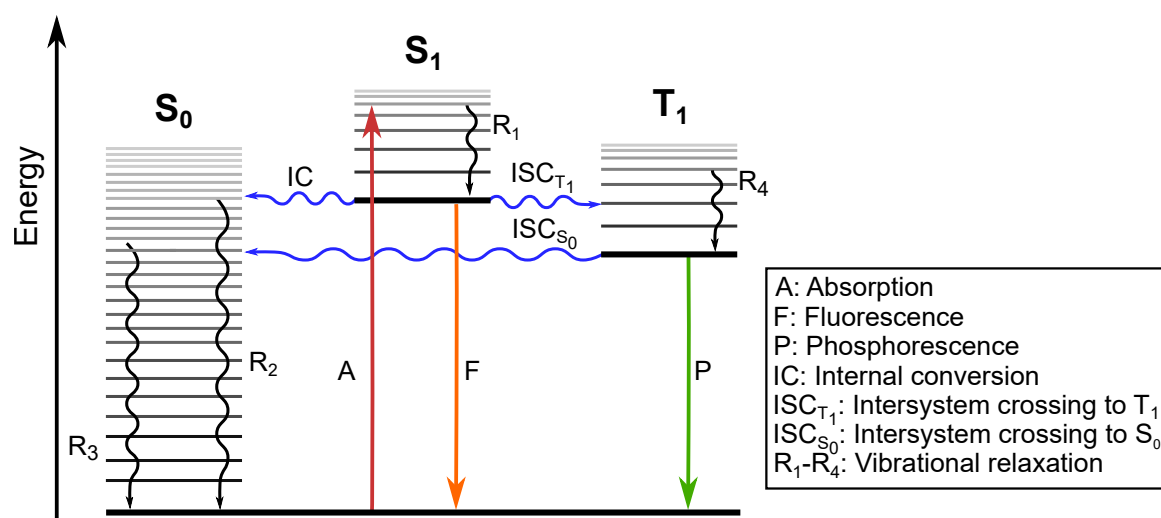


Figure 1.5 Jablonski diagram depicting the electronic and vibrational transitions following the absorption of a photon. S_0 represents the singlet ground state, S_1 and T_1 are the first singlet and triplet excited states. Straight and squiggly arrows indicate radiative and non-radiative processes respectively. Figure adapted from reference.⁵⁰

Fluorescence and phosphorescence are both monomolecular processes, however bimolecular processes such as exciton-exciton annihilation (EEA) may occur under higher light intensities. EEA describes the process when two singlet excitons (S_1) ‘collide’ with each other to generate a higher excited state (S_n) and a GS (S_0). Once formed, S_n most likely decay back to S_1 via internal conversion. The bimolecular nature of EEA suggests that its rate depends on how frequently excitons interact, hence on the excitation density. This process usually occurs when the excitation density is much higher than that under normal solar irradiation. That is, EEA has a negligible role under standard PV operating conditions but may become dominant under pulsed laser excitation such as in transient absorption measurements with a high excitation fluence. As such, unless otherwise stated, low excitation densities have been employed when probing the dynamics in organic films/devices in this thesis.

In summary, Figure 1.5 is a simplified representation of the fate of absorbed photon energy and elementary electronic processes involved in organic semiconductors. When moving to multi-component systems involving more than one semiconductor such as planar or bulk heterojunction OSCs, other non-radiative processes including electron transfer and energy transfer can also occur, leading to the formation of other electronic states such as charge-transfer and charge-separated states. Based on this, a modified Jablonski diagram is needed to illustrate relevant processes, which will be further discussed in Section 1.5.1.

1.3.4 Electron transfer

Electron transfer (ET) is one of the most important chemical reactions and governs the basis in numerous chemical and biological systems.⁵² In nature, ET occurs in photosynthetic reaction centres, allowing the subsequent oxidation of water to form oxygen.⁵³ In OSCs, ET from D^* to A (or hole transfer from A^* to D) enables the separation of tightly bound excitons to generate CT states and subsequently polarons.⁵⁴ This section discusses two widely accepted theories to describe ET processes, the Marcus theory and the Onsager theory.

Marcus theory

One of the most generally accepted frameworks to understand the ET mechanism is Marcus theory, first proposed by R.A. Marcus in the 1950s.^{55–57} This section begins with a brief overview of the fundamentals of Marcus theory, followed by its application to organic solar cells.

During ET, electronic transitions happen very fast so that the nuclear structure stays unchanged, as stated in the Franck-Condon principle. In Marcus theory, the total energy of the reactant R (DA^*) and product P (D^+A^-) states are represented by two parabolic potential energy surfaces (PESs), as depicted in Figure 1.6. The originally proposed model is only valid under the assumption that there is little overlap of the electronic wavefunctions (weak coupling) between the reactant and product states.⁵⁶ Here, the ET reaction occurs at the crossing point between the two PES curves where the barrier is overcome. This barrier (between the minima of the PES of R and the crossing point), also known as Gibbs free energy of activation, $\Delta G^\ddagger$, is quadratically dependent on the Gibbs free energy of reaction, ΔG° :

$$\Delta G^\ddagger = \frac{(\Delta G^\circ + \lambda)^2}{4\lambda} \quad (1.5)$$

where λ is the reorganisation energy, defined as the Gibbs free energy required to rearrange the molecule so that it reaches the equilibrium geometry of the product state without ET. The Gibbs free energy of reaction, ΔG° , is also known as the ‘driving force’ for the ET reaction. Regarding ET processes in the context of OSCs, the reactant would be the first singlet excited state (S_1), i.e. either D^*A or DA^* depending on the incident photon energy, while the product would be the CT state formed at the D:A interface. The free energy difference between the S_1 and CT states thus stands for the driving force for ET in OSCs, which is defined here as:

$$\Delta G^\circ = E_{S_1} - E_{CT} - T\Delta S \approx E_{S_1} - E_{CT} \quad (1.6)$$

where ΔS is the entropy change of electron transfer. It is worth noting here that Equation 1.6 takes into account the binding energy of CT states compared to cases in the literature where

the driving force is sometimes defined as the energy difference between the S_1 and E_{el} of the D:A blend (i.e. $IP_D - EA_A$).⁵⁸⁻⁶⁰

Based on the Fermi's golden rule, the ET rate, k_{ET} , in the semi-classical Marcus theory can therefore be expressed as:

$$k_{ET} = \frac{2\pi}{\hbar} H_{RP}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right) \quad (1.7)$$

where H_{RP} represents the electronic coupling between the reactant and the product (i.e. S_1 and CT states in OSCs), and $k_B T$ is the thermal energy..

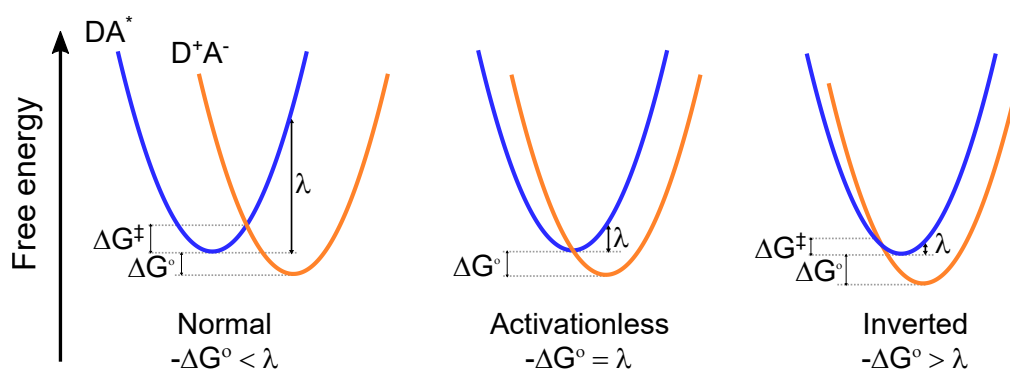


Figure 1.6 Schematic for Marcus theory: blue and orange parabola represent the potential energy surfaces for the reactant R (DA) and the product P (D^+A^-). $\Delta G^\ddagger$ is the Gibbs free energy of activation, ΔG° is the Gibbs free energy of reaction, while λ is the reorganisation energy. Three regimes are shown here depending on the value of ΔG° .

Following Equation 1.7, three kinetic regimes exist depending on the value of ΔG° , namely normal region ($-\Delta G^\circ < \lambda$), activationless region ($-\Delta G^\circ = \lambda$) and the inverted region ($-\Delta G^\circ > \lambda$) which are shown in Figure 1.6. In the normal region, the driving force is small and k_{ET} becomes faster as ΔG° becomes more negative (i.e. when the reaction is more exergonic), following the thermodynamic framework. In contrast, in the inverted region, where the driving force is large, k_{ET} becomes slower as ΔG° becomes more exergonic. Finally, the highest k_{ET} is achieved in the activationless region.

Onsager theory

In addition to the microscopic Marcus theory, Onsager theory has also been adapted to understand ET processes including charge separation from 'hot' CT_n states in OSCs.^{61,62}

Specifically, Onsager theory as applied to OSCs describes ‘hot’ CT_n states as the formation of an unrelaxed electron/hole pair, which quickly thermalise at a distance, a , from each other (here the term ‘hot’ refers to either excess vibrational or electronic energy).^{61,63,64} These hot CT_n states can either dissociate into free charges or they can thermalise to ‘cold’ CT states. Onsager theory states that the dissociation of hot states is assisted with the excess energy within these states, which is reflected by the magnitude of a . As such, the Coulombic capture radius, R_c , defined as the distance at which the Coulombic potential energy equals to the thermal energy, was proposed by Onsager to rationalise the dissociation of such hot states, as shown in Equation 1.8.

$$R_c = \frac{q^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (1.8)$$

where q is the elementary charge, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant, and $k_B T$ is the thermal energy. In particular, Onsager theory states that if a is larger than R_c , then hot states are considered as fully dissociated into free charges, otherwise these states would undergo a rapid relaxation to thermalised states, such as the cold CT states at D:A junctions. As a result of the low dielectric nature within organic semiconductors and short thermalisation distances, the electron-hole pair within these thermalised CT states are bound by Coulombic potential energy, which typically has been reported to be higher than the thermal energy at room temperature.^{35,65} Consequently, upon the formation of these thermalised CT states, they can either dissociate with an escape probability, $P(E)$, as expressed in Equation 1.9, or undergo geminate recombination to the GS with a probability of $1 - P(E)$ (see more discussions on geminate recombination in Section 1.5.2).⁶⁶

$$P(E) = \exp\left(\frac{-R_c}{a}\right) \left(1 + \frac{qR_c}{2K_B T} E\right) \quad (1.9)$$

In Equation 1.9, R_c is the Coulombic capture radius, a is the carrier thermalisation distance at a given temperature (T), q is the elementary charge, E is the electric field strength, and K_B is the Boltzmann constant. As can be seen from Equation 1.9, a long thermalisation length and

the presence of an electric field can reduce the Coulombic potential energy barrier and hence enhance the escape probability.

The original Onsager theory of autoionisation in weak electrolytes was later modified by Braun where the finite lifetime of CT states in the solid state is accounted for.⁶⁷ While the field-dependent CT dissociation is still valid, the then new Onsager-Braun model includes the aforementioned two decay pathways of CT states, dissociation into free charges and geminate recombination to the GS, depicted by $k_d(E)$ and k_g , respectively, hence the escape probability, $P(E)'$ is rewritten as follows:

$$P(E)' = \frac{k_d(E)}{k_d(E) + k_g} = k_d(E)\tau(E) \quad (1.10)$$

where $\tau(E)$ is the lifetime of CT states. Equation 1.10 implies that if dissociation does not occur within the lifetime of CT states, they will then decay to the GS via geminate recombination.⁶⁷ Other refinements to the Onsager model consider, for example, the distance distribution of CT states, the energetic disorder, mobilities depending on the nature of material systems.^{66,68,69} Several studies have successfully implemented the Onsager(-Braun) model to explain charge separation processes in OSCs, correlating the excess energy and the yield of charge photogeneration, which will be further discussed in Section 1.5.1.^{59,70–75}

1.3.5 Energy transfer

In organic semiconductors, the transport of charge-neutral excitons is facilitated by intermolecular energy transfer, which can be mediated non-radiatively in two dominant pathways including Förster resonance energy transfer (FRET) and Dexter energy transfer.⁷⁶ Both are often one-step processes where the electronically excited energy donor gets de-excited while the ground-state energy acceptor gets excited via the coupling.^{47,77}

FRET occurs through a long-range dipole-dipole intermolecular coupling and requires overlap between the acceptor absorption and the donor emission spectrum. FRET typically happens at a length scale in the range between 1 nm to 10 nm, with its rate inversely proportional to the

sixth power of the distance between the donor and acceptor, as shown in Equation 1.11:

$$k_{FRET} = k_D \left(\frac{R_0}{r} \right)^6 \quad (1.11)$$

where k_{FRET} is the rate of Förster resonance energy transfer, k_D is the decay rate of the donor, r is the distance between donor and acceptor, and R_0 is the Förster radius.

Dexter energy transfer, on the other hand, occurs at a short-range with a length scale on the order of 0.1 nm to 1 nm. Dexter energy transfer requires a wavefunction overlap between the relevant states in the donor and acceptor, in which the donor and the acceptor exchange their electrons directly.⁵⁰

In organic semiconductors, energy transfer occurs for example when a singlet exciton encounters a nearby singlet exciton, generating a higher singlet state, S_n , and a GS, S_0 , followed by the decay of S_n and dissipation of its energy to phonons, as shown below:

$$S_1 + S_1 = S_0 + S_n = S_0 + S_1 + \text{phonons} \quad (1.12)$$

Equation 1.12 depicts the exciton-exciton annihilation process, which is only significant at high excitation densities, as described above.⁷⁸ Depending on the materials of interest and timescales, other types of annihilation involving triplets or polarons may also occur.

1.4 Development of organic solar cells

Organic solar cells first emerged in the 1970s, and more recently have witnessed a surge in the device efficiency.^{54,79–81} OSCs employ organic semiconductors as the photon absorber to convert sunlight into electricity. The main advantage of OSCs is that they can be easily printed from an ink made by dissolving organic semiconductor materials in solvents. The printable nature of OSCs can therefore potentially result in lower cost and higher throughput manufacturing compared to silicon PV. Additionally, their modules can be light-weight and flexible if deposited on plastic substrates. Future portable and durable devices can be made possible with OSCs.⁸²

The commercialisation has been exemplified by companies including Heliatek (using evaporated small molecules) and InfinityPV. Nevertheless, the OSC modules produced by those pioneering companies lack the efficiency and stability to compete directly with silicon PV in most market applications. To widen the application of OSCs, more research is thus needed to resolve these issues. The semi-transparency in OSCs remains an attractive unique selling point for this technology. To date, the champion module efficiency has reached 11.7% in 2019 by ZAE Bayern, while the best research cell efficiency has reached 17.6% in January 2020.⁵⁴

As discussed in Section 1.3.2, unlike inorganic semiconductors which can directly generate free charge carriers upon photoexcitation, coulombically bound excitons are generated in organic semiconductors upon photoexcitation. OSCs thus typically rely on energy offsets at D:A heterojunctions to assist the separation of excitons into charges.⁸³ Figure 1.7 shows the architecture of a complete OSC device, consisting of the photoactive layer, hole transport layers (HTLs), electron transport layers (ETLs) and electrodes to govern its operation. Depending on the number and the layout of semiconductor materials within the photoactive layer, OSCs can be fabricated either in a homojunction, a planar heterojunction or a bulk heterojunction, as will be further discussed below.

1.4.1 Homojunction organic solar cells

Homojunction OSCs can be most simply made by inserting a single layer of the organic photoabsorbing materials between two electrodes.^{79,84} Under illumination, photogenerated excitons are expected to be split into charges by the electric field provided by the difference in the work functions of the two electrodes. However, this field is often too weak to break apart excitons as a result of their strong Coulombic binding energies. Therefore, device performance could only reach 0.01% in the 1970s.⁸⁵ Subsequently, chemical doping with electron acceptors was introduced to generate p-type organic semiconductors, which was observed to enhance charge generation efficiency.⁸⁵ Early studies suggested that charge-transfer complexes are formed at the dopant sites, which could facilitate exciton dissociation.^{85–87} In recent years, an extensive research effort has focused on incorporating ‘double-cable’ polymers and molecules containing donor and acceptor units to fabricate homojunction OSCs, where the strong intramolecular charge

transfer nature is employed to enhance charge generation efficiency.^{88–90} In 2017, the efficiency of homojunction OSCs reached 5.58% based on a D-A polymer, which matched the efficiency of an equivalent two-component heterojunction device.⁹¹ The record efficiency was further pushed to 6.3% in July 2019.⁹² Currently, homojunction OSCs are still attracting extensive research interest due to their potential to achieve low voltage losses, simplify device fabrication and stabilise the photoactive layer morphology.⁹³ However, despite the progress of homojunction OSCs to date, their device efficiency remain substantially too low to be commercialised.^{94,95}

1.4.2 Planar heterojunction organic solar cells

Planar heterojunction OSCs (also known as bilayer OSCs) utilise two organic semiconductors deposited sequentially, layer by layer, as shown in Figure 1.7a. The two organic semiconductors possess different moieties and function as the electron donor (D) and the electron acceptor (A), respectively. The first planar heterojunction OSC was reported by Tang in 1986, in which copper phthalocyanine (CuPc) was employed as the donor and a perylene tetracarboxylic derivative as the acceptor.⁹⁶ It reached an efficiency of 1% and a relatively high fill factor (FF) of 65%. This work pioneered the development of the OSC research field and established the concept of ‘heterojunctions’ in OSCs. Furthermore, this work pointed out that an interface between two organic materials with different electron affinities and ionization potentials can be crucial in determining the photovoltaic performance, and laid a solid foundation for future research.⁸⁵ This layer-by-layer concept has also been extended to multi-layer OSCs fabricated via vacuum evaporation, for example, an 8.4% efficient three-layer OSC was made possible using small molecules with complementary absorption in 2014.⁹⁷ However, the optimum thickness of planar heterojunction OSCs can often be limited by the exciton diffusion length, which is typically on the order of 3 nm to 20 nm and therefore may result in insufficient photon absorption (see further discussions in Section 1.5.1). Nevertheless, the single well-defined interface within the planar heterojunction has the potential to suppress charge recombination.⁹⁸

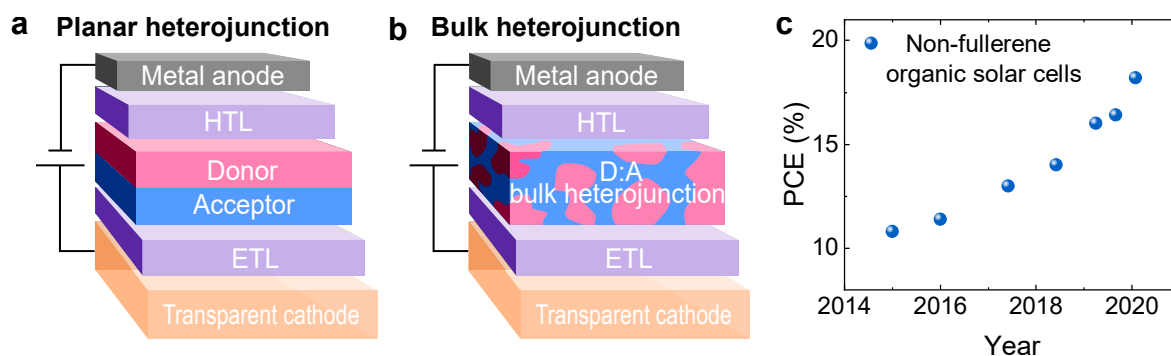


Figure 1.7 Inverted device architecture for **a**, a planar heterojunction organic solar cell and **b**, a bulk heterojunction organic solar cell, where ETL and HTL represent electron and hole transport layers respectively. **c**, Power conversion efficiency (PCE) progress for bulk heterojunction organic solar cells in recent years, where data points were extracted from individual papers and plotted against the year they were published in.^{54,99–104}

1.4.3 Bulk heterojunction organic solar cells

In the 1990s, the discovery of ultrafast electron transfer from polymers to a fullerene acceptor, C_{60} , in a planar heterojunction OSC made researchers realise that it is possible to further enhance the efficiency by increasing the interfacial areas between the two materials.¹⁰⁵ In 1995, Yu et al. first reported a then state-of-the-art efficient OSC made from a bi-continuous network of polyphenylene vinylene (PPV) polymer donor with a soluble fullerene derivative as the acceptor, one of the first examples to demonstrate the ‘bulk heterojunction’ concept.^{106,107} In such a bulk heterojunction OSC, D and A materials were blended in a solution which then undergoes phase separation during the film fabrication process to form an interpenetrating network as shown in Figure 1.7b. In contrast to the single interface within a planar heterojunction, the bulk heterojunction drastically increases the interfacial areas between D and A, leading to a higher exciton dissociation yield and a rise in the overall efficiency. For nearly two decades, research mostly focused on the design of various polymers to match with soluble fullerene acceptors such as [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), however, recent studies have transitioned towards the design of various non-fullerene acceptors (NFAs), such as EH-IDTBR, ITIC, Y6, to name a few.¹⁰⁸ To date, the efficiency of non-fullerene based OSCs have surpassed that of fullerene-based OSCs and bulk heterojunction remains the most common morphology for current state-of-the-art OSCs.⁵⁴ This thesis focuses on the photophysical studies of those non-fullerene based OSCs in all three architectures introduced above.

1.5 Photophysics of organic solar cells

1.5.1 Basic operation: from exciton generation to charge separation

In general, photocurrent generation in heterojunction OSCs can be broken down into five steps: (1) light absorption and exciton generation, (2) exciton diffusion, (3) exciton dissociation and charge transfer, (4) charge separation, (5) charge transport and extraction, as depicted in Figure 1.8a. Absorption of a photon above the band gap generates Coulombically bound excitons, which have to diffuse to the D:A interface before their dissociation can happen unless generated at the interface. This dissociation refers to the process of transferring an electron from the D to A or a hole from the A to D, leading to the formation of CT states as discussed above. Charges are then separated/generated when the electron and hole separation distance exceeds the Coulombic capture radius. Finally, the photocurrent generation is achieved by charge transport towards the right electrodes where charges are then extracted. This section discusses in detail the basics of each step towards photocurrent generation, while the following section 1.5.2 presents the main recombination pathways during the operation of OSCs.

1. Light absorption and exciton generation

The photoactive layer in D:A OSCs usually comprises organic molecules with complementary absorption to cover a broad range of the solar spectrum. Those organic molecules typically have high extinction coefficients of around 10^5 cm^{-1} , enabling strong light absorption even with a thin layer of 100 nm.¹⁰⁹ Following light absorption, excitons are generated in D and/or A molecules depending on the excitation wavelength (Step 1 in Figure 1.8a). This exciton generation process is illustrated in Figure 1.8b, where the excitation of the GS, S_0 , populates the first singlet excited state, S_1 . In practice, higher excited states, S_n , can also be populated but would undergo rapid internal conversion to S_1 , which in Figure 1.8b are neglected for simplicity. As a result of the strong Coulombic binding energy within excitons, the electron and hole cannot escape each other unless in the presence of an external gradient such as an electric field or an energetic offset.¹¹⁰ In the rare occasions where the electron hole pair do separate without any external gradient, these materials can be employed in homojunction OSCs as further discussed

in Chapter 5 and 6, yet often the yield is relatively low.^{111,112} The excitation density of excitons, defined as the carrier density per volume, can thus be estimated from the excitation fluence and the sample thickness following the calculations described in Section A.1. The excitation density can greatly affect the behaviour of carriers and therefore the separation and recombination processes, for example, the occurrence of exciton-exciton annihilation at high excitation densities as discussed in Section 1.3.3.

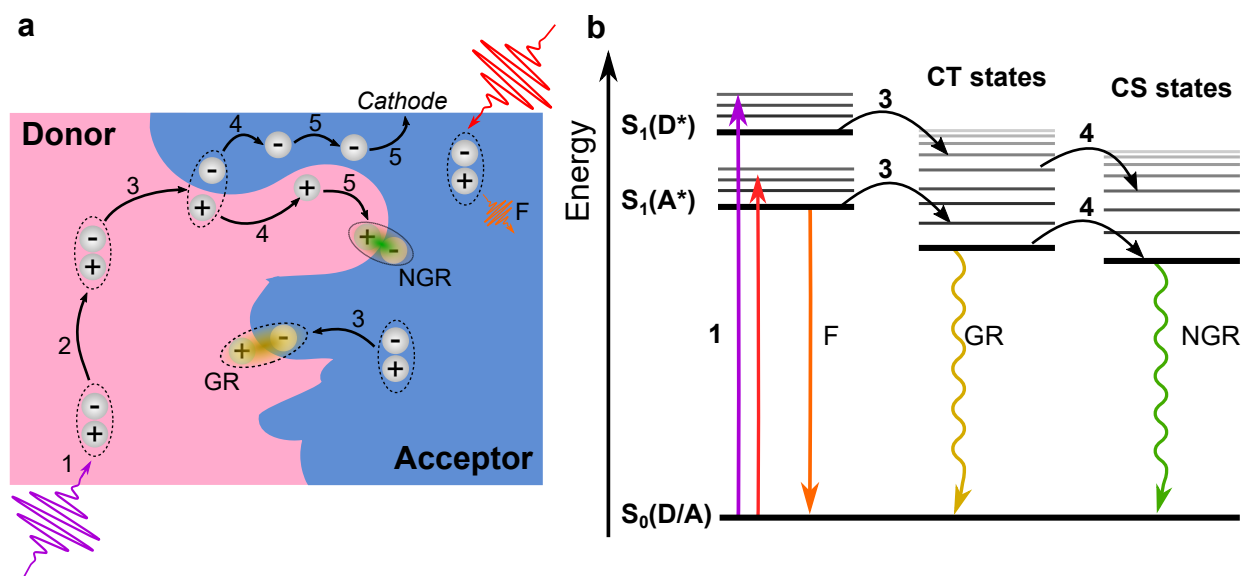


Figure 1.8 Schematic and energy level diagram illustrating various processes leading to the photocurrent generation in organic solar cells (OSCs). **a**, Schematic showing the mixed phase of a donor and an acceptor in a bulk heterojunction OSC under illumination. **b**, Energy level diagram summarising relevant electronic states and transitions between them which lead to photocurrent generation as well as recombination processes.

2. Exciton diffusion

Excitons are localised on single molecules and mainly transport via a random walk model in order to diffuse towards the D:A interface where charge transfer occurs (see Step 2 in Figure 1.8a).^{47,113,114} However, this diffusion must be faster than the main competing process, which is the exciton recombination to the ground state as previously presented in Figure 1.5. The average distance that excitons can travel within their lifetime (τ) is known as the exciton diffusion length, L_D , and Equation 1.13 describes the relationship between τ and L_D . Following this relationship, typical values of L_D in organic semiconductors in OSCs are found to be between 3 nm to 20 nm,^{29,113,115} with the exception of some recently developed crystalline NFAs reported to show L_D values exceeding 50 nm in an extremely dilute film.^{116,117} However, the dilute film

is not representative of the optimised blend morphology employed in efficient OSC devices, thus may not reflect the real exciton diffusion length under device operational conditions. In optimised non-fullerene based D:A films, strong intermolecular interactions of those NFAs can lead to a highly aggregated film morphology, which therefore tends to lower the excitation density threshold for the occurrence of exciton-exciton annihilation, as will be further discussed in Chapter 4. The short exciton diffusion length limits the thickness of planar heterojunction OSCs and hence a lot of research effort has been spent to enhance exciton diffusion lengths in order to enable the fabrication of thicker devices or bulk heterojunctions with larger domain size and enhance the device performance.^{118,119}

$$L_D = \sqrt{D\tau} \quad (1.13)$$

where L_D is the exciton diffusion length, D is the diffusivity, and τ is the exciton lifetime.

3. Exciton dissociation and charge transfer

Following Onsager theory, exciton dissociation and charge transfer at the D:A interface form ‘hot’ CT_n states with excess vibrational or electronic energy, which can dissociate directly into free charges or undergo rapid internal conversion to the lowest-lying CT states, also referred as thermalised/localised CT states.^{59,120–123} Whether charge separation is mediated by hot CT_n states or thermalised CT states is still under debate. While several studies have indeed shown the successful dissociation of hot CT_n states into free charges, two opposing viewpoints have been proposed to rationalise this result. Some studies have attributed the origin for CT_n dissociation to the excess energy within hot states, under the framework of Onsager theory presented in Section 1.3.4.^{59,124} These results are further supported by the observation of the dependence of charge separation yield on the driving force as well as the excitation energy.^{42,59,125,126} However, others have challenged this viewpoint based on the observation of an increase in photocurrent from an additional IR push pulse but at the same time no change in the charge generation yield for above-gap and sub-gap excitation.¹²¹ Together with theoretical calculations, this instead suggests that hot CT_n dissociation is facilitated by the presence of delocalised states.¹²¹ The main conclusion from this study is similar to those reported for ‘ballistic’ charge generation

model, in which case rapid charge motion in delocalised states within fullerene domains was attributed to be the origin of efficient charge generation.¹²² Other studies have suggested that charge generation is governed by the dissociation of thermalised CT states, supported by the excitation energy independent charge separation yield as well as internal quantum efficiency.^{127–132} Furthermore, Bässler et al. have suggested that efficient charge separation from thermalised CT states can occur with the aid of charge delocalisation and electrostatic screening at the D:A interface.¹³³

The rate and yield of exciton dissociation can be influenced by various factors such as blend morphology, the driving force for charge separation (as shown in Equation 1.6), and coupling between D and A. For example, several studies have suggested that a more intermixed blend morphology can result in a faster exciton dissociation and electron transfer (equivalently valid for hole transfer) rate.^{134–136} Charge transfer yield correlates with the driving force for charge separation, as shown by many studies.^{42,83,125} In addition, different models have been reported to correlate the CT kinetics with the driving force. In OSCs with relatively large driving forces, the standard ‘two-state’ model applies by taking into account only the transition between the CT state and the GS, while a ‘three-state’ model has been proposed instead for OSCs with small driving forces, in which case the hybridisation/mixing between the CT state and the S_1 state is no longer negligible.^{137,138} These charge transfer models will be further discussed in Chapter 4. Experimentally, the exciton dissociation rate can be probed by transient spectroscopies including time-resolved photoluminescence (PL) and transient absorption spectroscopy, while the exciton dissociation yield can be characterised by steady-state measurements such as PL spectroscopy (see Chapter 2 for more details on the techniques).

4. Charge separation from charge-transfer states

Various reports have discussed the crucial role of CT states in the operation of OSCs, for example, the CT state separation efficiency determines the photocurrent generation efficiency and the CT state energetics directly influence the photovoltage.^{31,139,140} As discussed in Section 1.3.4, the charge separation process from CT states can be understood under the framework of Onsager-Braun theory, which means that the Coulombic binding energy within CT states must

be overcome prior to dissociation into free charges, unless the initial thermalisation length is long, as also suggested by a few groups.^{63,141} Several studies have shown that, indeed, charge separation efficiency is related to the excitation energy for example by Grancini et al. and others.^{126,141–143} In addition, several reports also have shown that the charge separation efficiency is determined by the energetic offset, for example, Scharber et al. have reported that a minimum offset of 0.3 eV is needed to ensure efficient charge separation.⁶⁰ However, as the field transitions towards lower driving force systems, more studies are suggesting that charge separation can happen even in the absence of a significant energetic offset.^{144,145} Though, more recently, it has been pointed out that a minimum ionisation potential offset of 0.5 eV is still necessary for efficient charge generation in NFA based OSCs.⁸³ Nevertheless, the entropy increase during charge separation can stabilise the charge separated (CS) states relative to CT states, thus driving charge separation, as also suggested by several theoretical studies.^{64,146,147} Thus, more research effort is needed to address this new and contradictory observation in order to understand the charge separation mechanism in state-of-the-art efficient OSCs.

5. Charge transport and collection

The final step leading to photocurrent generation involves the transport of polarons through the photoactive layer and the subsequent extraction to the correct electrodes, which usually occurs over the nanosecond to microsecond timescale.

1.5.2 Recombination processes

Recombination is simply the reverse of the generation process and can be pictured as the transition of an electron from a higher energy state to a lower energy state.¹⁴⁸ Charge recombination refers to the recombination between an electron and a hole, which may occur via radiative or non-radiative pathways, releasing either photons or phonons respectively. Radiative recombination is unavoidable, while non-radiative recombination can often be tuned or even suppressed via careful control of material properties and device engineering.^{149–152} Understanding the fundamental recombination mechanisms would allow researchers to recognise the efficiency-limiting factors for OSCs and guide future material and device design towards a higher efficiency regime. This

section looks at different types of recombination processes involved in OSCs. Details on the elementary decay pathways within a single organic semiconductor molecule have already been discussed in Section 1.3.3, which is therefore neglected in this section.

Geminate recombination

Geminate recombination (GR) describes the recombination between an electron and a hole originated from the same precursor, for example the molecular excited state S_1 .¹⁵³ In the context of D:A OSCs, exciton dissociation leads to the formation of CT states, which can undergo either geminate recombination to the ground state or dissociation into free charges. Generally speaking, GR is often absent in OSC systems with large driving forces but has been reported to become more significant as the driving force is reduced, especially in some non-fullerene based OSCs.¹²⁵ Moreover, GR is also strongly influenced by the blend morphology, where a well-mixed blend is usually associated with more significant GR losses, while the presence of neat domains has often been shown to be able to suppress the GR losses as they provide a charge percolation pathway.^{154–157}

As mentioned above, geminate recombination of CT states competes with its dissociation into free charges, that is, if CT states cannot dissociate into charges within their lifetime, then they will recombine to the GS. Specifically, Onsager theory states that the ‘geminate pair’ would recombine to the GS when the distance between the electron and hole falls within the Coulomb capture radius R_c .

The first measurement of the relaxation and dissociation of geminate pairs is based on the pump-push technique, proposed by Braun and Scott in 1983.¹⁵⁸ This work lays the foundation for the more recent pump push photocurrent measurements on OSCs, which has been adapted to address the geminate recombination dynamics and the binding energy of CT states, as will be presented in Chapter 3. A more common approach to interrogate the GR is based on a pump-probe technique, i.e. transient absorption spectroscopy. Since GR is a monomolecular process, one would expect the kinetics to follow a monoexponential decay with the same decay rate irrespective of the excitation density, in contrast to bimolecular recombination. Both analyses are employed in this thesis as will be discussed later.

Non-geminate recombination

The process of an electron encountering a hole generated from different excitation events and their subsequent decay is known as non-geminate recombination (NGR). NGR, in principle, can be both radiative or non-radiative. For example, the NGR of the injected charge carriers governs the operation of OLEDs. In the case of OSCs, the majority of the NGR occurs when the electron and hole collide at the D:A interface and fall within the Coulomb capture radius (see Equation 1.8), before decaying to the ground state. As a result of the strong phonon interactions, this process is primarily non-radiative.

NGR is ideally a second-order process in which its rate depends on how likely the electron and hole will find each other. In other words, NGR rate scales linearly with the product of the electron and hole density, as shown in Equation 1.14. However, this only applies when the electron and hole densities are similar. In the case when one type of carriers is in excess compared to the other one, it will become a pseudo-first-order monomolecular process. However, for materials with a large energetic disorder, the reaction order observed in OSCs can be higher than 2.¹⁵⁹ Characterisation of NGR in OSC devices can for example be probed by transient photovoltage measurements over nanosecond to millisecond timescales.^{160,161} When it comes to an OSC device under operational conditions, NGR may compete with charge transport and collection by the electrodes.

$$R = k_{bi}np \approx k_{bi}n^2 \quad (1.14)$$

where k_{bi} is the bimolecular rate constant, n and p are the carrier densities for electrons and holes respectively.

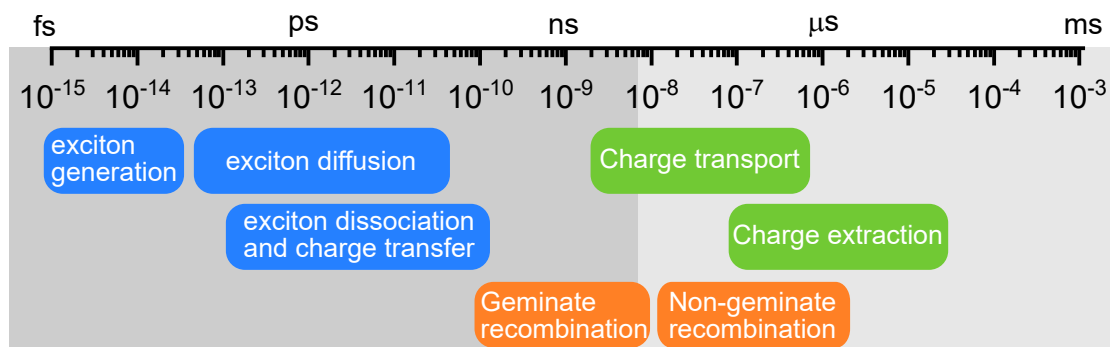


Figure 1.9 Relevant timescales for the photophysical processes governing the photocurrent generation in organic solar cells.

In summary, whether a specific OSC system suffers from GR or NGR can be identified by the reaction order with the help of transient absorption spectroscopy. The rule of thumb is that GR follows a monomolecular decay manner, while the NGR is often a second, or higher, order process. Moreover, GR and NGR usually occur on different timescales, where the former happens over hundreds of ps to tens of ns and the latter happens over ns to ms (for charge densities relevant to OSC operation).⁴⁷ One of the reasons that the efficiency of OSCs still lags behind their inorganic counterparts is because of significant non-radiative voltage losses, associated with non-radiative recombination processes. This has prompted a research direction to minimise the non-radiative losses in order to boost the efficiency of OSCs.^{149,162,163} Finally, Figure 1.9 shows the relevant timescale for the generation and recombination processes occurred during typical OSC operation.

1.5.3 Binding energy and dynamics of charge-transfer states

As mentioned in previous sections, charge transfer across the D:A heterojunction in OSCs can lead to the formation of interfacial CT states, a state related to the GS by a CT transition.^{31,43} There is compelling evidence to suggest that CT states act as the intermediate state from exciton dissociation to charge separation and has a significant impact on both J_{SC} and V_{OC} in the operation of OSCs.¹³¹ Understanding the nature of CT states and its impact on the photovoltaic performance has been one of the main research directions within the field. However, these studies often present contradictory results and offer various photophysical models to describe the CT mechanism, hence establishing a model that reconciles all these results is a key challenge. Herein, this section aims to summarise a few key questions and current understandings in the literature on the nature of CT states, which have inspired the research presented in Chapter 3 and Chapter 4. Most studies on CT states rely on steady-state absorption or emission-based techniques;^{45,164,165} while these are crucial to determine CT state energetics, time-resolved spectroscopy can more directly reveal the transient properties of CT states including CT dissociation and recombination dynamics. Commonly utilised time-resolved spectroscopies include time-resolved photoluminescence, transient absorption spectroscopy and pump push photocurrent spectroscopy, to name a few.^{33,126,166,166–176} In addition, other device characteristic

measurements at various temperatures have also been valuable to understand the dissociation of CT states.^{177–179}

The GS wavefunction overlap between D and A governs the optical transition strength between the GS and CT states. It has been reported that the coupling between the GS and CT states is much weaker compared to that between the GS and the S_1 state in a neat semiconductor, resulting in a lower oscillator strength for the CT transition.¹⁸⁰ As a result of this, the presence of CT states is often detected by techniques based on the steady-state absorption and emission spectroscopy with high sensitivities and is often observed at lower energy than exciton states.³¹ Absorption based techniques include external quantum efficiency (EQE) spectroscopy, photothermal deflection spectroscopy,^{165,181} Fourier-transform photocurrent spectroscopy⁴⁵ as well as electroabsorption spectroscopy.^{182,183} In terms of emission-based techniques, methods such as photoluminescence (PL) and electroluminescence (EL) spectroscopy are often employed to quantitatively detect CT states.^{140,164} Some tools are often used in conjunction, for example, EL and EQE together serve as a convenient way to probe the energetics of CT states.^{45,137}

Whether the electron-hole pair within CT states is Coulombically bound or not is still constantly under debate.⁶² Generally speaking, both Coulombically bound and loosely bound CT states have been reported in various D:A blends, where the former tends to undergo geminate recombination and the latter tends to dissociate into free carriers, consistent with Onsager-Braun model.^{67,184} Additionally, both bound and unbound CT states can be present in one D:A blend depending on the local microstructures.¹⁸⁵ Measuring the binding energy of CT states is thus the most straightforward way to examine the bound nature of CT states, often achieved by in-situ T -dependent characterisation as further discussed below.^{186,187} Table 1.1 summarises a few experimentally measured CT state binding energies for various D:A blend systems reported over the last decade, together with the measurement techniques used. For example, Kern et al. measured the steady-state PL under external biases for the MDMO-PPV:PCBM blend film and deduced a CT binding energy of around 203 ± 18 meV based on the Onsager-Braun model in 2011.¹⁸⁶ At the same time, the CT binding energy for a large driving force system, PFB:F8BT, was estimated to be around 250 meV.³⁵ In 2015, T -dependent time-resolved PL measurements were employed to determine the CT binding energy in the PTB7:PCBM blend.¹⁷¹ This work

indicated that only a small amount of energy of around 30 meV is required to separate CT states, indicating that this weak binding nature within CT states is the main reason for efficient charge separation in the PTB7:PCBM blend.¹⁷¹

Table 1.1 Binding energies of charge-transfer states for various D:A blend systems reported in the literature.

D:A system	Binding energy (meV)	Technique	Published in
MDMO-PV:PCBM	203 ± 18	PL	2011 ¹⁸⁶
PFB:F8BT	250	TRPL	2011 ³⁵
P3HT:PCBM ^a	35.3 ± 4.6	TRPL	2015 ¹⁷¹
MDMO-PPV:PCBM ^b	90 ± 50	PPPc	2017 ¹⁸⁸
PCPDTBT:PCBM	23.5 ± 3.4	TDCF	2018 ¹³¹
PfBT4T-2OD:EH-IDTBR	100 ± 6	PPPc	2019 ⁶⁵ (this thesis)

^a The binding energy listed here is for the blend with a 60% PCBM ratio.

^b Various PCBM derivatives were employed including mPCBM, bPCBM and tPCBM.

In 2017, pump push photocurrent (PPPc) spectroscopy was employed to investigate CT state binding energies in various fullerene blend devices.¹⁸⁸ In comparison with the steady-state measurements on devices, PPPc measurements can directly access the bound CT states on an ultrafast timescale and hence eliminates the potential drawback of T -dependent device characteristic measurements which may be limited by the slow charge extraction. Moreover, it is useful to examine those non-fullerene blends with low driving forces, where the closely aligned CT and exciton energy levels make it difficult to distinguish the CT emission from the exciton emission peaks. However, PPPc spectroscopy also has its own Achilles' heel—it cannot probe the subset of CT states which are loosely bound, meaning that they will eventually separate into free carriers without any additional push pulse. More recently, the combination of different tools including photothermal deflection spectroscopy and PPPc was also successfully used to address the nature of CT states.¹⁸⁹

In addition to the aforementioned PL and PPPc measurements, bias and T -dependent time-delayed collection field (TDCF) has also been employed to study the dissociation of CT states and examine the dominant charge generation pathway in OSCs.^{128,131} For example, in 2018, Kurpiers et al. measured an activation energy of 23.5 meV for the CT dissociation in the

PCPDTBT:PCBM blend, while pointing out that the energetic/structural disorder can easily increase this dissociation barrier by two-fold.¹³¹

The binding energy of CT states describes the minimum energy required to dissociate these states. However, even with sufficient energy, CT states must dissociate within their lifetime before decaying to the ground state. The dissociation of thermalised CT states directly competes with the geminate recombination of these states. It is thus important to measure the lifetime of CT states and elucidate its impact on the CT dissociation. Additionally, geminate recombination can become more severe when the driving force gets smaller, hence it is crucial to unravel how the driving force would impact on the lifetime of CT states. Chapter 4 will address this unexplored issue and discuss the correlation between CT lifetimes with material energetics in polymer:non-fullerene OSC blends.

1.6 Aim and scope of the thesis

1.6.1 Aim

Following the invention of the bulk heterojunction concept and the recent growth in non-fullerene acceptor materials, the field has witnessed a surge in the efficiency of organic solar cells from 11% in 2015 to nearly 18% in 2020.⁸¹ While material development and device engineering have made rapid progress, the underlying photophysics is still lagging, especially regarding the role of driving force on charge separation and recombination dynamics as well as the origin behind charge generation.¹⁰⁸ What lies at the core of the photophysics in heterojunction OSCs are the CT states, acting as the key precursor for charge generation and recombination. Concerning studies on CT states, pioneering work has been established to confront how their energetics affect the device open-circuit voltage, and consequently the voltage losses, based on steady-state characterisation and numerical modellings. However, as previously discussed, studying the dynamics of CT states on the timescale of their dissociation/recombination is also of great importance but remains rather limited in the literature compared to research on energetics and voltage losses analysis. Herein, a combination of steady-state and time-resolved spectroscopic tools are employed to examine the unique physics of CT states in non-fullerene based bulk

heterojunction OSCs. The work covered in this thesis aims to address some of the unexplored but important issues and will be presented throughout Chapter 3 to Chapter 4, exploring the role of driving force on the CT state dynamics in non-fullerene based D:A bulk heterojunction OSCs.

Despite the fact that the bulk heterojunction architecture leads the efficiency record in OSCs, homojunction OSCs have their distinctive advantages and rich photophysics, making them an ideal system to investigate the origin behind exciton dissociation and charge generation. While the majority of the research focuses on materials with co-existing electron donating and accepting moieties, those materials without such structures have not been thoroughly investigated. Chapters 5 and 6 explore how the molecular electrostatics and electric field can drive charge generation in homojunction OSCs employing small molecule materials.

1.6.2 Scope

The scope of this thesis can be broken down as follows:

Chapter 1 provides an overview of the motivation behind the current research and state-of-the-art understandings on the photophysics in organic solar cells. It begins with the motivation for this thesis, together with the history of organic solar cells development. This is followed by the fundamental photophysics in organic semiconductors with a focus on their electronic structures, the fate of excited states, as well as charge transfer and energy transfer processes. The last section discusses the current understandings on photocurrent generation mechanism within organic solar cells, and how those lead to the motivation for this thesis.

Chapter 2 covers the technical details and the working principles for the experimental methods employed for the research carried out in this thesis including sample fabrication, steady-state absorption and photoluminescence spectroscopy, time-correlated single photon counting, transient absorption spectroscopy, electroabsorption spectroscopy, pump push photocurrent spectroscopy as well as the data analysis approach, namely the genetic algorithm.

Chapter 3 addresses the unique photophysics in an OSC blend with a low driving force for charge separation, namely PffBT4T-2OD:EH-IDTBR. *T*-dependent pump push photocurrent

(PPPC) measurements determined a binding energy of CT states of around 100 meV. Combining PPPc and transient absorption measurements, a photophysical model depicting the charge generation and separation was proposed, which can also be applied to other OSC systems with low driving forces.

Chapter 4 continues to strengthen the understanding of the dynamics of CT states by comparing the TA kinetics for seven different non-fullerene based OSC blends, which all undergo significant geminate recombination of CT states. Herein, it is shown that reducing the driving force leads to a faster CT recombination as a result of the hybridisation/mixing between S_1 and CT states. By correlating with the exciton lifetime of the lower gap components, it is evident that the CT lifetime is intrinsically limited by the exciton lifetime in those low-offset systems.

Chapter 5 discusses how the molecular electrostatics can drive charge generation in pristine organic small molecules and how this can be employed to make efficient homojunction solar cells based on α -sexithiophene (α -6T). Using a mixture of standing and lying α -6T molecules can efficiently generate charges as evidenced by TA and time-resolved photoluminescence measurements. This is attributed to the formation of an interfacial energy offset of 0.4 eV between the standing and lying domains.

Chapter 6 discusses how the electric field drives charge generation in a homojunction OSC device based on chloroboron subnaphthalocyanine chloride (SubNc). Detailed analysis of TA measurements shows that free charges can only be generated in the SubNc device, while only thermal modulation was observed in the pristine film. Further measurements on the planar heterojunction α -6T/SubNc device investigates how charge generation in pristine materials (both α -6T and SubNc) affects the charge generation efficiency as well as carrier dynamics in planar heterojunctions and provides a useful guideline for future material design.

Chapter 7 summarises the key conclusions of this thesis and an outlook for future research direction.

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Chapter 2

Experimental Details

This chapter talks about the experimental details used in this thesis consisting of sample preparation, characterisation and analytical methods. It begins with sample fabrication methods, and is followed by basic characterisation techniques including absorption spectroscopy, steady-state and time-resolved fluorescence spectroscopy. The remaining part of this chapter discusses more advanced techniques including transient absorption spectroscopy and genetic algorithm analysis, as well as electroabsorption spectroscopy and pump push photocurrent spectroscopy.

2.1 Sample fabrication

2.1.1 Film and device fabrication via spin coating

All the materials were used as received without any further purification. Where complete devices were studied, these were fabricated with the aid of Dr Pabitra Shakya Tuladhar and Dr Hyojung Cha, unless otherwise specified.

Film fabrication: films were deposited on glass substrates with a size of 1 cm by 1 cm unless otherwise specified. The glass substrates were cleaned with water, acetone, and isopropanol. Finally, the substrates were treated with oxygen plasma before the spin coating of the active layer on top. The details about the active layer solution ratios and spin coating parameters will be explained in each chapter.

Device fabrication: devices were fabricated in an inverted architecture with the configuration of ITO/ZnO/Blend/MoO₃/Ag unless otherwise stated. Initially, ITO (indium tin oxide) substrates were treated with oxygen plasma before the spin coating of zinc acetate dihydrate precursor solution (60.4 μ l of 1-ethanolamine in 2 ml 2-methoxyethanol). ZnO layers were annealed at 150° for 10 min. The blend solutions were spun onto the ITO substrates in a nitrogen glovebox. Finally, MoO₃ (10 nm) and Ag (100 nm) layers were deposited by vacuum evaporation through a mask with an active area of 0.045 cm² in each device. Current-voltage characteristics were measured with a Keithley 2400 source meter under AM 1.5 illumination from a xenon lamp (Oriel Instruments).

2.1.2 Film and device fabrication via vacuum evaporation

All the materials were purified twice after bought by vacuum gradient sublimation. Samples were encapsulated in a nitrogen atmosphere with a transparent encapsulation glass, fixed by UV hardened epoxy glue unless otherwise stated. Fabrication was carried out by Vasileios C. Nikolis at TU Dresden.

Device fabrication: devices were processed by thermal evaporation in a custom-built vacuum system (Kurt J. Lesker, USA) with a base pressure of 10⁻⁷ mbar. During the evaporation, a

combination of masks and movable shutters of different sizes allow the variation of the device stacks and processing parameters. Devices were fabricated onto pre-structured ITO substrates (Thin Film Devices, USA), which underwent an ozone plasma treatment before processing. This was followed by the evaporation of the active layer and the thick Ag cathode (100 nm). The active area of devices was 6.44 mm^2 .

2.2 Steady-state measurements

2.2.1 Ultraviolet-visible absorption spectroscopy

Ultraviolet-visible (UV-vis) absorption spectroscopy is a fundamental technique to measure the ground state (GS) absorption in materials. When light passes through materials, the absorption in the energy of certain wavelengths allows electronic transitions from the GS to the excited state (ES). Absorbance is calculated by comparing the difference in the transmitted light intensity with and without the sample according to the equation below:

$$A(\lambda) = -\log T(\lambda) = -\log \frac{I(\lambda)}{I_0(\lambda)} \quad (2.1)$$

where $A(\lambda)$ is the absorbance at wavelength λ , $T(\lambda)$ is the transmittance at wavelength λ , $I(\lambda)$ is the light intensity transmitted through the sample and $I_0(\lambda)$ is the light intensity received by the sample. For homogeneous systems, the absorbance is related to the optical path length, sample concentration as well as the light attenuating ability of the sample, this is stated in the Beer-Lambert law:

$$A(\lambda) = \epsilon(\lambda)cl \quad (2.2)$$

where $\epsilon(\lambda)$ is the molar attenuation coefficient, also known as the extinction coefficient, representing how strongly the sample can attenuate the light. c is the concentration of the sample and l is the optical path length.

All absorption spectra in this thesis were measured with a spectrophotometer (UV-2600, Shimadzu) with an interval step of 1 nm. It is equipped with integrating spheres (ISR-2600, Shimadzu) and a photomultiplier (PMT) tube R928 detector, allowing measurements ranging

from 300 nm to 1100 nm in the electromagnetic spectrum with a ‘double beam - single detector configuration’. The absorption spectra were obtained with the *UVProbe* software with a normal S/R (sample/reference) mode. During the measurements, a deuterium lamp was employed to cover 300 nm to 323 nm while a halogen lamp was used to cover 323 nm to 1100 nm and the slit width was set to 5 nm. For T -dependent absorption measurements, a water bath was used to modulate the temperature of the sample holder to the desired temperature whilst carrying out the in-situ measurement. The baseline was corrected with a pristine sample substrate.

2.2.2 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy measures the spontaneous emission of photons when carriers relax from an ES to the GS. Following the absorption of photons at a certain wavelength in the sample, the photons can emit in random directions, yielding a typical PL spectrum where the photon counts are plotted as a function of wavelength. According to the Kasha’s rule, internal conversion from the higher ES to the lowest ES occurs rapidly, therefore the PL only originates from the carriers in the lowest ES.¹ PL serves as a great tool to study the charge/energy transfer within Donor:Acceptor (D:A) systems.² More specifically, in the case of D:A OSC blends, PL is often used to examine the PL quenching efficiency (PLQE) of the blend relative to either neat donor or neat acceptor materials. PLQE is an approximate measure of the additional non-radiative exciton quenching in the blend relative to neat films, assigned primarily to charge/energy transfer, representing the exciton dissociation efficiency. This is estimated by taking the PL intensity maxima for the blend and that for the neat material using the equation below:

$$PLQE = 1 - \frac{PL_{blend}}{PL_{neat}} \quad (2.3)$$

where PL_{blend} and PL_{neat} are the PL maxima for the blend and the neat material normalised to their absorbance at the excitation wavelength, respectively.

All PL spectra in this thesis were measured on a Fluorolog-3 spectrofluorometer (FL 3-22, Horiba Jobin Yvon). Samples were excited at various wavelengths from a Xenon lamp source ranging from 240-750 nm. The emitted photons were collected in the front face geometry (with

a 60 ° angle to the excitation light) with a photomultiplier tube (PMT) R928P detector with a slit width of 5 nm. Collecting the emission in this front face geometry minimises reflected and scattered light.

2.2.3 Determination of the optical gap

Organic semiconductors often exhibit broad absorption features with shallow absorption tails, which has been related to the material disorder and low-frequency vibrations by several studies.³⁻⁵ As such, an elegant way to determine the optical gap (E_{opt}) of these materials relies on the combination of their absorption and PL spectra.⁴ In this approach, the optical gap is estimated from the crossing point between the reduced absorption and PL spectra, corresponding to the 0-0 transition from the lowest vibrational state of the GS to the lowest vibrational state of the ES, as shown in Figure 2.1b.⁴

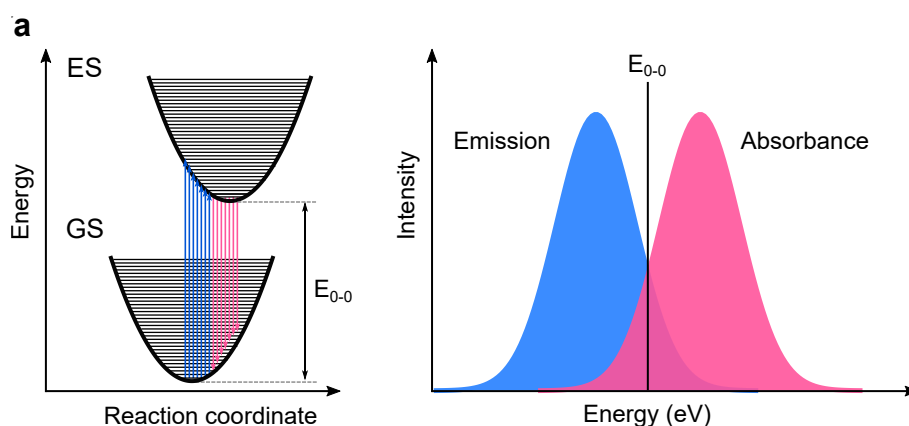


Figure 2.1 Schematic depicting how to determine the optical band gap of an organic semiconductor. **a**, Energy level diagram illustrating the optical transition from the ground state (GS) to the excited state (ES) taking into account the spectral broadening effect arising from low-frequency vibrations, and **b**, Reduced absorption and photoluminescence spectra representing the optical transition processes mentioned in **a**.

2.3 Time-resolved photoluminescence spectroscopy

Time-resolved PL spectroscopy measures the recombination lifetime of materials. Specifically, it can provide insight into the competition processes between radiative and non-radiative processes.

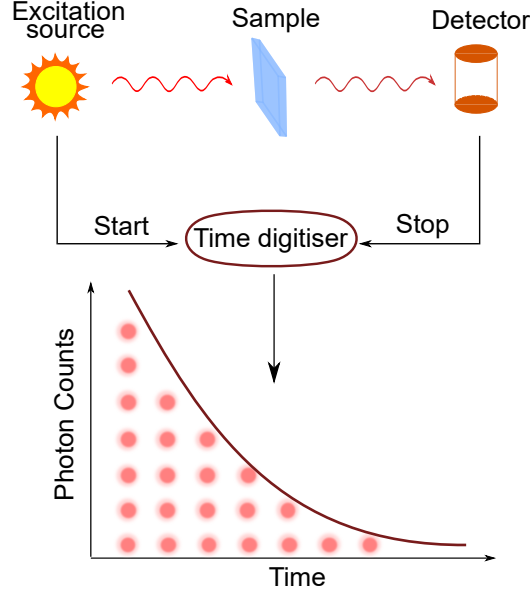


Figure 2.2 Schematic for the time-correlated single photon counting set up.

Time-resolved PL spectroscopy is based on the time-correlated single photon counting (TCSPC) set up as shown in Figure 2.2. During the measurement, an excitation source is employed to excite carriers from the GS to ES. The time digitiser is triggered by the start of the excitation pulse and is stopped when the detector receives a single photon. The arrival time of the single photon is thus measured in this way in respect to the reference signal, the excitation source. This step is repeated many times and eventually yields a histogram of the accumulation of photon counts against time. The lifetime measured in TCSPC is reciprocally related to the sum of the radiative and non-radiative recombination rates as shown below:

$$\tau = \frac{1}{k_r + k_{nr}} \quad (2.4)$$

where k_r is the radiative recombination rate, k_{nr} is the non-radiative recombination rate and τ represents how long it takes to decay to $1/e$ of its original intensity.

In addition to measure the TCSPC kinetics at a single emission wavelength, this set up also allows the measurement of time-resolved emission spectra (TRES). In TRES measurements, a set of kinetics across a wavelength range can be obtained with a fixed interval step of 10 nm, for example. The measurement run-time for each kinetics is fixed to allow the same number of incident photons. By the end of the measurement, a 3D plot of the photon counts against both wavelength and time will be obtained.

For this thesis, a laser diode (635 nm, NanoLED-02B, Horiba) was used as the excitation source, which produces pulses with a duration of < 200 ps and a repetition rate of 1 MHz. The emitted photons were probed with a photomultiplier tube (PMT) detector (PPD-900) which allows the detection of photons between 300-900 nm. For all the measurements, an instrument response function (IRF) was measured with a pristine sample substrate at the excitation wavelength (635 nm). In addition, long-pass filters were placed before the detector to filter the scattering from the excitation source for some measurements.

2.4 Transient absorption spectroscopy

Transient absorption (TA) spectroscopy is often employed to study the mechanisms of chemical processes involving short-lived excited states following the absorption of photons. It is a pump-probe technique which uses the pump to excite the sample and the probe to interrogate the transmittance after a defined pump-probe delay time.

2.4.1 Set up

A commercially available broadband pump-probe femtosecond (fs) transient absorption spectrometer Helios (Spectra Physics, Newport Corp.) was used to measure the TA spectra and kinetics for thin film and device samples. Ultrafast laser pulses (800 nm, < 100 fs pulse duration) were generated by a 1 kHz Ti:sapphire regenerative amplifier (Solstice, Spectra Physics, Newport Corp.). One portion of the 800 nm pulse was directed to an optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (Niruviz, Light Conversion) to tune the visible pump pulses to various wavelengths. The pump pulses were modulated at a frequency of 500 Hz by a mechanical chopper. The rest of the 800 nm pulse was routed onto a mechanical delay stage (with a 6 ns time window) and directed through a crystal (sapphire for the visible region and yttrium aluminium garnet (YAG) for the NIR region) to generate a white light probe ranging from 400 nm to 1600 nm. The probe pulse was split into two by a neutral density filter. One portion of the probe pulse served as the reference and was directly sent to the fibre-optic coupled multi-channel spectrometers (CCD and InGaAs sensors). The rest of the probe pulse together

with the pump pulse were focused onto the same spot on the samples with a beam size of around 0.5 mm^2 before sending it to the spectrometer. A detailed layout of the set up is shown in Figure 2.3. The pulse energies were measured with an energy meter (VEGA P/N 7Z01560, OPHIR Photonics) equipped with a pinhole of $500 \mu\text{m}$ diameter. During the measurements, samples were kept in a quartz cuvette under continuous nitrogen flow unless the samples were encapsulated. To compensate for the fluctuations, the measured spectrum was normalised to the reference spectrum and averaged for several scans to achieve a good signal-to-noise ratio. Data analysis was performed with the commercialised *Surface Xplorer* software and genetic algorithm (see Section 2.4.3).

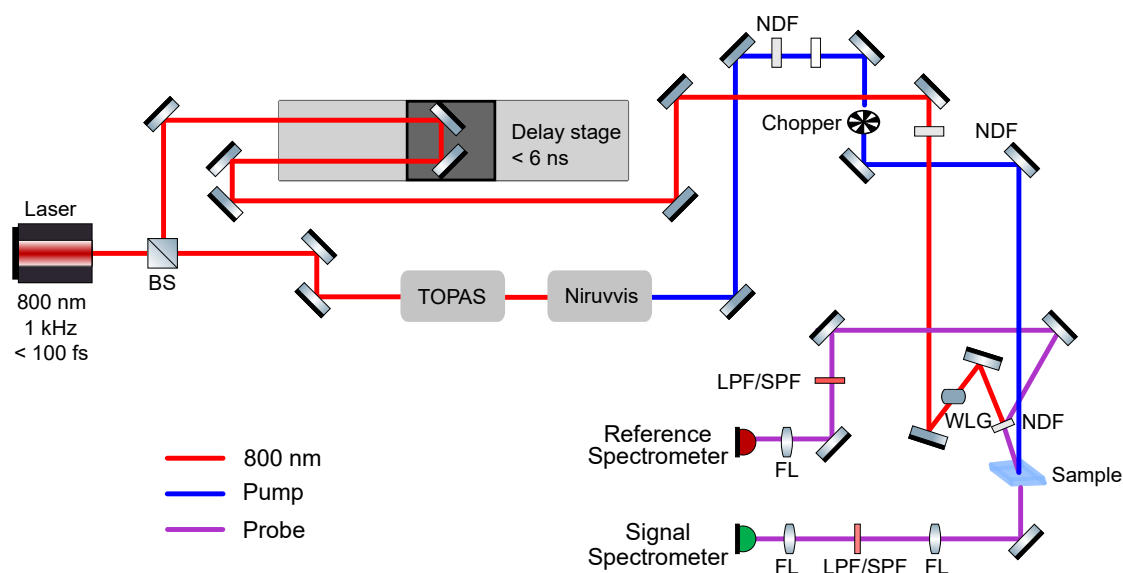


Figure 2.3 Layout of the transient absorption spectroscopy set up. BS: beam splitter; LPF: long-pass filter; SPF: short-pass filter; NDF: neutral density filter; WLG: crystals for white light generation; FL: focal lens; TOPAS: optical parametric amplifier, Niruvvis: frequency mixer. The polarisation of the pump and probe beams were set at the magic angle of 54.7° to each other.

2.4.2 Typical signals

Change in optical density

In TA spectroscopy, changes in absorbance (ΔA) or alternatively optical density (ΔOD) are measured by detecting the difference in the light intensity transmitted through the sample with the pump on and off, respectively. At each pump-probe delay time, this change in transmittance (ΔT) is recorded across the whole probe wavelength range using a spectrometer. Based on the

logarithmic relation between transmittance (T) and absorbance (A) described in Equation 2.1, ΔOD can thus be related to ΔT as follows:

$$\Delta OD = OD_2 - OD_1 = -\log\left(\frac{I_2}{I_0}\right) - \left[-\log\left(\frac{I_1}{I_0}\right)\right] = -\log\left(\frac{I_2}{I_1}\right) \quad (2.5)$$

where I_0 is the light intensity received by the sample, I_2 and I_1 are the transmitted light intensities with the pump on and off respectively. As the difference in the detected light intensity with pump on and off in TA measurements is relatively small ($\sim 10^{-3}$), Equation 2.5 can be approximated to:

$$\Delta OD = -\log\left(1 + \frac{I_2 - I_1}{I_1}\right) = -\log\left(1 + \frac{\Delta I}{I_1}\right) = -\frac{1}{2.3} \times \ln\left(1 + \frac{\Delta I}{I_1}\right) \approx -\frac{1}{2.3} \times \frac{\Delta I}{I_0} \quad (2.6)$$

That is, the change in absorbance is directly proportional to the change in light intensity, now commonly expressed as $\Delta T/T$.⁶ Following the Beer-Lambert law presented in Equation 2.2, the change in absorbance can thus reflect the transient concentration of the photogenerated excited-state species.⁶

Ground state bleach, stimulated emission and photoinduced absorption

Typical signals in TA measurements are shown in Figure 2.4 and are explained as follows.

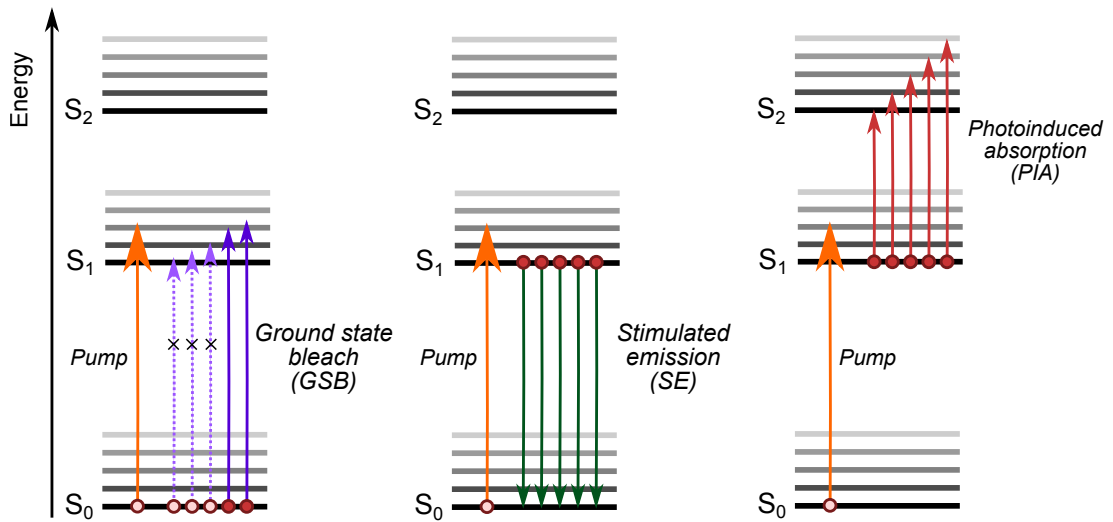


Figure 2.4 Typical signals observed in transient absorption spectra including ground state bleach, stimulated emission and photoinduced absorption.

- (1) Ground state bleach (GSB): the pump pulse promotes the molecules from the ground state (GS) to the excited states, leading to a reduction in the population of the GS molecules. Hence, the GS absorption is decreased in the excited sample in comparison with the non-excited sample. This is reflected as a negative signal in a ΔA plot. The identification of the GSB signal can be retrieved by comparing the TA spectra with the steady-state UV-vis absorption spectra.
- (2) Stimulated emission (SE): SE describes the process when the photon from the probe pulse induces the emission of another photon from the excited state, following the population of excited-state species by the pump. This occurs when the incident photon energy matches the energy difference between the excited state and ground state. The detector sees an increased light intensity passing through the sample when the pump is on, therefore it is shown as a negative signal in a ΔA plot, which can spectrally overlap with the GSB signal at very short delay times but mostly resembles the PL signal. This is different from that in steady-state PL spectroscopy described in Section 2.2.2, which is also known as the spontaneous emission.
- (3) Photoinduced absorption (PIA): upon the pump excitation, a fraction of molecules gets promoted to the excited states, these excited-state species can then take part in further optically allowed transitions. Consequently, it exhibits a positive signal in a ΔA plot. In the organic semiconductors studied within this thesis, commonly observed PIA signals originate from excitons, charge-transfer states and polarons, for example.

2.4.3 Data analysis

The routine treatments for the TA data were carried out using the built-in functions in *Surface Explorer*, which involve the subtraction of the background noise and scattering light, chirp correction as well as ‘time-zero’ correction. In addition, genetic algorithm (GA) was also employed to decipher the complicated information embedded in the TA data, as further described below.

In TA data, the simultaneous presence of multiple excited-state species results in the overlapping of different signals. At each wavelength, there is often contributions from more than one species unless their population is negligible. This makes the kinetics and spectra hard to analyse due to

the convolution of signals. To tackle this, a model-free approach called the genetic algorithm (GA) was employed to deconvolute signals in the TA data. The GA code used in this thesis was originally built by Simon G  linas.⁷ Unlike other model-based analysis, GA only requires a genetic representation of the solution and a fitness function to evaluate the solution.⁸

In a typical TA measurement excited with a fixed fluence, there are only two variables: time (t) and wavelength (λ). Starting with a simple system where only one species is present, the TA data can be summarised into Equation 2.7:

$$\frac{\Delta T}{T}(t, \lambda)_{\text{data}} = S(\lambda) \times A(t) \quad (2.7)$$

where $\frac{\Delta T}{T}(t, \lambda)$ is a $m \times n$ matrix, $S(\lambda)$ is a $m \times 1$ matrix representing the spectrum and $A(t)$ is a $1 \times n$ matrix representing the time-dependent population amplitude. If there are in total x species present, then the TA data can be rewritten as Equation 2.8:

$$\frac{\Delta T}{T}(t, \lambda)_{\text{data}} = \sum_{i=1}^x S_i(\lambda) \times A_i(t) \quad (2.8)$$

By rearranging Equation 2.7, $A(t)$ can be represented with $S(\lambda)$ and $\frac{\Delta T}{T}$ as shown in Equation 2.9:

$$A(t) = S^{-1}(\lambda) \times \frac{\Delta T}{T}_{\text{data}} \quad (2.9)$$

Now the solution obtained from GA is solely dependent on the spectra and the original TA data as shown in Equation 2.10:

$$\frac{\Delta T}{T}(t, \lambda)_{\text{solution}} = \frac{\Delta T}{T} \left(S(\lambda), \frac{\Delta T}{T}_{\text{data}} \right)_{\text{solution}} \quad (2.10)$$

The analysis starts by generating random populations representing the solution. In TA spectroscopy, this specifically refers to different spectra representing each species generated by the pump excitation. Each spectrum has its weights and consists of a random Gaussian function with additional noise. This can be simply represented by Equation 2.11 where the data is

written in a product of various species at the wavelength domain $w_{species\ n}$ multiplied by their kinetics at the time domain $k_{species\ n}$. It is also possible to add an initial estimate of spectra to this initialisation step. For example, if exciting only the acceptor material in the studied blend, the acceptor exciton spectra obtained from a separate TA measurement for the pristine acceptor film can serve well as an initial estimate in addition to the randomly generated population. The aim is to achieve a minimum mean square difference between the model TA_{model} and the experimental data $TA_{\text{experimental}}$.

$$TA_{\text{model}} = \begin{bmatrix} w_{\text{species } 1} & w_{\text{species } 2} & \dots & w_{\text{species } n} \end{bmatrix} \times \begin{bmatrix} k_{\text{species } 1} \\ k_{\text{species } 2} \\ \dots \\ k_{\text{species } n} \end{bmatrix} \quad (2.11)$$

The next step is the evolution. Firstly, the fitness of each species within the population was measured based on the fitness function. The best individual species were selected as the ‘parents’ for further evolution. Secondly, GA variants, including crossover and mutation, were applied to produce the offspring of the next generation, creating new populations. Such processes were repeated for several iterations and the best fit was evolved when the fitness function reached the global minimum.

2.5 Electroabsorption spectroscopy

Electroabsorption spectroscopy is employed to understand the field-induced absorption in organic solar cells, which is often associated with exciton/CT state generation.⁹

2.5.1 Set up

Electroabsorption (EA) spectroscopy was measured on a complete OSC device using the TA set up as described in Section 2.4.1 but in a reflectance geometry. During the measurement, an electric field was applied across the device using a digital delay generator (Stanford Research Systems DG645) and was modulated at 500 Hz, which is half of the probe frequency. A square

voltage of up to 5 V with a time duration of 100 μ s was applied. The difference in the reflected probe light intensity with the electric field on and off was averaged over multiple scans, which yields the EA spectra under different electric fields.

2.5.2 Typical signals

EA spectroscopy measures the change in material absorption under an electric field, an effect known as the Stark effect, in which case the electric field is understood to be able to perturb the electronic structures and shift the energy levels.¹⁰ The field-induced absorption change is reflected as a shift in the absorption peak with and without the field as shown in Figure 2.5a. As such, the amount of absorption shift in the energy of a ground state transition from 0 to n induced by the electric field can be expressed as:

$$\Delta E = E(F) - E(0) = -m_{0n}F - \frac{1}{2}p_{0n}F^2 \quad (2.12)$$

where m_{0n} is the change in the permanent dipole moment, p_{0n} is the change in the polarisability for the 0 to n transition and F is the electric field strength.^{9,11}

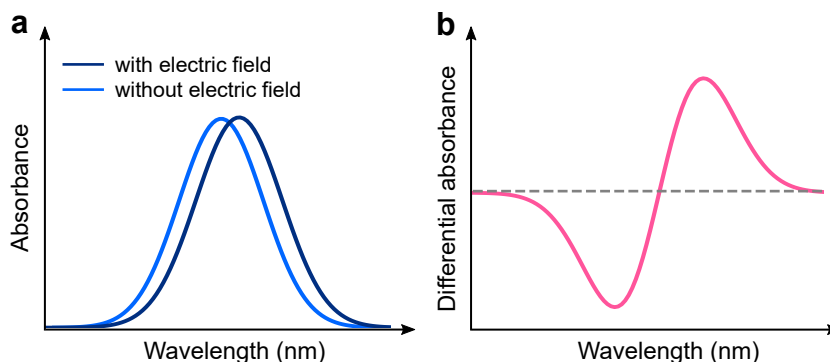


Figure 2.5 **a**, Representative absorption spectra with and without the electric field; **b**, Differential absorption spectrum by taking the difference of the absorbance with and without the electric field, representing the electroabsorption signal.

The electric field can result in a change of polarisability or dipole moment. When the field induces a change in the polarisability, this molecular polarisability change would interact with the field to induce a dipole moment, which is oriented in the direction of the field.¹² This results in the absorption spectrum to shift towards a higher or lower energy and the EA spectrum thus follows the first derivative of the absorption spectrum as shown in Figure 2.5b. When the field

induces a change in the dipole moment such as a transition to a charged state, the EA spectrum would follow the lineshape of the second derivative of the absorption spectrum instead.^{9,10,13} In disordered organic semiconductors, it has been reported that the EA often consists of a combination of both first and second derivative lineshapes.¹³ Since the 1990s, steady-state EA spectroscopy has been widely employed to study the built-in potentials in OSCs.^{14,15} More recently, time-resolved EA spectroscopy has been employed to investigate the charge separation dynamics across the interface in both planar and bulk heterojunction OSCs.^{16,17} In the context of D:A OSCs, such an electric field can originate from a local electric field induced by the electron-hole pair at the D:A interface, or the macroscopic field applied by external biases.

2.6 Pump push photocurrent spectroscopy

2.6.1 Set up

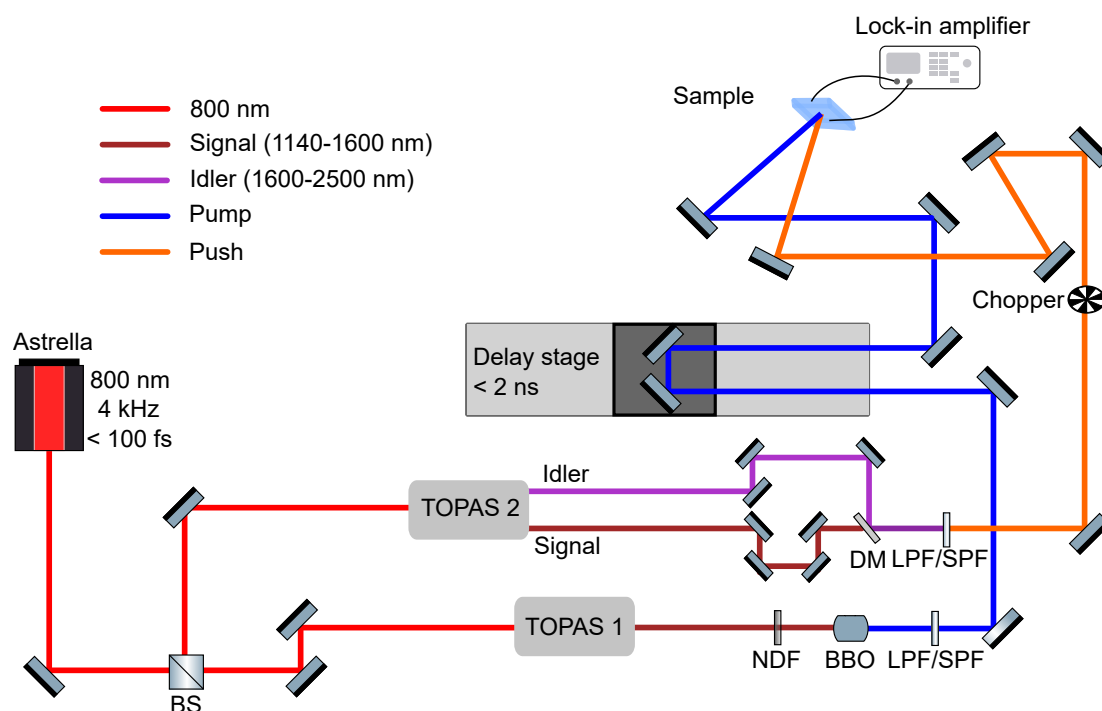


Figure 2.6 Layout of the pump push photocurrent spectroscopy set up. BS: beam splitter; LPF: long-pass filter; SPF: short-pass filter; NDF: neutral density filter; DM: dichroic mirror.

A layout of the pump push photocurrent (PPPC) spectroscopy set up is shown in Figure 2.6. A 4 kHz Ti:sapphire regenerative amplifier (Astrella, Coherent) was used to generate the pump pulses (800 nm, 35 fs). These pulses were routed onto two optical parametric amplifiers (TOPAS

Prime, Coherent). The 1200 nm output from one TOPAS passed through a frequency-doubling barium borate (BBO) crystal to generate the pump pulse at 600 nm. The pump pulse was then directed onto a mechanical delay stage which varies the time delay between the pump and push pulses. The 2000 nm output from the other TOPAS served as the push pulse, which was mechanically modulated at 1.1 kHz. Both pump and push pulses were aligned onto a single spot onto the device pixel. During the measurements, the OSC devices were connected to a lock-in amplifier (SR830, Stanford Research Systems) and were measured under short-circuit conditions unless otherwise stated. The reference photocurrent J is measured at the pump frequency of 4 kHz, and the push induced photocurrent ΔJ was measured at the push frequency of 1.1 kHz.

2.6.2 Typical signals

Different energetic states involved in a PPPc measurement are depicted in Figure 2.7. When PPPc spectroscopy is carried out on an OSC device, the visible pump pulse populates carriers into ‘hot’ exciton states (S_n), followed by rapid internal conversion to the lowest exciton state (S_1) or dissociation at the D:A interface to form ‘hot’ CT_n states. Based on the Onsager theory discussed in Section 1.3.4, a portion of these ‘hot’ CT_n states can dissociate into free charges, while the rest undergo relaxation and stay bound at the D:A interface as thermalised CT states. After a certain pump-push delay time, the near-infrared (NIR) push pulse excites those bound CT states to CT_n states and the excess energy provided hence dissociates them into CS states, leading to an increase in the photocurrent, termed as ΔJ .

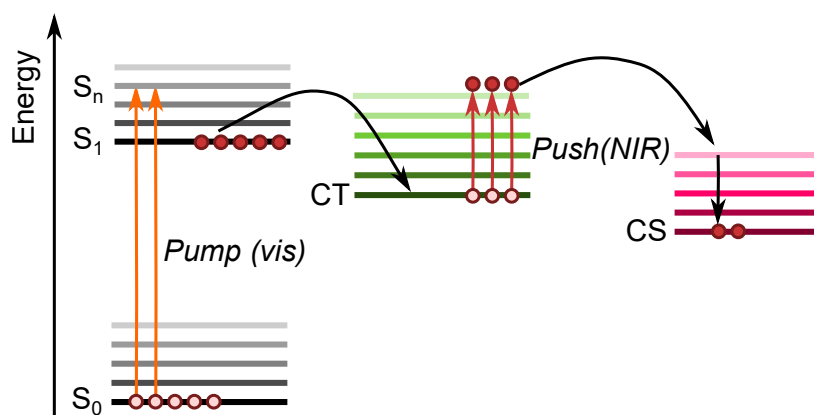


Figure 2.7 Relevant photophysical processes involved in pump push photocurrent (PPPC) measurements, where S_0 denotes the ground state, S_1 denotes the singlet exciton states, CT denotes the charge-transfer states and CS denotes the charge-separated states. For simplicity, other irrelevant photophysical processes are ignored in this figure.

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Chapter 3

The Binding Energy and Dynamics of Charge-transfer States in Low-offset Organic Solar Cells

This chapter is reproduced from ‘The binding energy and dynamics of charge-transfer states in organic photovoltaics with low driving force for charge separation. *J. Chem. Phys.* **150**, 104704 (2019)’, with the permission of AIP Publishing.¹ This chapter describes a detailed ultrafast spectroscopic study of a representative low-offset organic solar cell system based on a polymer donor PffBT4T-2OD and a small-molecule non-fullerene acceptor EH-IDTBR. Transient absorption kinetics suggest that a slow (15 ps) formation of charge-transfer (CT) states is followed by significant geminate recombination, limiting the device photocurrent. This contrasts with the ‘reference’ PffBT4T-2OD:PC₇₁BM system where the bimolecular recombination of free charges dominates. Using *T*-dependent pump push photocurrent spectroscopy, the activation energy for the dissociation of bound CT states in PffBT4T-2OD:EH-IDTBR was estimated to be 100 ± 6 meV. An additional activation energy of 14 ± 7 meV was also observed, which is associated with the de-trapping of charge carriers. This chapter aims to provide a comprehensive picture of the photophysics around CT states in a system representing the new generation of low-offset OSC blends.

3.1 Introduction

The rapid rise in bulk heterojunction OSC efficiencies over the past few years largely relies on the material design as well as minimising the energetic driving force for charge separation, as defined in Section 1.3.4.²⁻⁷ One of the non-fullerene acceptor (NFA) based benchmark systems with a low driving force for charge separation is PffBT4T-2OD:EH-IDTBR, which exhibits a high open-circuit voltage (V_{OC}) of 1.08 V, while only 0.8 V can be achieved using PffBT4T-2OD:PC₇₁BM as shown in Figure 3.1.⁸ In addition, devices employing EH-IDTBR can be easily fabricated without any additives such as DIO which can often result in the instability of fullerene-based devices.⁹⁻¹³ PffBT4T-2OD is a polymer donor which was first reported by Liu et al.¹⁴. It exhibits strong aggregation ability and tends to form highly crystalline domains.¹⁵ The NFA EH-IDTBR was reported by Holliday et al. in 2016,¹⁶ which is based on an indacenodithiophene (IDT) core with ethyl hexyl side chains. The planar conjugation together with the highly electron-rich core raises the energy level of the lowest unoccupied molecular orbital (LUMO), thereby showing potential to reduce voltage losses relative to fullerene-based blends.¹⁷ Additionally, EH-IDTBR exhibits a higher absorption coefficient and a higher photoluminescence (PL) quantum yield than some polymer donors.¹⁸ This opens up the possibility for hole transfer to be as equally important as electron transfer for charge generation in devices, which was not the case in fullerene-based systems due to their relatively weak absorbance.

Cha et al. previously compared the two OSC blends, PffBT4T-2OD:EH-IDTBR and PffBT4T-2OD:PC₇₁BM, and showed that the device stability has been greatly enhanced when using EH-IDTBR as the acceptor while the device suffered a significant burn-in degradation with PC₇₁BM as the acceptor.⁸ In terms of the photophysics, relatively slow exciton quenching times (30 ± 2 ps) in both blend systems were reported, yet they are still much shorter than the exciton lifetime in the neat PffBT4T-2OD (~ 300 ps). The shorter lifetimes in the blends are in agreement with the PL quenching yield (77% and 80% for EH-IDTBR and PC₇₁BM systems, respectively). Although similar exciton quenching kinetics and yields were observed, the yield of free charge carriers in the former system is lower, leading to a drop in the short-circuit current density (J_{SC}) (in Figure 3.1). Cha et al. attributed this to the smaller energy offset and a greater degree of geminate recombination in the PffBT4T-2OD:EH-IDTBR blend.⁸ However,

in-depth analysis of the transient absorption (TA) data had not previously been performed, for example, exciton and charge dynamics, as well as the dynamics of charge-transfer (CT) states have not been clearly identified. The enhanced stability and the high V_{OC} together with the complimentary absorption between PffBT4T-2OD and EH-IDTBR make this blend an interesting system for in-depth spectroscopic studies. Other studies have indicated the promising potential of OSC blends with overlapping absorption features. For example, Baran et al. have reported that blending PTB7-Th with EH-IDTBR leads to stable and efficient OSCs with minimal recombination losses, even when the absorption of PTB7-Th and EH-IDTBR are largely overlapped.¹⁹ Also Krückemeier et al. have recently pointed out that overlapping absorption between D and A is preferable and beneficial for efficient OSC performance if the active layer thickness is relatively thin, which is commonly observed among polymer:NFA OSCs.²⁰ Furthermore, minimising the driving force has been one of the main focuses recently to enhance the OSC efficiencies.^{21,22} As the PffBT4T-2OD:EH-IDTBR blend is a prototypical low energy offset system, understanding what governs the charge generation and recombination in this representative low-offset OSC system is thus crucial towards future material design and device performance.

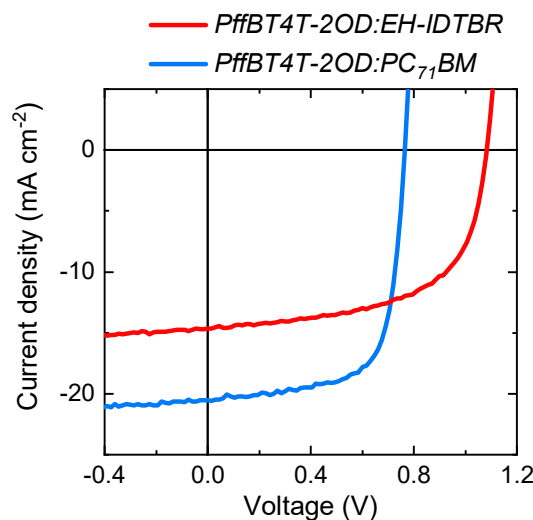


Figure 3.1 Current-voltage characteristics for PffBT4T-2OD:EH-IDTBR and PffBT4T-2OD:PC₇₁BM devices, respectively. Figure adapted from reference⁸.

This chapter goes beyond the previous work and focuses on investigating the carrier dynamics in PffBT4T-2OD:EH-IDTBR with different types of ultrafast spectroscopic tools and genetic algorithm (GA) analysis of the TA data following the methods described in Chapter 2. The use

of GA identifies the spectral ‘footprints’ for PffBT4T-2OD excitons, EH-IDTBR excitons, and charged states including both free charges and CT states. It reveals that the excitons in PffBT4T-2OD and EH-IDTBR decay with a similar lifetime in the PffBT4T-2OD:EH-IDTBR blend under illumination. However, the subsequent exciton dissociation appears to be slow (~ 15 ps). Rather than separating into free charges, a significant proportion of CT states remain bound and undergo geminate recombination. This differs from the ‘reference’ PffBT4T-2OD:PC₇₁BM system where charge separation is more efficient and the geminate recombination has been greatly suppressed. In other words, all separated charges undergo bimolecular recombination, which is in great contrast with the EH-IDTBR blend where not all CT states can separate. To understand the nature of CT states in PffBT4T-2OD:EH-IDTBR devices, the temperature-effect on charge generation and recombination were further investigated using pump push photocurrent (PPPC) spectroscopy by addressing the dynamics of CT states in these blend devices. The early-time (i.e. at a pump-push delay time < 100 ps) PPPC kinetics were found to resemble the CT state dynamics extracted from the TA data measured at the same temperature, implying that the same photophysical process governs the formation of CT states in thin films and devices. Arrhenius analysis fitting the early-time PPPC traces measured under different T determines an activation energy (E_a) for CT state dissociation to be on the order of 100 ± 6 meV.

3.2 Experimental details

All the materials were used as received without further purification. Substrates have undergone ozone treatment prior to the spin coating process. Device samples were fabricated by Dr Hyojung Cha.

Pristine PffBT4T-2OD, pristine EH-IDTBR and pristine PC₇₁BM films

PffBT4T:2OD was dissolved in DCB (concentration 10 mg ml^{-1}), which was then heated under 120°C for 1 h and under 60°C for 12 h until all PffBT4T:2OD has been dissolved. To prepare the films, the solution was spin coated onto the pre-cleaned and pre-heated glass substrates (80°C) at 1500 rpm for 60 s. EH-IDTBR was dissolved in DCB (concentration 10 mg ml^{-1}) and

was heated under 60 °C for 2 h. The solution was then spin coated onto the pre-cleaned glass substrates at 2500 rpm for 60 s. PC₇₁BM was dissolved in DCB (concentration 10 mg ml⁻¹) and was heated under 60 °C for 2 h. The solution was then spin coated onto the pre-cleaned glass substrates at 2500 rpm for 60 s.

Blend films and devices

A blend solution of PffBT4T-2OD and EH-IDTBR (D:A weight ratio of 1:1.2 and polymer concentration of 10 mg ml⁻¹) was prepared in DCB. A blend solution of PffBT4T-2OD and PC₇₁BM (D:A weight ratio of 1:1.4 and polymer concentration of 10 mg ml⁻¹) was prepared in CB and DCB (1:1 volume ratio) with 3 vol% DIO. Active layer solutions were stirred on a hot plate at 120 °C for 1 h and then at 60 °C for another 12 h. Thin films were prepared by spin coating each solution onto the pre-cleaned and pre-heated glass substrates (80 °C) at 1500 rpm for 60 s. Devices were fabricated based on the methods described in Chapter 2.

3.3 Results

3.3.1 Material properties

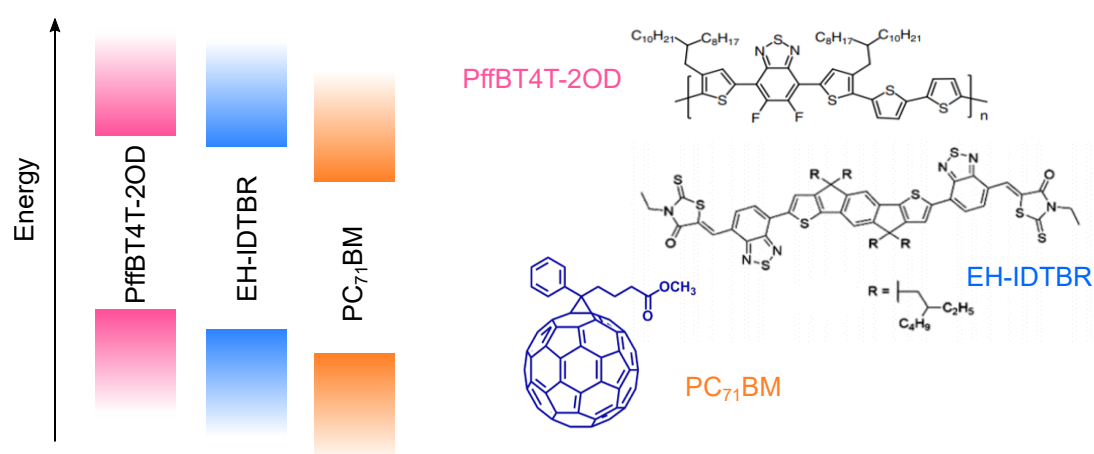


Figure 3.2 Left: Materials investigated including PffBT4T-2OD, EH-IDTBR and PC₇₁BM; Right: chemical structures of each material.

The two blend systems investigated herein are PffBT4T-2OD:EH-IDTBR and PffBT4T-2OD:PC₇₁BM, where PffBT4T-2OD acts as the electron donor, EH-IDTBR or PC₇₁BM acts as the electron

acceptor, respectively (see Figure 3.2 for chemical structures of each material and their band alignments).

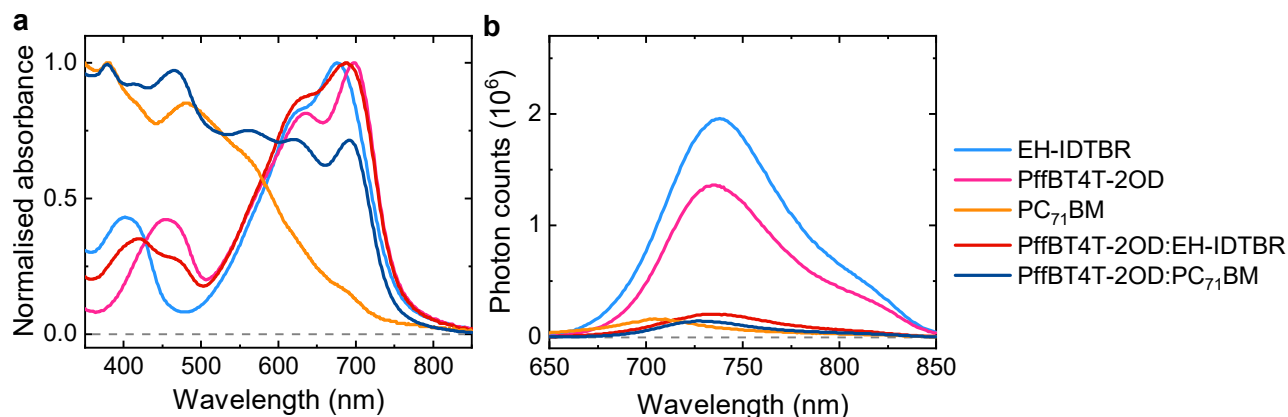


Figure 3.3 **a**, Normalised absorption spectra and **b**, Photoluminescence (PL) spectra for the studied materials and the corresponding blends: PffBT4T-2OD (pink), EH-IDTBR (light blue), PC₇₁BM (orange), PffBT4T-2OD:EH-IDTBR (red) and PffBT4T-2OD:PC₇₁BM (dark blue). For PL measurements, the PC₇₁BM film was excited at 400 nm while the rest of the samples were excited at 600 nm.

Figure 3.3a displays the absorption spectra for PffBT4T-2OD, EH-IDTBR, PC₇₁BM, and the two corresponding blends. PffBT4T-2OD shows a pronounced absorption peak at 700 nm, which is closely related to its high crystallinity and aggregation. This strong peak can only be achieved when the films were spin coated at a low spin rate from a hot solution which therefore allows the aggregation of PffBT4T-2OD during the film making process. EH-IDTBR exhibits an absorption peak at a similar wavelength of 675 nm. The absorption spectra of the two pristine materials are largely overlapped between 500 nm to 800 nm. Blending the two results in peak shifts in the absorption spectra, which may suggest the formation of CT states showing slightly red-shifted ground state absorption.²³ In PffBT4T-2OD:PC₇₁BM, the absorption spectrum of the blend resembles the sum of the two individual materials with PC₇₁BM mainly absorbing in the UV region, suggesting relatively weak CT state absorption. PL spectroscopy was employed here to probe the exciton dissociation efficiency. As shown in Figure 3.3b, EH-IDTBR shows the highest PL yield, followed by PffBT4T-2OD and then PC₇₁BM, peaking at 734, 738 and 704 nm, respectively. When PffBT4T-2OD was blended with EH-IDTBR, the PL yield was quenched by 85% with respect to PffBT4T-2OD and 89% with respect to EH-IDTBR. When blended with PC₇₁BM, a similar yield of 85% was observed. The PL quenching yields are relatively low compared to other well-mixed blends, which can be attributed to the high crystallinity and

aggregation of donor molecules, PffBT4T-2OD. While the similar quenching yield in two blends indicates that the morphology is likely to be dominated by the PffBT4T-2OD aggregation, with similar PffBT4T-2OD exciton dissociation efficiencies for both blends.²⁴

3.3.2 Identification of excited-state species

TA spectroscopy was employed to study the carrier dynamics in PffBT4T-2OD:EH-IDTBR and PffBT4T-2OD:PC₇₁BM blend films in the near-infrared (NIR) region (900 nm to 1400 nm), which serves as a great tool to investigate the excited state species and the mechanism for charge generation as well as recombination dynamics.

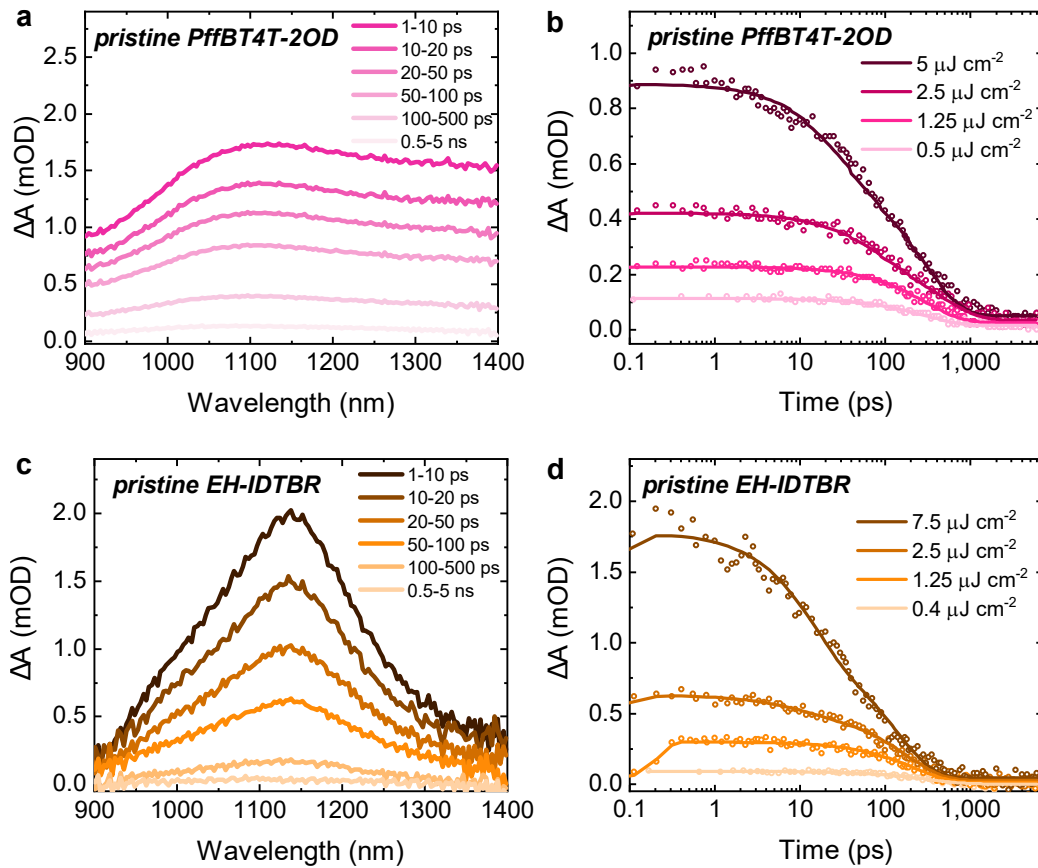


Figure 3.4 **a,c**: Transient absorption spectra for pristine PffBT4T-2OD and pristine EH-IDTBR thin films as a function of pump-probe delay time with a pump fluence of 20 $\mu\text{J cm}^{-2}$; **b,d**: Transient absorption kinetics for pristine PffBT4T-2OD and pristine EH-IDTBR thin films measured at various pump fluences. Both samples were excited at 700 nm under a continuous N₂ flux.

Figure 3.4a,c show the TA spectra of pristine PffBT4T-2OD and pristine EH-IDTBR thin films as a function of pump-probe delay time. PffBT4T-2OD films exhibit a broad photoinduced

absorption (PIA) peak centring at 1100 nm, whereas EH-IDTBR films exhibit a sharper and narrower PIA signal, peaking at 1150 nm. In both materials, the PIA features stay the same across the measurement time window up to 6 ns, indicating that only one excited state species is present under photoexcitation. Since the intersystem crossing is relatively slow in these materials, this PIA feature is thus attributed to singlet excitons. Figure 3.4b,d show the kinetics for pristine PffBT4T-2OD and pristine EH-IDTBR as a function of the pump fluence (only low fluences below $10 \mu\text{J cm}^{-2}$ are shown here). In both materials, the decay becomes faster as the excitation fluence increases due to exciton-exciton annihilation. When the fluence reaches below $1.25 \mu\text{J cm}^{-2}$, the kinetics do not vary as a function of the fluence anymore, indicating that the only recombination pathway probed now is the singlet exciton monomolecular decay back to the ground state. By fitting the kinetics at excitation fluences below $1.25 \mu\text{J cm}^{-2}$, the exciton lifetime for PffBT4T-2OD and EH-IDTBR were extracted to be 313 ± 8 ps and 328 ± 10 ps respectively, which are of similar magnitudes and maybe as a result of their similar optical gaps.^{25,26}

Turning to the TA spectra for the two blends, the spectra at 1 ps immediately after the excitation were compared against that observed for each pristine material. Under the excitation at 700 nm, only PffBT4T-2OD was excited in the PffBT4T-2OD:PC₇₁BM blend, whereas both PffBT4T-2OD and EH-IDTBR were excited in the PffBT4T-2OD:EH-IDTBR blend. In Figure 3.5, the PffBT4T-2OD:PC₇₁BM blend film shows a PIA peak at 1100 nm, consistent with the spectrum shape of PffBT4T-2OD exciton PIA (in Figure 3.4a). In the PffBT4T-2OD:EH-IDTBR blend, the initial PIA peak lies at 1125 nm, whereas the PIA peaks for pristine PffBT4T-2OD and pristine EH-IDTBR are at 1100 nm and 1150 nm, respectively. Additionally, the spectrum shape at 1 ps for the PffBT4T-2OD:EH-IDTBR blend differs from either one of the pristine materials' spectra. The difference could be resulting from the co-existence of both PffBT4T-2OD and EH-IDTBR excitons. As will be further discussed below, GA confirmed that the initial PIA peak at 1125 nm in this blend is indeed due to the combination of exciton absorption from both materials.

To understand the evolution of the excited state species in each blend, TA spectra were normalised and plotted as a function of pump-probe delay time in Figure 3.6. In the PffBT4T-

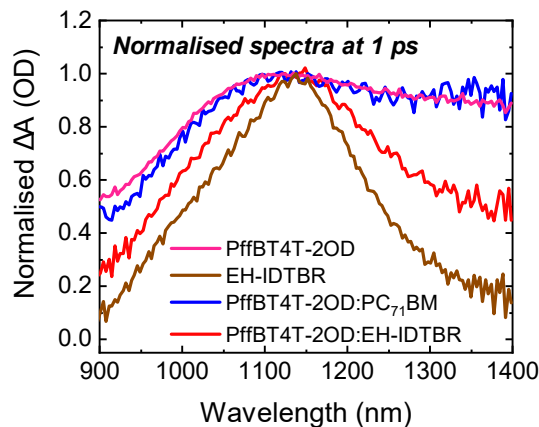


Figure 3.5 Normalised transient absorption spectra at the pump-probe delay time of 1 ps for: PffBT4T-2OD, EH-IDTBR, PffBT4T-2OD:EH-IDTBR, and PffBT4T-2OD:PC₇₁BM thin films. Samples were excited at 700 nm with a fluence of $10 \mu\text{J cm}^{-2}$.

2OD:EH-IDTBR blend, the initial PIA peak at 1125 nm gradually shifts to 1080 nm over 50 ps. As mentioned above, the peak at 1125 nm is due to absorption of both PffBT4T-2OD and EH-IDTBR excitons. Additionally, this is possibly due to the energy transfer between PffBT4T-2OD and EH-IDTBR, which will be discussed further in GA. The shift of the PIA peak to 1080 nm over 50 ps is likely due to the photoinduced electron and hole transfer between PffBT4T-2OD and EH-IDTBR. In the PffBT4T-2OD:PC₇₁BM blend, the PIA peak remains at 1100 nm, but the lower energy shoulder (from 1100 nm to 1400 nm) becomes narrower within the first 100 ps. The distortion in the blend spectra indicates the appearance of another species while PffBT4T-2OD excitons decay. As only PffBT4T-2OD was excited, charges formed through photoinduced electron transfer from PffBT4T-2OD to PC₇₁BM are the most likely species. After 100 ps, there is no further change in the spectra. Therefore, the PIA after 100 ps is attributed solely to charges since all excitons have decayed to the ground state.

The co-existence of donor and acceptor excitons in NFA OSC blends has also been reported in other non-fullerene based OPV systems. For example, Laquai and co-workers observed the co-existence of cations and anions in TA formed through electron and hole transfer in PTB7-Th:CDTBM under the co-excitation of both materials.²⁷ However, few studies indicate the individual dynamics of donor and acceptor exciton decay. Bearing this in mind, GA analysis was employed herein to decouple the spectrum features for individual excited state species and their corresponding kinetics in the following section.

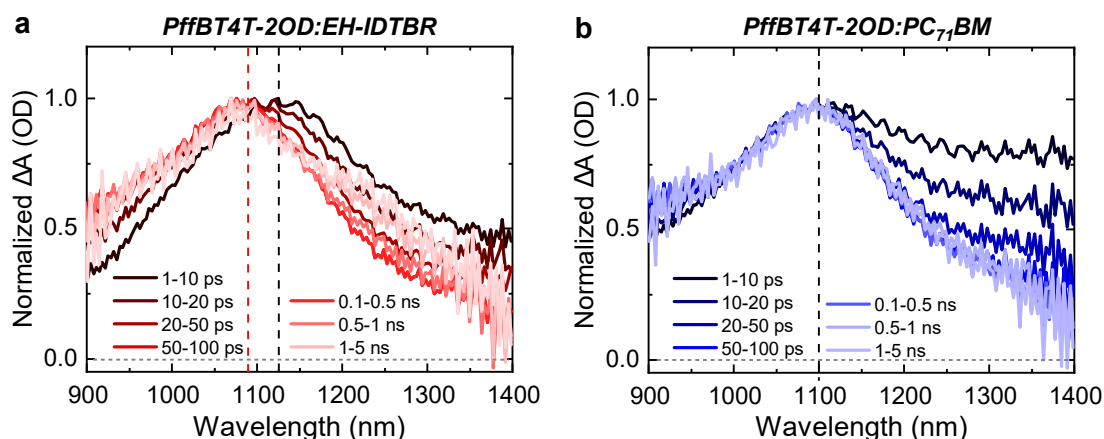


Figure 3.6 Normalised transient absorption spectra for **a**, PffBT4T-2OD:EH-IDTBR and **b**, PffBT4T-2OD:PC₇₁BM thin films as a function of pump-probe delay time. Both samples were excited at 700 nm with a fluence of $10 \mu\text{J cm}^{-2}$.

3.3.3 Charge generation and recombination dynamics

This section aims to provide a detailed analysis for carrier dynamics and an understanding of the underlying mechanism for charge generation and recombination in PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blends.

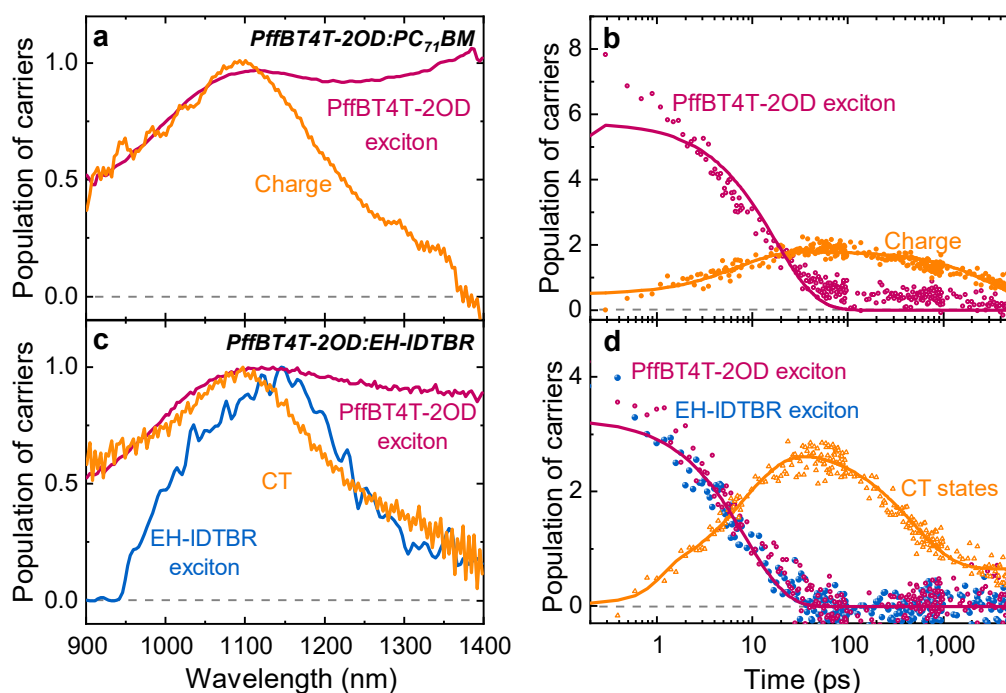


Figure 3.7 Genetic algorithm analysis summary including the spectral components for **a**, PffBT4T-2OD:PC₇₁BM and **c**, PffBT4T-2OD:EH-IDTBR thin films as a function of wavelength. The kinetics components are shown in **b**, for PffBT4T-2OD:PC₇₁BM and **d**, for PffBT4T-2OD:EH-IDTBR thin films as a function of pump-probe delay time.

The raw data shown in Figure 3.6 comprises multiple excited-state species with overlapping absorption features. To gain a better understanding of individual kinetics, these raw data were deconvoluted with GA. The validity of the GA results was tested by inputting different spectra as reference(s) and it was found out to be consistent regardless of the input reference spectra. Regarding the data discussed herein, the spectrum of the charges (orange line in Figure 3.7a) was fixed for the PffBT4T-2OD:PC₇₁BM blend, while for the PffBT4T-2OD:EH-IDTBR blend, the spectra of PffBT4T-2OD excitons and charge features were fixed (purple and green lines in Figure 3.7c). Figure 3.7a,b show the deconvoluted spectra and the corresponding kinetics for the PffBT4T-2OD:PC₇₁BM blend. The results clearly indicate the presence of two excited state species when PffBT4T-2OD was selectively excited at 700 nm. By comparing the deconvoluted spectra with the neat PffBT4T-2OD spectra in Figure 3.4, the broad spectral feature centred at 1100 nm was assigned to PffBT4T-2OD excitons. The other spectrum with a narrower absorption band at 1100 nm represents the charges, which are slowly formed over tens of ps. In summary, the corresponding kinetics in Figure 3.7b show one component with a fast decay rate and another component being gradually formed with a longer lifetime. The fast-decaying component is PffBT4T-2OD excitons since its absorption spectrum follows the shape of neat PffBT4T-2OD excitons as discussed above, and the apparent faster decay kinetics relative to that in neat PffBT4T-2OD TA spectroscopy ($\tau = 313$ ps) indicates the efficient exciton dissociation as a result of the electron transfer to PC₇₁BM. The other component is hence due to the charges that are generated as a result of electron transfer. Fitting the kinetics in Figure 3.7b yields a quenching time of 15 ps for PffBT4T-2OD excitons. A notable feature here is the slow formation of charges, which is in contrast with other well-intermixed OSC blend systems where charge generation is usually ultrafast (< 200 fs).^{28,29} However, the phase segregation can lead to slower charge generation due to the diffusion limit as observed in this case. The slow generation here may be associated with the relatively large domain size of PffBT4T-2OD aggregates in the PffBT4T-2OD:PC₇₁BM blend as reported.¹⁴

Turning to the PffBT4T-2OD:EH-IDTBR blend, Figure 3.7c,d present the deconvoluted spectra and kinetics for each species. Figure 3.7c indicates the presence of three distinct PIA spectra centred at 1080 nm, 1100 nm, and 1150 nm individually. Comparing the PIA spectra at 1100 nm and 1150 nm with the pristine material spectra (Figure 3.4), the broad PIA feature centring

at 1100 nm can be assigned to PffBT4T-2OD excitons and the narrower PIA at 1150 nm to EH-IDTBR excitons. As shown in the TA data (Figure 3.6), the PIA peak of the long-lived charges shifts to 1080 nm. The third component with an absorption peak at 1080 nm is thus assigned to the feature of charges. Turning to the kinetics in Figure 3.7d, both PffBT4T-2OD and EH-IDTBR excitons decay with the same quenching time of 9 ps, comparable to previous studies.⁸ The same decay time of both excitons would be consistent with both PffBT4T-2OD and EH-IDTBR excitons going through ultrafast energy transfer due to their similar exciton energies (1.73 and 1.75 eV, respectively, measured from the intersection between reduced absorption and PL spectra as shown in Figure A.5a,b of the Appendix). While the excitons decay, charges are generated with a similar lifetime of 10-15 ps, followed by a subsequent decay. It is worth noting that the yield of charges at 6 ns is relatively low in the PffBT4T-2OD:EH-IDTBR blend (only 25% of charges escape the recombination on this timescale and contribute to the long-lived charge generation). To further understand the recombination dynamics and to exclude the contribution due to the exciton-exciton or exciton-charge annihilation at high excitation fluences, TA measurements and GA under various excitation fluences were carried out for both blends.

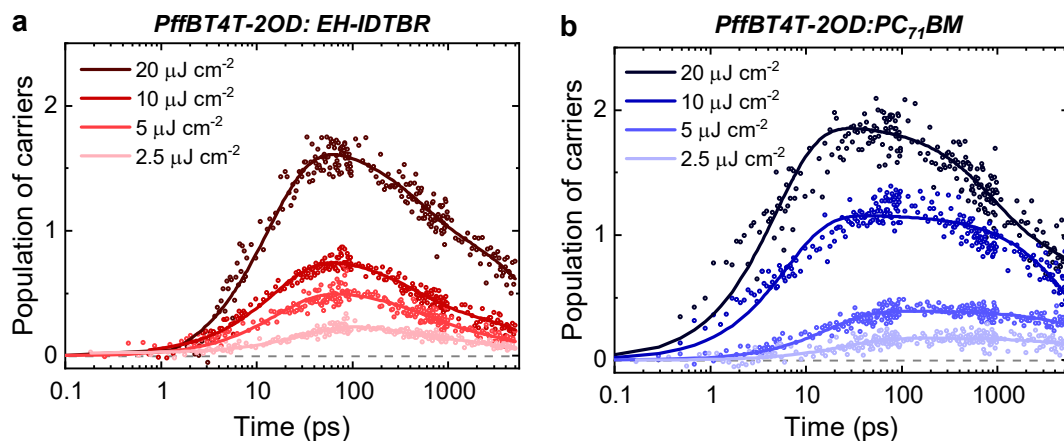


Figure 3.8 Transient absorption kinetics for **a**, PffBT4T-2OD:EH-IDTBR and **b**, PffBT4T-2OD:PC₇₁BM thin films at various excitation fluences including 2.5, 5, 10 and 20 $\mu\text{J cm}^{-2}$. Both samples were excited at 715 nm.

Figure 3.8b displays the charge dynamics at various excitation fluences extracted from GA for PffBT4T-2OD:PC₇₁BM. As the excitation fluence decreases, the amplitude representing the population of charge carriers drops proportionally (see also Figure A.1 in the Appendix). While the generation kinetics are mostly independent on the excitation fluence, the recombination kinetics are strongly fluence-dependent. At a lower excitation fluence, a much slower decay was

observed with more charges remaining across the measurement time scale. The charge lifetime in the PffBT4T-2OD:PC₇₁BM blend gradually increases from 0.8 ns to 15 ns as the fluence decreases from 20 $\mu\text{J cm}^{-2}$ to 2.5 $\mu\text{J cm}^{-2}$, in agreement with the bimolecular recombination model of charges as discussed in Section 1.5.2 and it hence indicates negligible geminate losses. Figure 3.8a displays the charge kinetics for PffBT4T-2OD:EH-IDTBR extracted from GA for TA carried out at various fluences. When compared to the PC₇₁BM based blend, here the charge generation time is slower (15 ps) at the same fluence of 2.5 $\mu\text{J cm}^{-2}$, however it is still much faster than the pristine exciton lifetimes of either PffBT4T-2OD or EH-IDTBR (313 ± 8 ps and 328 ± 10 ps, respectively), in agreement with the reasonably high PL quenching yields discussed above. The recombination kinetics exhibit fluence-independent behaviour, which indicates that the geminate recombination pathway dominates. In other words, the electron-hole pairs stay bound at the interface and recombine before having a chance to separate into free charges. A significant amount of charges were already recombined by 5 ns even at the lowest fluence (2.5 $\mu\text{J cm}^{-2}$). Comparing the kinetics of charges in these two blends at the same fluence, a higher recombination loss and faster decay kinetics were always observed in the PffBT4T-2OD:EH-IDTBR blend.

3.3.4 The binding energy of charge-transfer states

To isolate and address the nature of bound CT states, pump push photocurrent (PPPC) spectroscopy was employed here to study their dissociation dynamics and binding energy by probing the photo-induced current change in PffBT4T-2OD:EH-IDTBR devices.

When illuminating a bulk heterojunction OSC device, charge transfer across the D:A interface generates ‘hot’ CT states which can then go through relaxation to the low-lying localised/thermalised CT states or separate into free charge carriers, leading to a branching between the localised CT states and CS (charge-separated) states as stated in the Onsager-Braun model.^{30,31} The dissociation efficiency from CT states into free charge carriers directly impacts on the photocurrent in devices, where a higher dissociation efficiency can normally lead to a higher photocurrent. In PPPC measurements, the illumination of the pump pulse at 650 nm on the PffBT4T-2OD:EH-IDTBR device generates a reference photocurrent, J , which is proportional

to the product of the yield of free charge carriers and the charge extraction efficiency (η_{ext}). The later arrival of the IR push pulse at 2000 nm is then able to excite localised immobile charged states including CT states formed at short delay times and/or shallow trap states at long times. It is worth pointing out here that even though all the localised CT states can be excited to higher energy states by the push pulse, only those bound CT states can lead to an increase in the additional photocurrent as a result of their dissociation since the ‘weakly bound’ CT states are able to dissociate by themselves without the aid of such a push pulse. Here, the dissociation probability of those localised bound CT states into free carriers is defined as P_{dis} . As a result of this push pulse, extra photocurrent (ΔJ) is generated. The additional photocurrent, ΔJ , is linked with the product of the number of bound CT states (N_{CT}), the dissociation probability (P_{dis}), and the charge extraction efficiency (η_{ext}). Hence, the PPPc amplitude ($\Delta J/J$) reflects the population of bound CT states, though this may also be correlated with the population of trapped charges at longer pump-push delay times, as will be discussed in detail below.

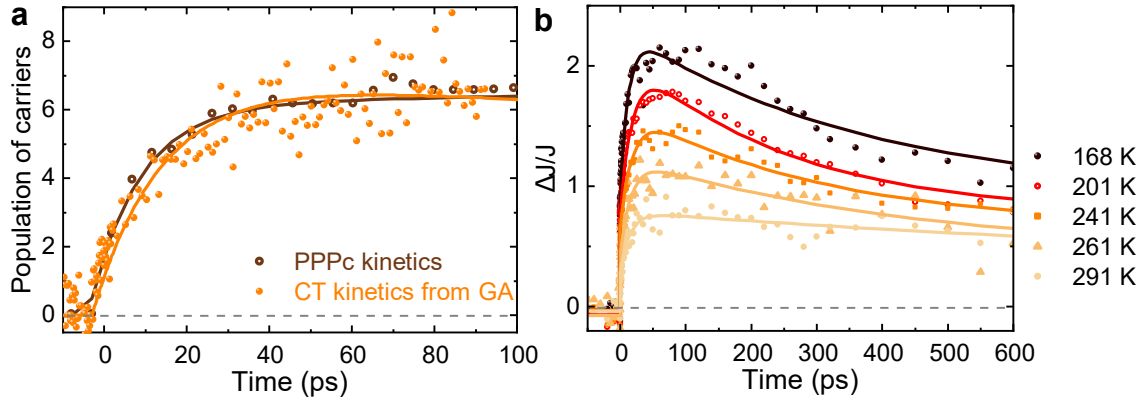


Figure 3.9 Pump push photocurrent (PPPc) characterisation for a PffBT4T-2OD:EH-IDTBR device. **a**, Kinetics for bound CT states from the TA data (extracted via genetic algorithm) for a PffBT4T-2OD:EH-IDTBR blend film (orange) and the PPPc kinetics for a PffBT4T-2OD:EH-IDTBR device (brown); **b**, PPPc measurements for a PffBT4T-2OD:EH-IDTBR device under various temperatures from 168 K to 291 K. The solid lines are multi-exponential fittings as a guide to the eye.

Varying the time delay between pump and push pulses allows the extraction of information on how the population of bound CT states would change as a function of the delay time.³² Figure 3.9a presents the PPPc kinetics for a PffBT4T-2OD:EH-IDTBR device measured at 298 K over a time window of 100 ps. The PPPc kinetics (brown dots) shows a slow rise with a time constant of 15 ps, which agrees well with the TA kinetics measured at the same T representing the CT states (orange dots) in Figure 3.9a. This rise is thus attributed to the formation of bound CT

states in both films (measured by TA) and devices (measured by PPPc). As mentioned before, the slow diffusion of excitons across the relatively large PffBT4T-2OD domains could be one of the reasons for this slow generation of CT states. Another possible reason could be the high activation barrier to form CT states, which will be examined later. In any case, the similarity between the TA kinetics and the PPPc kinetics indicates that the generation of CT states is governed by the same mechanism in films and devices.

To further understand if the CT state dissociation is thermally activated, PPPc measurements were carried out at different temperatures. As shown in Figure 3.9b, the $\Delta J/J$ amplitude increases by nearly three-fold when T was lowered from 298 K to 168 K, indicating the presence of more bound CT states at a lower T . As T varies, the branching ratio between the CT states and CS states also changes accordingly. Specifically, fewer CT states can overcome the energy barrier and hence not able to directly dissociate into free carriers at a lower T . This is also supported by the widely reported device photocurrent measurements in the literature, which shows a drop in photocurrent as T is decreased, attributed to less separated charges but more bound CT states.^{33,34} Therefore, the push pulse has a greater impact at a lower T since there are more bound CT states that can be pushed and dissociated, hence generating more photocurrent as indicated by the increase of the $\Delta J/J$ amplitude. Extending the measurement time window to 2 ns allows the probe of slower electronic processes. As shown in Figure 3.10a, the signal flattens out and even exhibits a growth after a few hundreds of ps. This delayed growth feature can not be due to the bound CT states since CT states have a shorter lifetime based on the previous TA analysis. Additionally, the push pulse at 2000 nm was previously reported to be able to excite trapped carriers.³⁵ Furthermore, the growth also happens on a similar time scale as the charge trapping. Therefore, this rise is most likely related to the de-trapping of charges.

For a more quantitative analysis of the T -dependence, an Arrhenius analysis was applied (Figure 3.10b). Based on the previous work,^{33,35} the amplitude at early times (at 2 ps) from Figure 3.10a were extracted and plotted against the reciprocal T (brown dots in Figure 3.10b). The dependence can be described by two activation energies. At the high T regime (> 200 K), the dominant process responsible for the T -dependence has an E_a of 100 meV, which is attributed to the binding energy of CT states. At the low T regime (< 200 K), the behaviour changes,

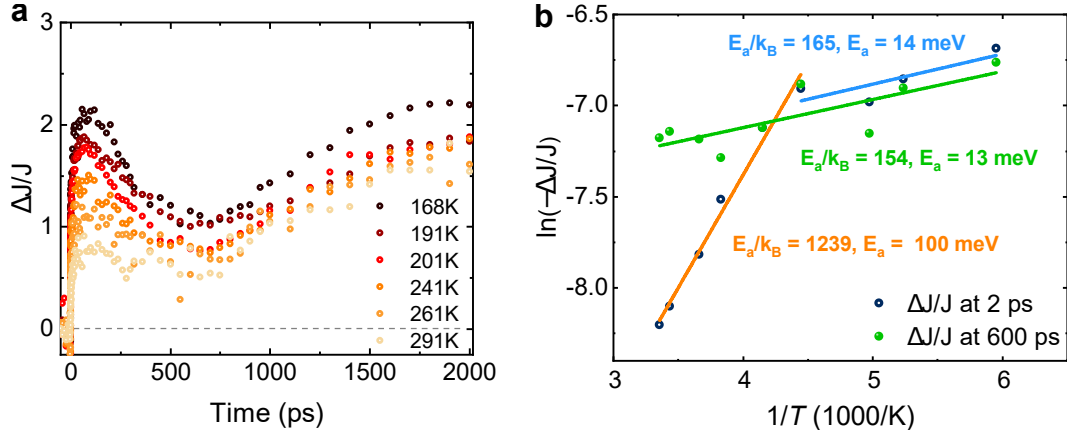


Figure 3.10 **a**, Pump push photocurrent kinetics for a PffBT4T-2OD:EH-IDTBR device under various temperatures from 168 K to 291 K; **b**, Arrhenius plot of the $\ln$ value of the $\Delta J/J$ amplitude at 2 ps (extracted from **a**) as a function of the reciprocal T represented by the circle symbols. Solid lines indicate the linear fitting based on the equation $\ln(-\Delta J/J) = -E_a \times K_B T$, where k_B is the Boltzmann constant. Linear fittings in the high- T regime (the orange solid line) and the low- T regime (the blue solid line) yield an activation energy of 100 and 14 meV, respectively.

and carrier extraction is limited by a different process with an E_a of 14 meV limiting carrier extraction, which is discussed further below.

Indeed, the T -dependence of the PPPc signal measured at 600 ps reveals a lower activation energy of 14 meV. Although the push pulse has a minimal effect on mobile carriers near the band edge, it is able to elevate free charge carriers from low energy states to mobilise them again and thus generate additional photocurrent. Therefore, this late-time signal is attributed to the de-trapping of separated charges. Furthermore, this E_a is the same as the 14 meV observed for the early time data at temperatures below 200 K. Therefore, it can be concluded that carrier trapping can be as important for charge separation as the CT state binding energy at low T .

3.4 Discussion

Evaluation of the CT state binding energy has been a long-standing question in application to polymer-polymer and polymer-fullerene OSCs, and various values have been reported based on different techniques.^{36–38} For example, G  linas et al. have reported a binding energy of 250 meV for CT states in the PFB:F8BT system using PL and TA over the nanosecond time window.³⁹ Gao et al. have also interpreted the activation energy for charge separation to be between

9-25 meV depending on the morphology of the P3HT:PC₆₀BM using external quantum efficiency (EQE) measurements.⁴⁰ Specifically, thermal annealing treatment reduces the activation energy from 25-9 meV, allowing efficient charge generation at room temperature. More recently, Neher and co-workers have reported the activation energy for charge formation from thermalised CT states to be around 25 meV using time-delayed collection field.⁴¹ These recent results from Gao et al. and Neher et al. both reveal a low activation energy of similar magnitudes or lower than the thermal energy at room temperature. However, these low activation energies do not agree with the fact that CT states are strongly localised electron-hole pairs. Further work is still needed to reconcile these contradicting observations. One must note that the activation energy values for the same OSC blend might also vary depending on the technique and the time scale selected, attributed to the fact that different techniques can probe the different subsets of CT states. In this chapter, the CT state behaviour was probed at relatively early times using a femtosecond laser pulse, which exclusively involves charge generation from bound states. This differs from values extracted from other techniques that usually address a steady-state material/device performance that can be controlled by a combination of electronic processes. In PffBT4T-2OD:EH-IDTBR blends, the dissociation energy of CT states was found to be of 100 meV, serving as the first experimentally determined binding energy for CT states in non-fullerene based OSCs with a small driving force for charge separation. This binding energy of 100 meV is of similar magnitude to other fullerene systems, which indicates that the smaller driving force has little effect on the CT state generation.³³ Similarly, in some fullerene-based blends, charge generation may also be independent of the energetic offsets.³⁵

Bringing together PL, TA, and PPPc results, a model for charge generation in PffBT4T-2OD:EH-IDTBR was proposed in Figure 3.11 which summarises the photophysical processes occurring in this blend. Upon illumination, (a) excitons are formed in both PffBT4T-2OD and EH-IDTBR. (b) Excitons dissociate at the D:A interface with a lifetime of 15 ps to form bound CT states. (c) A significant fraction of the initially formed CT states undergoes a rapid relaxation to localised bound states. (d) Another portion of the initially formed hot CT states directly separates into free carriers. (e) When the push pulse arrives, localised CT states can be excited to higher energy states to dissociate into free carriers. (f) The subsequent dissociation of CT states into free carriers happens with different efficiencies depending on the temperature. The activation

barrier was found to be 100 meV from T -dependent PPPc measurements. (g) A portion of CT states remains bound and recombines to the ground state via geminate recombination. (h) Free carriers transport including trapping, de-trapping, and hopping between different states where the trap depth is estimated to be 14 meV. (i) Free carriers can then undergo bimolecular recombination or get extracted to the electrodes. This model can also be applied to other OSC systems with low driving forces.

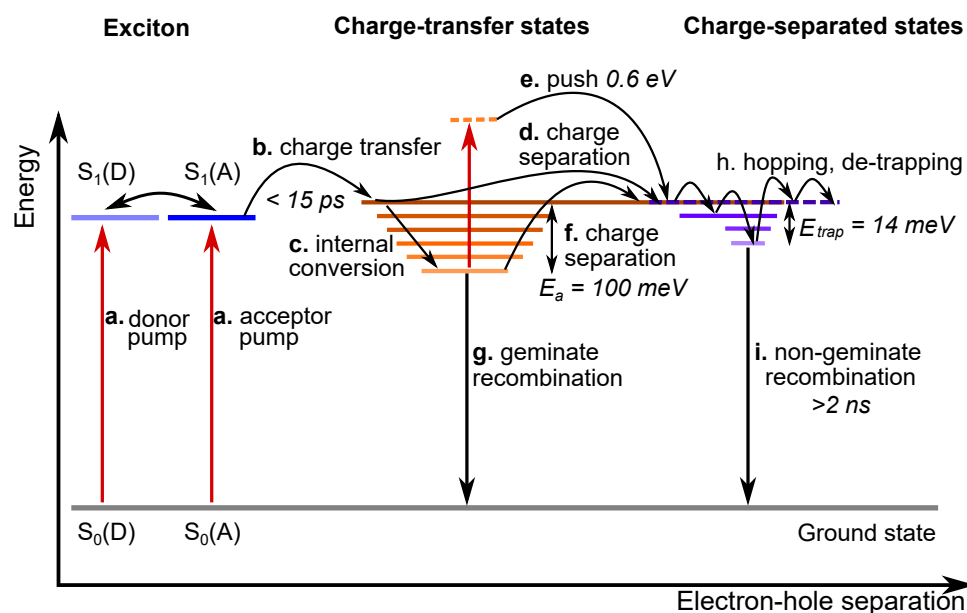


Figure 3.11 Photophysical model summarising the charge carrier dynamics for a representative low-offset organic solar cell blend, PffBT4T-2OD:EH-IDTBR.

Finally, based on the model proposed in Figure 3.11, the origin of the difference in device performance between these two blends as shown in Figure 3.1 are further discussed. In the PffBT4T-2OD:PC₇₁BM blend, efficient electron transfer occurs from PffBT4T-2OD to PC₇₁BM, generating free charge carriers under illumination, which agrees with what has been reported by others.⁴² This has led to a high J_{SC} of 18.7 mA cm^{-2} .⁴³ However, only 14 mA cm^{-2} was achieved when blending PffBT4T-2OD with EH-IDTBR. Under illumination, both electron and hole transfer between PffBT4T-2OD and EH-IDTBR can happen, leading to the generation of interfacial CT states as shown previously in TA measurements. In this case, most of the CT states remain bound at the interface without separating into free charges which go through geminate recombination eventually, therefore leading to a reduction of the overall photocurrent. Geminate recombination is detrimental to the device performance, especially the current density. Previous analysis for a wide range of non-fullerene based PffBT4T-2OD blends shows a linear

correlation between the amplitude of the remaining CT states/charge population in TA against the current density.⁸ Even though the low driving force in the state-of-the-art non-fullerene blends greatly suppresses the voltage losses, it sometimes comes with sacrificing the current density, like in the case of PffBT4T-2OD:EH-IDTBR. For future development, it is crucial to design systems where the trade-off between voltage and current can be eliminated, therefore exploring the possibility for charge generation in pristine materials with the help of field or energetics could be useful.

3.5 Conclusions

In summary, two transient spectroscopic tools, transient absorption (TA) and pump push photocurrent (PPPc) spectroscopy were employed to elucidate the charge carrier dynamics in a low energy offset non-fullerene based OSC blend PffBT4T-2OD:EH-IDTBR, which show overlapping donor and acceptor absorption profiles. TA analysis indicates the occurrence of rapid energy transfer between PffBT4T-2OD excitons and EH-IDTBR excitons following photoexcitation. The dissociation of excitons at the D:A interface generates CT states slowly with a time constant of 15 ps, which then suffer significant geminate recombination subsequently. The resemblance between the PPPc (carried out on devices) and TA (carried out on films) kinetics suggests that the same mechanism governs the charge generation in both blend films and devices. The main loss mechanism in the PffBT4T-2OD:EH-IDTBR blend is geminate recombination of CT states, hence leading to a lower current density. T -dependent PPPc suggests a relatively low CT state binding energy of 100 ± 6 meV for the dissociation of CT states. A rise in the PPPc amplitude at long pump-push delay time was also observed which has been attributed to the charge trapping with a trap activation energy of 14 ± 7 meV. Together with the reasonably high PL quenching yield, these results suggest that the main limiting factor in PffBT4T-2OD:EH-IDTBR performance is not the exciton dissociation but the ability of charges to escape the bound CT states at the D:A interface.

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Chapter 4

Correlating Charge-transfer State and Exciton Lifetimes with Material Energetics in Organic Solar Cells

Minimising the energy offset between the lowest exciton and charge-transfer (CT) states, i.e. the driving force for charge separation, is a widely employed strategy to minimise the energy losses ($E_g/q - V_{OC}$) in bulk heterojunction polymer:non-fullerene acceptor (NFA) organic solar cells, yet the impact of the minimised energy offset on CT state dynamics remains unclear. This chapter builds upon the previous chapter and continues to investigate the CT state dynamics, focusing on its correlation with material energetics. In this chapter, transient absorption spectroscopy was employed to determine exciton and CT lifetimes in a series of pristine NFA films and low energy loss polymer:NFA blends. The exciton decay is observed to show an energy gap law dependence, with lifetimes ranging from 51 ps to 328 ps. In contrast, the CT state lifetime is observed to show an inverse energy gap law dependence and gets shorter as the energy loss is reduced. This behaviour is assigned to increased mixing/hybridisation between these CT states and shorter-lived excitons as the energy offset ΔE_{CT-S_1} is reduced. This study highlights how achieving longer exciton and CT state lifetimes has the potential for further enhancement of organic solar cell efficiencies.

4.1 Introduction

As discussed in the previous chapter, state-of-the-art OSCs utilise a bulk heterojunction blend of electron donor (D) and electron acceptor (A) materials, which are usually polymer donors and non-fullerene acceptors (NFAs).^{1–4} Under illumination, excitons can dissociate at the D:A interface to form charge-transfer (CT) states.⁵ These CT states are key determinants of OSC device efficiencies, for example, the energy of the CT state (E_{CT}) has been correlated with the open-circuit voltage (V_{OC}) and voltage losses.^{6–8} Reducing the driving force for charge separation, i.e. the energy offset between the lowest singlet exciton (S_1) state and the CT state (ΔE_{CT-S_1}) can reduce energy losses, leading to a higher V_{OC} , but may also have a detrimental effect on the yield of free charges.^{9–12} In many D:A blends, monomolecular CT state recombination (*geminate recombination*) has been reported to be a key limitation on device photocurrent generation.^{13–15} The lifetime of these CT states is a key consideration for device function, influencing how efficiently these states can dissociate into free charges as well as the free charge recombination via these CT states.^{16–21} However, relatively few studies have addressed the parameters determining CT lifetimes in such blends. Herein, this chapter aims to address this issue, focusing in particular upon how CT state lifetime is influenced by material energetics and exciton lifetimes.

Analysis of non-radiative voltage losses in small molecule:fullerene OSCs have indicated that CT states can exhibit energy gap law decay kinetics, accelerating as the CT state energy is reduced.^{22,23} Such energy gap law behaviour for CT decay has been assumed in several other analyses of voltage losses in OSCs.^{24,25} Direct confirmation of this behaviour has been provided by Collado-Fregoso et al., who observed from transient absorption (TA) studies an acceleration of CT state decay lifetime with a decreasing CT state energy.²⁶ However the Collado-Fregoso study was limited to a series of relatively large driving force small molecule:fullerene blends with a highly dilute D:A ratio.²⁶ The OSC field is now increasingly focusing on lower energy offset, high-efficiency blends employing NFAs.²⁷ Several recent studies have indicated that a low energy offset between the exciton and CT state may result in the hybridisation or mixing of these states.^{24,28–30,30} This hybridisation or mixing can be expected to impact substantially upon the CT state lifetime, such that it may no longer exhibit energy gap law behaviour. This chapter

investigates this possibility, determining the impact of material energetics upon CT state lifetime in high-performance, low energy offset polymer:NFA OSCs. Specifically, TA spectroscopy was employed to investigate singlet exciton and CT decay dynamics for seven polymer:NFA blend films, which were prepared following the same processing methods as for optimised devices (see Table A.1 in the Appendix for chemical names and device performance). These results suggest a strong correlation between the CT state lifetime and V_{OC} , where an acceleration in CT state lifetime was observed with an increasing V_{OC} , revealing an ‘inverse energy gap law’ behaviour.

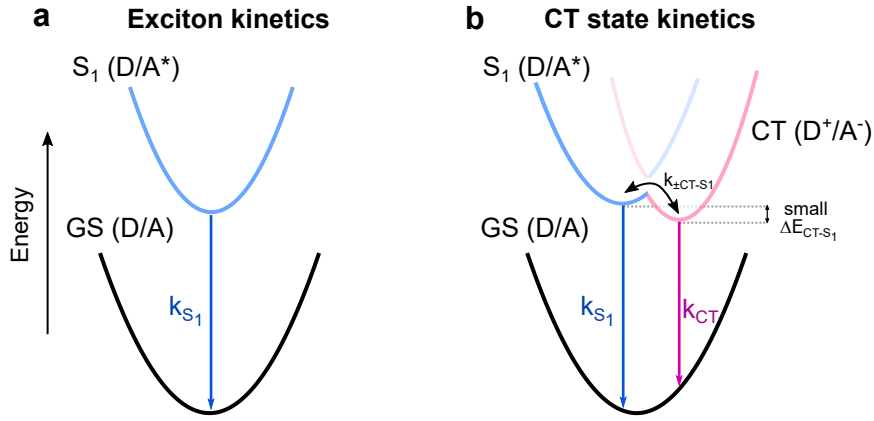


Figure 4.1 Potential energy surface diagrams illustrating **a**, singlet exciton S_1 decay to the ground (k_{S_1}) in a pristine organic semiconductor film and **b**, the impact of additional CT states in a low-offset polymer:non-fullerene blend. For low energy offset ΔE_{CT-S_1} blends, the S_1 and CT states can be expected to be in rapid thermal equilibrium as illustrated by $k_{\pm CT-S_1}$, as well as quantum mechanical hybridisation. Both k_{S_1} and k_{CT} include possible decay to lower energy triplet states, which is assumed to be irreversible, and both radiative and (predominately) non-radiative processes.

Figure 4.1 illustrates the impact of blend formation on the lifetime of singlet exciton and CT states in low energy offset polymer:NFA OSCs. In a pristine semiconductor, the rate of exciton decay (k_{S_1}) mostly depends on the coupling between the S_1 and ground state (GS), as depicted in Figure 4.1a. Whereas in a low-offset blend, the impact of quantum mechanical hybridisation and/or thermal mixing of these states on the CT decay dynamics is likely to depend strongly on the relative magnitudes of k_{S_1} and k_{CT} . In particular if $k_{S_1} > k_{CT}$, one would expect k_{S_1} to limit the CT lifetime when the mixing between the two states becomes dominant. As such mixing is expected to become stronger for smaller energy offsets, and consequently higher CT state energies, this mixing could thus give an opposite trend to the energy gap law behaviour reported previously,²⁶ therefore requiring a re-evaluation of the impact of CT lifetimes on non-radiative voltage losses in low energy offset OSCs. These two scenarios depicted in Figure 4.1

are often referred to as the two-state and three-state models, respectively. Detailed theoretical understandings and the validity of these models for relevant systems have been actively reported in the literature, which will not be discussed further in this thesis.^{28,31–33} However, it needs to be noted that for some NFAs, including in particular the crystalline, high-performance NFA Y6, the exciton decay rate k_{S_1} in pristine films is also the subject of conflicting recent reports,^{34,35} as addressed further below.

4.2 Experimental details

All the materials were used as received without further purification. Substrates have undergone ozone treatment prior to the spin coating process. Full details on device fabrication can be found in Chapter 2. Some of the samples investigated in this chapter were fabricated by Helen Bristow, Dr Hyojung Cha, Dr Jinho Lee and Dr Pabitra Shakya Tuladhar at Imperial College London. In addition, the raw transient absorption spectroscopy data on PffBT4T-2OD:FBR, PffBT4T-2DT:IDFBR, and PffBT4T-2OD:ITIC systems were provided by Dr Hyojung Cha.

Pristine IT-4F films

IT-4F was dissolved in DCB (concentration 10 mg ml^{-1}). The solution was heated under 120°C for 1 h and under 60°C for 12 h until all the materials has been dissolved. To prepare the films, the solution was then spin coated onto the pre-cleaned glass substrates at 2000 rpm for 60 s.

Pristine Y6 films

Y6 was dissolved (concentration 7 mg ml^{-1}) in CB/chloronaphthalene (CN) (99.5:0.5 vol%) solution. To prepare the films, the solution was spin coated onto the pre-cleaned glass substrates at 2000 rpm, followed by annealing at 100°C for 10 min.

Pristine PffBT4T-2OD films

PffBT4T:2OD was dissolved in DCB (concentration 10 mg ml^{-1}). The solution was heated under 120°C for 1 h and under 60°C for 12 h until all PffBT4T:2OD has been dissolved. To prepare the films, the solution was spin coated onto the pre-cleaned and pre-heated glass substrates (80°C at 1500 rpm for 60 s).

Pristine EH-IDTBR films

EH-IDTBR was dissolved in DCB (concentration 10 mg ml^{-1}) and was heated under 60°C for 2 h. The solution was then spin coated onto the pre-cleaned glass substrates at 2500 rpm for 60 s.

Pristine IDIC films

IDIC was dissolved in CF (concentration 10 mg ml^{-1}) and was heated 60°C for 2 h. The solution was then spin coated dynamically onto the pre-cleaned glass substrates at 2000 rpm to 3000 rpm. After spin-coating, the active layers were annealed at 140°C for 5 mins.

PBDB-T:EH-IDTBR blend films and devices

A blend solution of PBDB-T and EH-IDTBR (D:A weight ratio of 1:1 and a polymer concentration of 10 mg ml^{-1}) was prepared in CB. Active layer solutions were stirred on a hot plate at 120°C for 1 h and then at 60°C for another 12 h. Thin films were prepared by spin coating the dissolved solutions onto the pre-cleaned and pre-heated glass substrates (80°C) at 2500 rpm for 60 s, followed by annealing at 120°C for 10 mins.

PBDB-T-SF:IT-4F blend films and devices

A blend solution of PBDB-T-SF:IT-4F (D:A weight ratio of 1:1 and a polymer concentration of 10 mg ml^{-1}) was prepared in CB with 5 vol% DIO. The active layer solution was then spin coated at 2500 rpm for 60 s, followed by thermal annealing at 150°C for 10 mins.³⁶

PTQ10:IDIC blend films and devices

A blend solution of PTQ10:IDIC active layer (D:A weight ratio of 1:1.5 and a total concentration of 25 mg ml⁻¹) in CF, which were then deposited on substrates with a dynamic spin coating at 2000-3000 rpm. Following spin coating, the active layer was then annealed at 140 °C for 5 mins.³⁷

PfBT4T-2OD:FBR and PfBT4T-2OD:IDFBR blend films and devices

A blend solution of PfBT4T-2OD and FBR (D:A weight ratio 1:1.4 and a total concentration of 14 mg ml⁻¹) were prepared in CB:DCB (1:1 volume ratio) with 3 vol% of DIO, which was then heated on a hot plate at 110 °C for 3 h until the materials have been fully dissolved. Thin films and devices were made by spin coating the active layer solutions on preheated substrates.³⁸

4.3 Results

4.3.1 Charge-transfer state dynamics in a representative blend

As pointed out earlier, no systematic studies have been performed to address the CT state dynamics in low-offset OSCs. Nevertheless, it is of great importance to determine the CT state lifetime in high-performance, low driving force polymer:NFA blends, but at the same time remains challenging as the low energy offset between the S_1 and CT states makes the direct observation of CT state emission difficult.^{28,39} As such, TA measurements were employed herein to enable the separate tracking of both exciton and CT state dynamics, distinguishable by their distinct photoinduced absorption (PIA) peaks, as reported in previous works and also further discussed below.^{40–42}

As an example to illustrate how TA spectroscopy can probe the dynamics of S_1 and CT states separately, the characterisation for one of the blend systems, PBDB-T-SF:IT-4F, and its corresponding pristine IT-4F (the lower gap component in the blend) films are discussed in this section. Figure 4.2a shows the steady-state absorption and photoluminescence (PL) spectra for a pristine PBDB-T-SF film, a pristine IT-4F film and the blend film comprising a mixture of

the two materials. The pristine PBDB-T-SF thin film shows an absorption maxima situating at 625 nm, while the IT-4F thin film shows a red-shifted absorption peaking at 725 nm. As a result of the enhanced NIR absorption in IT-4F, the PBDB-T-SF:IT-4F blend was the first material system to demonstrate a power conversion efficiency (PCE) of 13% back in 2017.³⁶ In addition to the good device performance, the complementary absorption from PBDB-T-SF and IT-4F allows the selective excitation of the acceptor IT-4F, enabling the isolation of hole transfer kinetics (see further discussions below). Turning to the PL results in Figure 4.2b, exciting the pristine IT-4F film at 715 nm gives a rise to a pronounced and broad PL spectrum centring at 787 nm, corresponding to the emission from IT-4F S_1 states. Under the same excitation condition, the blend PBDB-T-SF:IT-4F shows a significantly reduced PL intensity and was found to be quenched by 97% relative to the pristine IT-4F film. The high PL quenching yield of 97% thus suggests an efficient dissociation of IT-4F excitons, implying a rather intermixed blend morphology, in contrast to the blend PffBT4T-2OD:EH-IDTBR examined in Chapter 3.

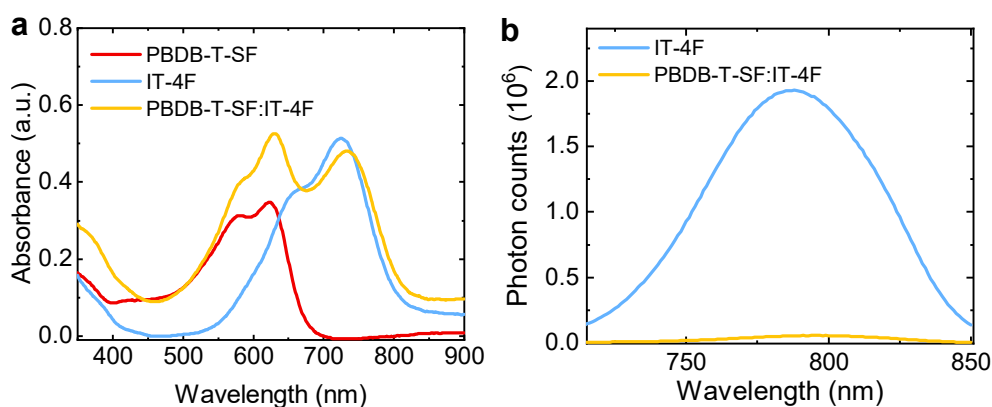


Figure 4.2 **a**, Steady-state absorption and **b**, photoluminescence spectra for a pristine PBDB-T-SF film, a pristine IT-4F film and a PBDB-T-SF:IT-4F blend film.

To directly assess the lifetime of S_1 and CT states, TA spectroscopy was carried out on the pristine IT-4F and the blend films. Herein, TA measurements only focus on the hole transfer kinetics for simplicity, where both the pristine IT-4F and the blend films were excited at 715 nm. As shown in Figure 4.3a, the pristine IT-4F shows a prompt photoinduced absorption (PIA) peak at 970 nm immediately following the excitation, which decays in amplitude as the pump-probe delay time increases but without any change in the spectrum shape. Moreover, this PIA decay becomes gradually accelerated as the pump fluence increases, as a result of the exciton-exciton annihilation. This PIA peak at 970 nm is therefore assigned to the lowest exciton S_1 state in IT-

4F. Under the lowest excitation fluence of $5 \mu\text{J cm}^{-2}$, this PIA signal exhibits a monomolecular decay with a lifetime of $51 \pm 3 \text{ ps}$ as shown in Figure 4.3c. In the PBDB-T-SF:IT-4F blend film, this PIA signal exhibits a peak shift from 970 nm to 1000 nm within $\sim 10 \text{ ps}$, assigned to hole transfer from IT-4F to PBDB-T-SF (apparent also as the fast decay phase for the blend film in Figure 4.3d. This ultrafast and efficient hole transfer is in good agreement with the high PL quenching yield of 97% shown in Figure 4.2b. The PIA peak at 1000 nm is thus assigned to CT/polaron absorption, and under a low excitation density, this feature also exhibits a monomolecular decay phase (at higher excitation densities, fluence-dependent and therefore bimolecular recombination kinetics are also observed), as further discussed below.

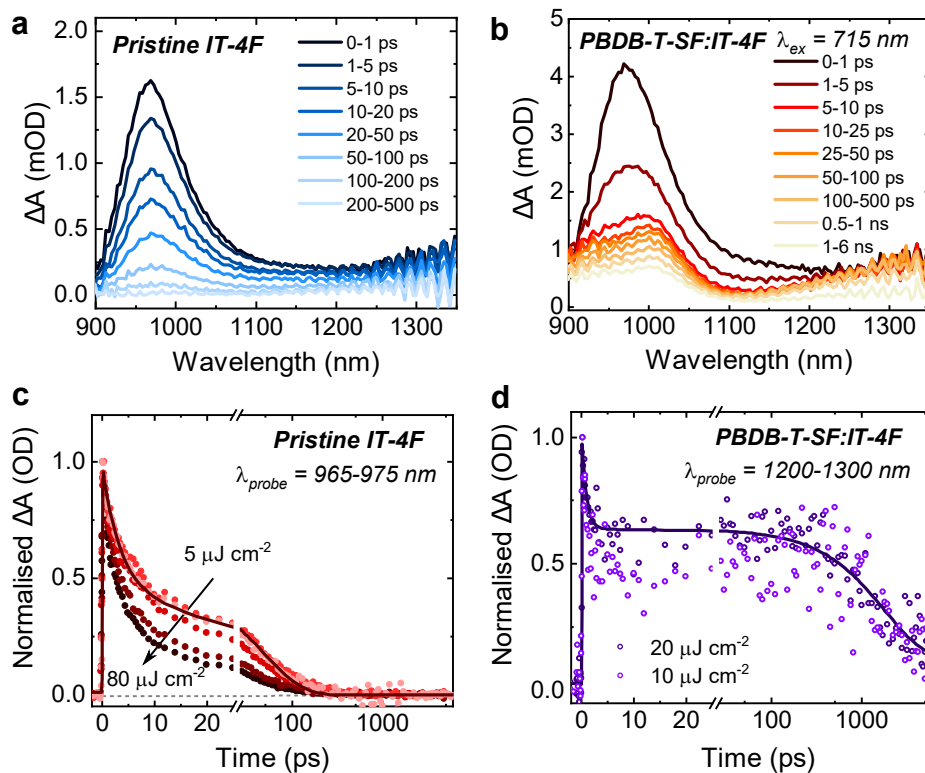


Figure 4.3 Transient absorption (TA) spectroscopy characterisation for a pristine IT-4F film and a PBDB-T-SF:IT-4F blend film. **a**, and **b**, TA spectra for **a**, a pristine IT-4F film and **b**, a blend PBDB-T-SF:IT-4F film; **c**, and **d**, TA kinetics under various pump fluences for **c**, a pristine IT-4F film and **d**, a blend PBDB-T-SF:IT-4F film. Both samples were excited at 715 nm.

The PIA signal in the blend (in Figure 4.3d) presents a biphasic decay, where the fast phase (at pump-probe delay time $< 10 \text{ ps}$) shows a minor fluence dependence and the slow phase (at pump-probe delay time $> 100 \text{ ps}$) shows no fluence dependence. Based on the previously discussed PIA peak assignment, the fast decay phase is thus assigned to the IT-4F exciton dissociation and the slow phase is the CT/polaron recombination. Clear CT state geminate recombination is

evidenced by these excitation fluence-independent TA kinetics at long pump-probe delay times (under low excitation fluences), thus eliminating the possibility of bimolecular recombination of free charges which would otherwise show a strong fluence-dependent behaviour as discussed in Section 1.5.2. Furthermore, the exciton decay has also been ruled out given the high PL quenching yield in the blends and the rapid peak shift in TA spectra upon blending, implying that exciton decay/dissociation occurs on a much faster timescale than the CT decay. Fitting the kinetics in Figure 4.3d with a biexponential function yields two lifetimes, among which the slow phase gives the CT lifetime of 1.74 ± 0.33 ns, which is more than an order of magnitude longer than the IT-4F exciton lifetime. It is worth noting that the CT state kinetics in the PBDB-T-SF:IT-4F blend film is accompanied with a significant drop in the TA amplitude, yet this device shows a reasonably high short-circuit current density of 19.3 mA cm^{-2} , suggesting that the built-in field in the device may play an important role in driving charge separation as reported previously in comparable low energy offset polymer:NFA blends.^{43,44}

4.3.2 Summary of exciton and charge-transfer state lifetimes

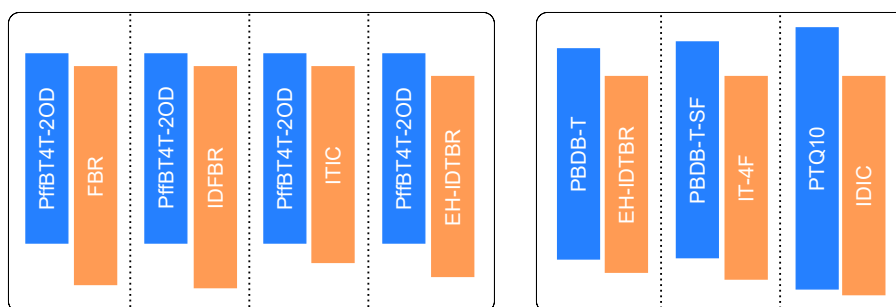


Figure 4.4 Summary of the polymer:non-fullerene blend systems investigated for their charge-transfer state lifetimes.

Extending the same characterisation method to all blends, analogous data were obtained for singlet exciton and CT state lifetimes in pristine and blend films respectively. Figure 4.4 presents a summary of the polymer:NFA blend systems investigated in this chapter including the PBDB-T-SF:IT-4F blend discussed above. Among these systems, the NFA exciton is the lowest energy exciton in the blend in most cases, with exciton and CT state dynamics monitored following direct excitation of the lower gap material in both pristine and blend films. These

NFAs exhibit optical band gaps from 1.5 eV to 2.0 eV, and include both relatively amorphous (e.g. EH-IDTBR) and crystalline (e.g. IDIC) materials, as reported in several studies.^{31,45,46}

Focusing first on exciton lifetimes in pristine films, for this material series, exciton lifetimes ranging from 51 ps to 328 ps were obtained. Figure 4.7a shows that these exciton lifetimes decrease with increasing optical band gaps, exhibiting a typical energy gap law behaviour. An analogous energy gap law behaviour has also been reported for a wide range of polymer excitons previously.⁴⁷ Similar tens to hundreds of picosecond for NFA exciton lifetimes have also been reported in other studies.^{33,48–51} In some cases, good agreement was observed between exciton lifetimes measured by TA (using low excitation density to avoid exciton–exciton annihilation) and time-correlated single photon counting (TCSPC) (see Figure A.2 in the Appendix on the EH-IDTBR exciton decay kinetics for example).

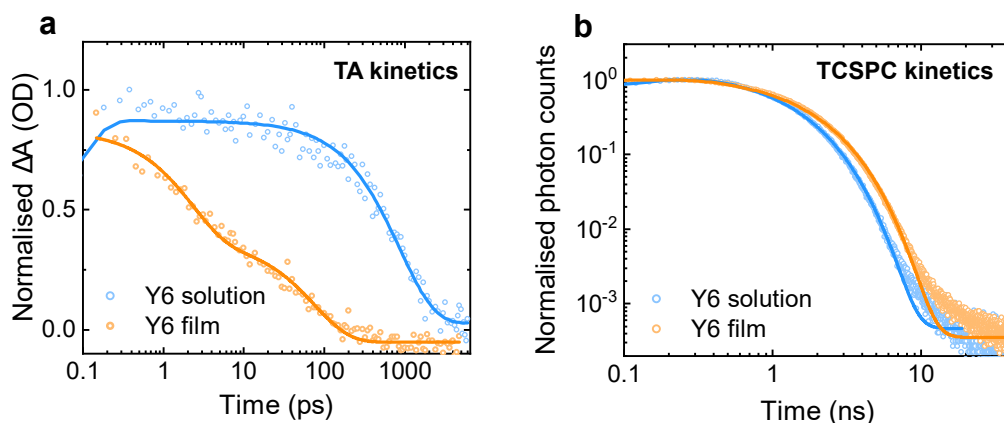


Figure 4.5 Exciton decay kinetics in Y6 solutions and films measured by **a**, Transient absorption spectroscopy, and **b**, Time-correlated single photon counting.

However in other cases, and most notably with the promising NFA Y6, widely divergent exciton lifetimes have been reported in the literature, ranging from ~ 50 ps to > 1 ns.^{34,35,52} To address this uncertainty, both TA and TCSPC measurements were employed to measure Y6 exciton decay times in solutions and pristine films. Typical TA decay kinetics are shown in Figure 4.5 for Y6 in a solution and as a pristine film (with full data sets in Figure A.3 of the Appendix), indicating an acceleration in decay kinetics from 1.5 ns in solution to 48 ps in the solid film. Comparison of UV-vis absorption spectra for Y6 in solutions and films also indicate substantive changes (as shown in Figure A.4a), indicative of strong intermolecular interactions in Y6 films, consistent with recent reports on the high Y6 crystallinity.³¹ In addition, a significant photocurrent was also observed in pristine Y6 homojunction OSC devices (with an external quantum efficiency

reaching nearly 5% in Figure A.4b of the Appendix), again indicative of strong intermolecular interactions. It must be noted that this lifetime change between film and solution was not observable in TCSPC kinetics in Figure 4.5b, most likely due to the limited time resolution of the TCSPC instrument (< 200 ps) preventing the observation of the fast decay phase observed in TA spectroscopy. The residual 1.5 ns TCSPC decay phase observed for Y6 films is therefore assigned to a small proportion of relatively amorphous/unaggregated Y6 molecules present in Y6 films. In summary, it can be concluded that the dominant exciton lifetimes in the pristine films studied herein range from 51 ps to 328 ps, exhibiting primarily non-radiative decay following energy gap law behaviour (as shown in Figure 4.7a).

Turning to the CT state kinetics observed in the blend films, TA spectroscopy measured CT lifetimes ranging from 0.27 ns to 1.74 ns as shown in Figure 4.6. In most cases, these were longer than the dominant exciton lifetimes in the corresponding pristine films of the lower gap materials, as observed for PBDB-T-SF:IT-4F detailed above in Figure 4.3c,d. For the shortest CT state lifetime of 270 ps, observed for PffBT4T-2OD:FBR (in Figure 4.6a), this lifetime was observed to be similar to the exciton lifetime observed for pristine PffBT4T-2OD films (of 313 ps).

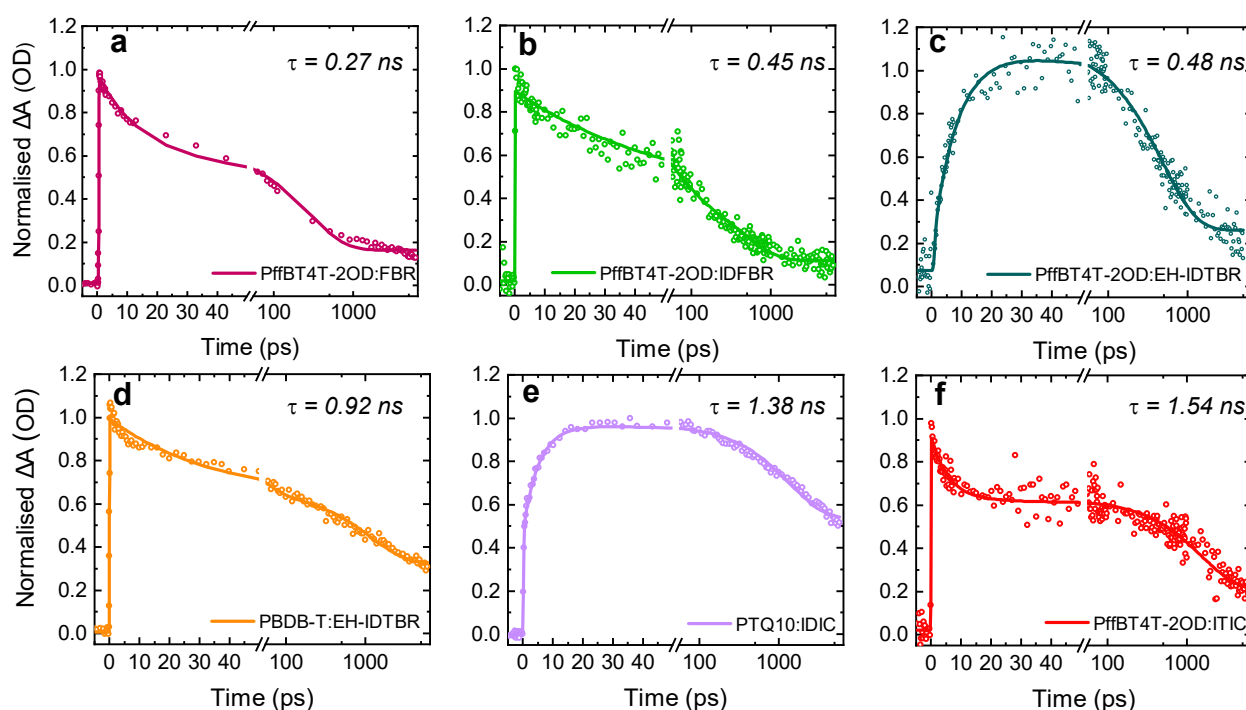


Figure 4.6 Transient absorption kinetics for the charge-transfer states in polymer:non-fullerene blends including **a**, PffBT4T-2OD:FBR, **b**, PffBT4T-2OD:IDFBR, **c**, PffBT4T-2OD:EH-IDTBR, **d**, PBDB-T:EH-IDTBR, **e**, PTQ10:IDIC, **f**, PffBT4T-2OD:ITIC.

Now turning to the correlation of the CT lifetime with blend energetics—for low energy offset polymer:NFA blends, the determination of CT state energies is particularly challenging, partly as for many blends the CT state emission can not be clearly resolved from the exciton emission, as previously discussed.^{25,28,39,53} In addition, the strong intermolecular interactions present in some films further complicate the determination of CT state energies (for example a shift in the highest occupied molecular orbital level for pristine Y6 and blend films of PM6:Y6 has been previously reported⁵²). On the other hand, it is well established that CT state energetics exhibits an approximately linear correlation with device V_{OC} .^{6,23} As such, V_{OC} was employed as a convenient assay of the trend in CT state energies among blends. Figure 4.7b plots the measured CT lifetimes versus device V_{OC} , showing that as V_{OC} increases from 0.84 V to 1.12 V, the CT state lifetime decreases from 1.74 ns to 0.27 ns. This observation of decreasing CT state lifetime with increasing V_{OC} , and therefore increasing CT state energy, is the inverse of that observed for the energy dependence of the exciton lifetime in Figure 4.7a. It is apparent that for this blend series, the CT state lifetimes do not exhibit energy gap behaviour, but rather the opposite trend, with the lifetime decreasing as the state energy increases.

In order to explore the origin of this ‘inverse energy gap law’ behaviour further, the CT state lifetime was further plotted against $E_g/q - V_{OC}$, with this energy difference being a proxy for the energy offset ΔE_{CT-S_1} between the S_1 and CT states. It is apparent from Figure 4.7c that a smaller energy offset leads to a faster decay of the CT state, with the lowest energy offset blend (PffBT4T-2OD:FBR) exhibiting a CT state decay with a similar time constant to the PffBT4T-2OD exciton observed in a pristine PffBT4T-2OD film. This dependence is indicative of increased mixing/hybridisation between CT and exciton states as their energy difference is reduced, as further discussed below.

Before discussing the implications of the trends of CT lifetimes with energetics observed in Figure 4.7b,c, the plot of CT state lifetimes versus V_{OC} was further extended to include the aforementioned Collado-Fregoso study on small molecule:fullerene blends.²⁶ As shown in Figure 4.8, the CT state lifetime shows a strong correlation with the device V_{OC} , with opposite trends observed in different V_{OC} regimes. In the low V_{OC} regime ($< \sim 0.9$ V), the CT state lifetime increases as the V_{OC} increases, as reported previously,²⁶ whereas in the high V_{OC} regime ($>$

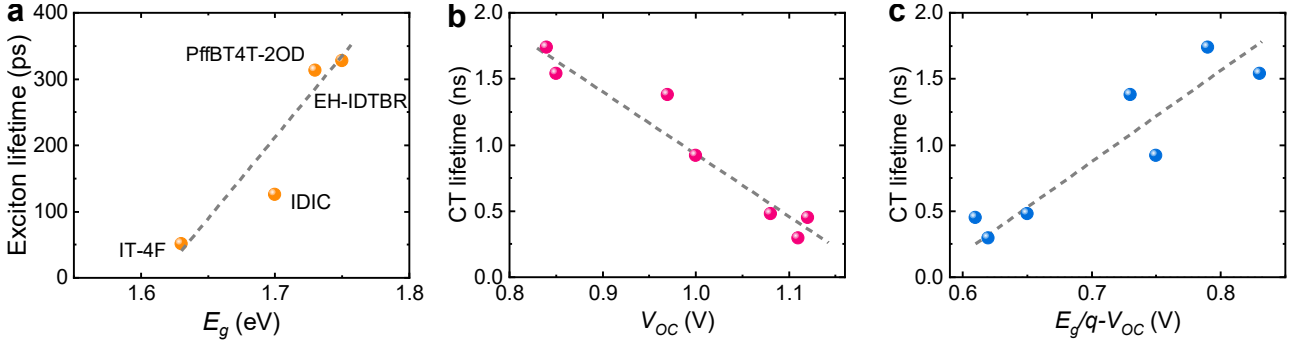


Figure 4.7 **a**, Exciton lifetimes plotted against their optical band gaps (PffBT4T-2OD and EH-IDTBR exciton lifetimes were taken from Chapter 3, and IDIC exciton lifetime was taken from the reference⁴⁸), and charge-transfer (CT) state lifetimes plotted against **b**, the open-circuit voltage, V_{oc} , and **c**, the total energy losses, $E_g - V_{oc}$, where q is the elementary charge.

~ 0.9 V), the CT state lifetime decreases as V_{oc} increases. The increase in CT state lifetimes with increasing V_{oc} observed in the low voltage regime can be understood in terms of an energy gap law dependence for k_{CT} , as reported previously.²³ Conversely the inverse behaviour in the high V_{oc} regime can be attributed to the concomitant reduction in the energy offset ΔE_{CT-S_1} with increasing V_{oc} (see Figure 4.7b). This results in increased mixing/hybridisation of the CT and exciton states, with the decay of the CT state becoming increasingly dominated by decay via the exciton decay pathway k_{S_1} . This conclusion is also supported by the work from Eisner et al. where the simulation results show that the hybridisation indeed leads to a shorter CT state lifetime in novel NFA based OSCs.²⁸ It is also consistent with reports that lowering the energy offset between S_1 and CT states enhances the radiative efficiency (i.e. a higher electroluminescence yield) in NFA based OSCs, as k_{S_1} will be typically dominated by a higher proportion of radiative recombination than k_{CT} as the S_1 state has a higher oscillator strength.

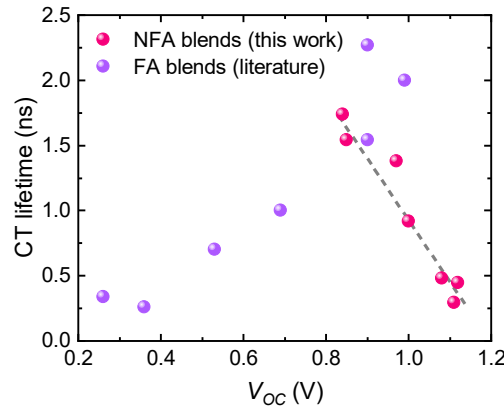


Figure 4.8 Charge-transfer (CT) state lifetimes plotted against the open-circuit voltage, V_{oc} , comparing this work and the reference.²⁶

4.4 Discussion

The conclusion herein that mixing of exciton and CT states results in a reduction in the CT state lifetime is likely to be in part determined by the relatively short exciton lifetimes observed for the lower gap materials, which in most cases are NFAs. PCBM, on the other hand, has a singlet exciton lifetime of > 1 ns in solid films,^{54–56} such that mixing of CT and PCBM S_1 exciton states would be unlikely to accelerate CT state decay. Furthermore, polymer donors are usually the lower gap component in polymer:fullerene OSCs. Similarly, most other polymer donors exhibit exciton lifetimes on the order of hundreds of picoseconds depending on their optical gaps,⁴⁷ again typically longer than the NFA exciton lifetimes observed herein. As such, in blends where the polymer donor is the lower band gap component, mixing of polymer exciton states with CT states is also less likely to cause a strong acceleration of CT state decay, unless the polymer donor has a short exciton lifetime of a similar magnitude to the NFA excitons here. As such, the strong reduction of CT lifetime as ΔE_{CT-S_1} is decreased, is likely to be particularly pronounced for blends where the lowest bandgap component has a relatively short exciton lifetime, as the polymer:NFA blends studied herein.

It has been previously pointed out that the short Y6 exciton lifetime limits the efficiency of hole transfer from Y6 excitons in the high-performing PM6:Y6 OSCs.⁵² The results herein suggest that this short exciton lifetime also accelerates the decay of CT states in this blend, due to either partial hybridisation of these states, or via thermally mixing driven $k_{\pm CT-S_1}$. In this regard, the relatively short NFA exciton lifetimes impact not only on the efficiency of exciton separation but also on the kinetics of both mono- and bi-molecular recombination processes proceeding via CT states. This emphasises the conclusion made previously by several studies,³⁴ that maximising the lifetime of NFA singlet excitons is a key challenge for the further enhancement of the performance of OSCs employing low band gap NFAs.⁵⁷ It can be further noted, as discussed above, that a particular challenge for some NFAs such as Y6 may be the undesirable acceleration of non-radiative exciton decay resulting from the intermolecular interactions generated by film formation (a process often referred to as ‘concentration quenching’).^{58–61}

4.5 Conclusions

In summary, this chapter elucidates the impact of material energetics on both exciton and charge-transfer (CT) state kinetics in low energy offset polymer:NFA blends with transient absorption spectroscopy. While the exciton lifetime in pristine materials and the CT lifetime in large offset systems follow the energy gap law with material energetics, the CT state lifetime in low-offset polymer:NFA blends exhibits an opposite trend, attributed to the mixing/hybridisation between these CT states and shorter-lived S_1 exciton states. Although suppressing the energy offset between S_1 and CT states is beneficial to reduce the energy/voltage losses, it can impose a limit on the CT state lifetime in cases when the exciton lifetime of the lower gap component is short. Designing acceptor materials with long exciton lifetimes in the solid state and eliminating the fast geminate recombination of CT states in low-offset systems can thus pave the way for further efficiency rises in polymer:NFA organic solar cells.

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Chapter 5

Orientation Dependent Molecular Electrostatics Drives Charge Generation in Homojunction Organic Solar Cells

This chapter is reproduced from ‘Orientation Dependent Molecular Electrostatics Drives Efficient Charge Generation in Homojunction Organic Solar Cells. *Nat Commun* **11**, 4617 (2020)’, with the permission of Springer Nature.¹ The use of a heterojunction blend between electron-donating and electron-accepting materials intrinsically limits the photovoltage and complicates the fabrication. This chapter shows that polycrystalline films of chemically identical alpha-sexithiophene (α -6T) molecules offer an alternative and the photoexcitation of α -6T films results in efficient charge generation. Spectroscopic studies show that charge generation happens in the bulk of the α -6T layer without the help of an electric field. Modelling and ambient photoemission spectroscopy studies attribute the origin of such efficient charge generation to the interfacial energy offset of 0.4 eV at the boundaries between α -6T domains with different orientations (standing and lying), promoting the formation of hybridised exciton/charge-transfer states at the interface. These findings open new avenues for the future of organic solar cell design where material energetics can be tuned through molecular electrostatic engineering and mesoscale structural control.

The results of this chapter come from a collaborative work. My contribution involves the overall coordination of the project, performing the absorption and photoluminescence measurements, as well as TCSPC and TAS measurements. The following results shown have been contributed by collaborators and their efforts are greatly acknowledged: Vasileios C. Nikolis fabricated all the samples and performed J-V and EQE measurements. Johannes Benduhn and Jonas Kublitski performed the sensitive EQE measurements. Felix Tahnack carried out the GIWAXS measurements. Yi-Chun Chin carried out the APS measurements. Gabriele D'Avino, Giacomo Londi, Luca Muccioli, David Beljonne and coworkers did the simulation studies.

5.1 Introduction

In Chapters 3 and 4, the photophysics of polymer:non-fullerene bulk heterojunction blends consisting of electron-donating (D) and electron-accepting (A) materials have been investigated. One of the main conclusions from the previous chapters is that the existence of an energy offset between D and A is crucial to facilitate fast and efficient exciton separation, hence the state-of-the-art OSCs often employ a blend of two materials with different electron moieties in order to provide an energy offset, as reported by others.^{2–5} However, optimisation of the blend morphology and preserving this morphology over time as well as finding the balance between long exciton diffusion length and efficient charge transport has always been challenging.^{6–12} Therefore, fabricating single photoabsorber material devices, as homojunction solar cells, remains as a highly attractive alternative, which offers the potential for relatively easy processing and morphology control, and could also lead to high photovoltages.¹³

Rare examples of such devices mostly rely on combining D and A moieties inside a single chemical entity as a large molecule or a copolymer with a D-A architecture.^{13–19} However, the complexity in synthesis and processing, as well as ultrafast recombination losses within such structures, has to date limited their further development.^{20,21} This chapter presents an alternative way of making homojunction OSCs, utilising an archetypal small molecule, alpha-sexithiophene (α -6T), which is widely known only as an electron donor and a p-type organic semiconductor, i.e. it is devoid of the D-A dual nature. It was previously shown by Duhm et al. that controlling the orientation of α -6T can lead to different ionisation potentials as a result of long-range intermolecular electrostatic interactions.²² However, the tantalizing idea of using molecular electrostatics engineering to fabricate efficient photovoltaic devices has not been realised in practice until this work.

This chapter shows the efficient charge generation in homojunction OSCs based on α -6T with mixed orientations of standing and lying molecules (relative to the substrate) in the absence of an electron-accepting material, reaching an EQE of up to 44% and a V_{OC} of 1.61 V. Transient absorption (TA) spectroscopy shows that photoexcitation of pristine α -6T films with mixed orientations leads to efficient and ultrafast charge carrier generation from excitons, indicating that charge generation happens in the bulk of the pristine α -6T. Using specific processing

parameters, films with two molecular orientations, mainly standing and mainly lying, were fabricated and an offset of 0.4 eV between the ionisation potentials at these two orientations were measured by ambient photoemission spectroscopy. Further theoretical calculations confirm the presence of this energy offset and reveal that this energy offset is dictated by intermolecular electrostatic interactions persisting at standing:lying grain boundaries, where the formation of low-lying excitation with hybrid intramolecular/charge-transfer character was promoted.

5.2 Experimental details

Sample fabrication, device characterisation and voltage losses analyses were carried out by Vasileios Nikolis (as shown in Figure 5.1, Figure 5.9 and Table A.3) and GIWAXS measurements were done by Felix Talnack at TU Dresden (Figure A.8). Ambient photoemission spectroscopy measurements were carried out by Yi-Chun Chin at Imperial College London (Figure 5.8). Theoretical calculations were carried out by Gabriele D’Avino and co-workers at Grenoble Alpes University (Figure A.9).

5.2.1 Sample fabrication

For both film and device fabrication, all the materials were purified twice in-house by vacuum gradient sublimation.

Film fabrication

Thin film samples with a thickness of 60 nm were prepared on ITO substrates (Thin Film Devices, USA). Three different fabrication methods were used to achieve the desired orientation. For the standing orientation, α -6T molecules were deposited at a low evaporation rate (of $0.1 \text{ \AA s}^{-1}$) on a heated substrate at 100°C . For the lying orientation, a thin layer of copper iodide (CuI) was first deposited on top of the ITO substrate as a template layer, α -6T molecules were then deposited on top of CuI at room temperature. For the mixed orientation, α -6T molecules were deposited at a high evaporation rate (of $1 \text{ \AA s}^{-1}$) at room temperature.

Device fabrication

Following the processing methods described in Section 2.1.2, α -6T molecules were deposited at a high evaporation rate (of $1 \text{ \AA s}^{-1}$) at room temperature to yield mixed orientations. A buffer layer of 10 nm and a layer of BPhen (8 nm) were deposited on top of the α -6T, followed by a silver (Ag) electrode of 100 nm. Various buffer layers were used to optimise the device performance including rubrene, C545T, DBzA, TCTA, TPBA, TBPe, TPBI (see Nomenclature for full chemical names). The active area of the device was 6.44 mm^2 , defined as the overlap between the anode and the Ag cathode. These devices were encapsulated in a nitrogen atmosphere with a transparent encapsulation glass using UV-hardened epoxy glue.

5.2.2 Device characterisation

Current-voltage measurements

Current-voltage measurements were performed on encapsulated devices in ambient conditions using a source measurement unit (SMU 2400 Keithley, USA) and a simulated AM1.5G illumination (16S-003-300-AM1.5G sunlight simulator, Solar Light Co., USA). Masks were used to minimise edge effects. A silicon photodiode (Hamamatsu S1337, calibrated by Fraunhofer ISE) was used as a reference.

External quantum efficiency (EQE) measurements

EQE measurements were carried out with a Xenon lamp (Oriel Xe Arch-lamp Apex, Newport, USA), a monochromator (Cornerstone 260 1/4m, Newport, USA), an optical chopper, and a lock-in amplifier (SR 7265, Signal Recovery, USA). An aperture mask (2.78 mm^2) was used.

Sensitive EQE (sEQE) measurements

sEQE measurements were carried out with a quartz halogen lamp (50 W), which was chopped at 140 Hz and coupled into a monochromator (Newport Cornerstone 260 1/4m, USA). The photocurrent of the device under the short-circuit condition was fed into a pre-amplifier and

then analysed with a lock-in amplifier (Signal Recovery 7280 DSP, USA). The time constant of the lock-in amplifier was set to 500 ms and higher amplification of the pre-amplifier was used to resolve low photocurrents. The sEQE was determined by dividing the photocurrent of the device by the flux of the incoming photons, which is obtained with calibrated silicon and indium gallium arsenide (InGaAs) photodiodes.

5.2.3 Ambient photoemission spectroscopy

Ambient photoemission spectroscopy was carried out with an APS04 system (KP Technology). During the measurement, a UV light (4.4 eV to 6.2 eV) was used to illuminate the samples. The photoemitted electrons then interact with air and generate radicals which are further collected by the positively biased tip. The energy levels were obtained by subtracting linearly from the cube root photoemission intensity to the baseline.

5.2.4 Grazing-incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS measurements were performed at the XRD1 beamline at the ELETTRA Synchrotron in Trieste. The thin films were illuminated under a grazing angle of 0.13° and the diffraction pattern was recorded with a PILATUS 2M area detector, placed at 35 cm behind the samples. The measurements were performed at a beam energy of 12.4 keV. The data were analysed with the WxDiff software.

5.3 Results

5.3.1 Device performance

α -6T is well known as an electron-donating material and has been paired with various fullerene and non-fullerene acceptors in organic solar cells.^{23–27} Herein, a homojunction OSC based on α -6T was fabricated, where the photon absorption and charge generation have been expected to be facilitated by the α -6T layer itself. The best performing device employs an architecture

of Glass/ITO/ α -6T/rubrene/BPhen/Ag as shown in Figure 5.1a, where the thickness of each layer was denoted in the bracket. Following the well-established processing parameters from the literature,²⁶ α -6T molecules adopt a mixed orientation including both standing and lying orientations (see further discussions below on each orientation). This device shows a remarkably high V_{OC} of 1.61 V, together with a J_{SC} of 3.6 mA cm⁻² and a FF of 50.2%, leading to an overall PCE of 2.9% (Figure 5.1b) and an EQE of 44%.

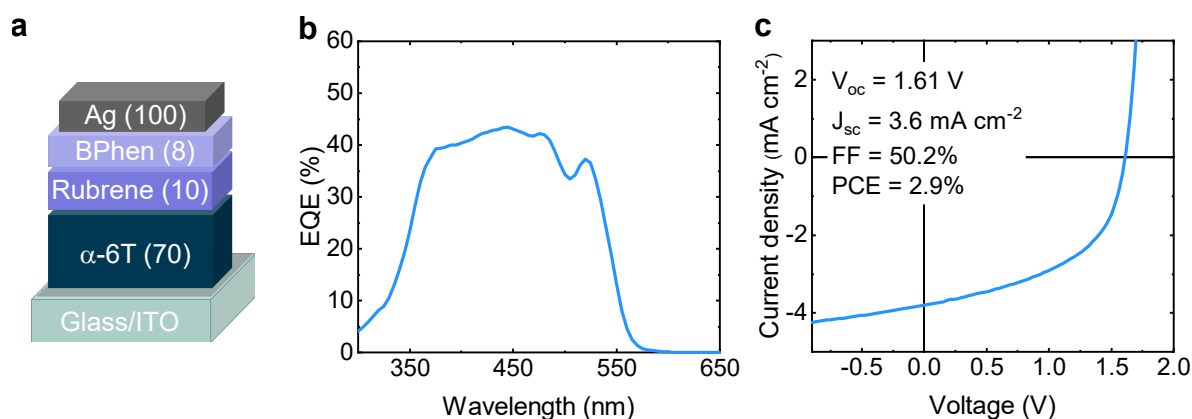


Figure 5.1 Device architecture and performance. **a**, Device architecture for an α -6T based homojunction organic solar cell (OSC): Glass/ITO/ α -6T/Rubrene/BPhen/Ag. The number in the bracket indicates the thickness of each layer in nanometers. **b**, External quantum efficiency spectrum and **c**, Current-voltage characteristics for an α -6T homojunction OSC. (Data measured by Vasileios C. Nikolis)

In the best performing devices, rubrene was used as a buffer layer (BL) to improve the selectivity but is not expected to facilitate charge generation across the α -6T/rubrene interface. The LUMO energy level mismatch between α -6T and rubrene (2.8 and 3.2 eV respectively) already suggests that charge generation is unlikely to happen across this interface,^{28–32} but tunnelling may play a role as a result of the low thickness (10 nm) of the rubrene layer. This is supported by sensitively measured EQE (sEQE) measurements which do not show any feature of subgap absorption, implying the absence of low-energy CT states originating from the α -6T/rubrene interface (See Figure 5.9c in Section 5.4). Further measurements including photoluminescence (PL) and TA targeting at the α -6T/rubrene bilayer film were also carried out to further substantiate this point and will be discussed later.

5.3.2 Mechanism of charge generation

While the spectroscopic studies of photoexcitation in α -6T thin films date back to the 1990s,^{33,34} the photophysical mechanism of charge generation in the α -6T based homojunction OSC remains unexplored. To investigate the mechanism of charge generation in these devices, TA spectroscopy was carried out on α -6T devices and pristine α -6T thin films fabricated on ITO substrates.

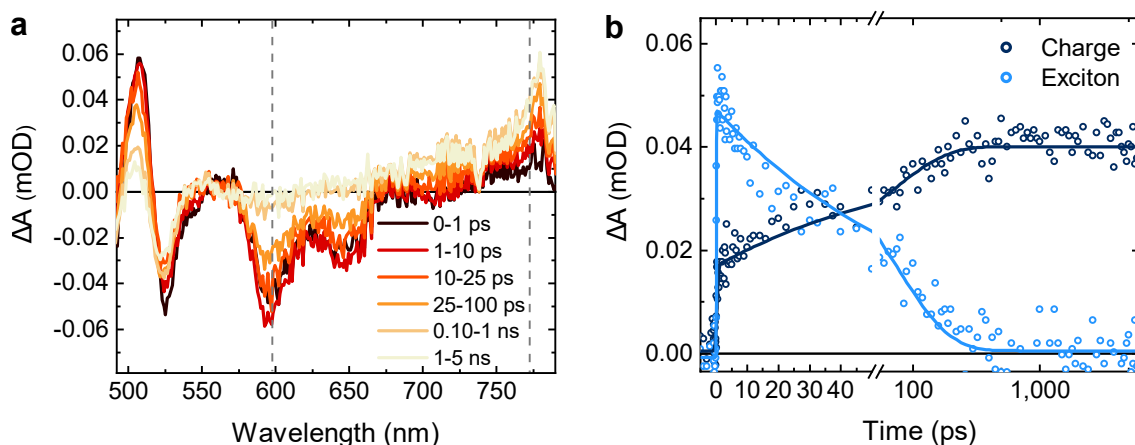


Figure 5.2 Transient absorption (TA) spectroscopy characterisation for a pristine α -6T film. **a**, TA spectra as a function of pump-probe delay time and **b**, TA kinetics at 593 nm (light blue) and 780 nm (dark blue) representing stimulated emission and photoinduced absorption signals respectively, where the lifetimes of exciton decay and charge generation can be extracted from individual dynamics. The solid lines are monoexponential fitting for the raw data (dots). A low ($5 \mu\text{J cm}^{-2}$) excitation fluence was used to minimise exciton-exciton annihilation and other bimolecular recombination processes). Samples were excited at 450 nm.

Figure 5.2a shows the TA spectra of an α -6T film fabricated with the same processing conditions as the α -6T based homojunction OSC described above. In these spectra, three negative bands peaking at 525 nm, 593 nm and 650 nm are apparent, as well as two sharp positive bands at 508 nm and 780 nm. In previous studies, the features at 525 nm and 508 nm have been assigned to electroabsorption (EA) signals associated with CT states.³⁵ Independently measured EA spectrum of the α -6T homojunction OSC (Figure A.7 in the Appendix) validated the resemblance between the EA and TA spectra, which further suggests that the strong signal at 525 nm and 508 nm in TA arises from the initially generated excitons having a high degree of CT character, most likely associated with the hybridisation between exciton and CT states (see further discussions below). The observation of similar EA signals has been reported for D:A bulk heterojunction OSCs.^{36,37} The 780 nm positive absorption feature has previously been assigned to α -6T charges by Watanabe et al. and others.^{33,38} Comparison between the absorption and

PL spectra (Figure A.6) indicate that ground state bleaching (GSB) is also likely to contribute to the 525 nm feature, whilst the negative features around 593 nm and 650 nm can be assigned to the stimulated emission (SE) from α -6T singlet excitons.

It is apparent from Figure 5.2b that the time evolution of the TA signal implies a decay of the negative exciton features at 593 nm and 650 nm, together with a partial decay of the 508 nm EA feature and a growth of the 780 nm signal attributed to charge carrier absorption. Fitting the kinetics at 593 nm with a monoexponential decay gives a lifetime of 71 ps, assigned to the exciton decay time (Figure 5.2b, light blue circles). The kinetics at 780 nm exhibits a prompt growth within the instrument response (< 200 fs), followed by a slower growth, with fits to this slower phase yielding a monoexponential rise time of 69 ps (Figure 5.2b, dark blue circles). The agreement between the exciton decay lifetime (measured at 593 nm) and charge absorption growth time (measured at 780 nm) indicates that charge generation correlates with the exciton decay. The observation of EA absorption features at the early time suggests that the initially generated α -6T excitons exhibit at least partial CT state character, as discussed further below. The decay of this EA feature on the timescale of free carrier generation is most likely associated with field screening as charges localise in separate domains.

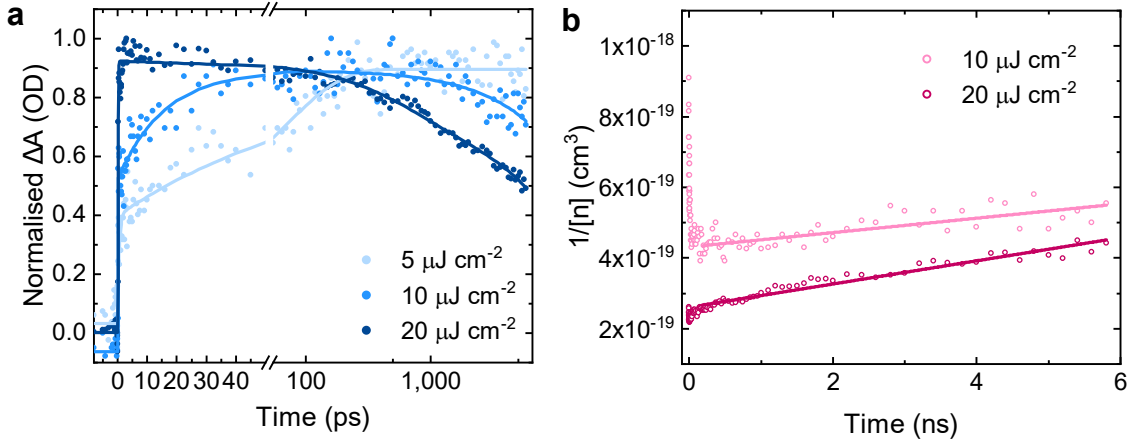


Figure 5.3 Characterisation of the charge kinetics. **a**, Transient absorption kinetics for the charges (at 780 nm) in an α -6T film with mixed orientations excited with various fluences including 5, 10 and 20 $\mu\text{J cm}^{-2}$ at 450 nm. **b**, Analysis of the bimolecular recombination rate constants from the TA decay at 780 nm. For a bimolecular recombination following the rate equation of $\frac{d[n]}{dt} = -k[n]^2$, the rate constant (k) can be extracted from the slope by plotting $\frac{1}{[n]}$ against t (shown in open dots). Solid lines are the linear fittings to the raw data in open dots.

To further strengthen the spectra assignment, TA measurements with different excitation fluences ranging from 5 $\mu\text{J cm}^{-2}$ to 20 $\mu\text{J cm}^{-2}$ were carried out for the pristine α -6T film (Figure

5.3a). The kinetics at 780 nm exhibits a strong dependence on the excitation fluence, with decay dynamics accelerating at higher fluences, characteristic of bimolecular recombination. By plotting the reciprocal of the excitation density, $[n]$, against the time, t , the bimolecular rate constants at various excitation fluences can be determined from the value of the corresponding slopes. As shown in Figure 5.3b, the slopes were fitted to be $1.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ respectively under excitation fluences of 10 and $20 \mu\text{J cm}^{-2}$. Here, the slightly higher bimolecular rate constant at $20 \mu\text{J cm}^{-2}$ is in agreement with the previously reported diffusion-limited recombination model involving an exponential tail of trapped charges, where the diffusion constant can be dependent on the carrier density.³⁹ These values are of similar magnitudes or slower than that observed in the state-of-the-art bulk heterojunction non-fullerene based OSCs,^{40–42} suggesting that using a single photoabsorber material in homojunction OSCs does not accelerate the bimolecular recombination rate. The fluence dependence, therefore, suggests that this PIA feature at 780 nm originates from free charge carriers rather than being caused by the formation of CT or triplet states. At a low excitation fluence, a negligible decay of this feature was observed for time delays up to 6 ns (plateau in Figure 5.3a), indicative of long-lived free charge carrier generation. In-situ steady-state absorption measurements carried out on an α -6T thin film at different temperatures suggest that the absorbance does not change as T varies from 293 K to 353 K, ruling out the contribution from thermal modulation (see Figure A.6 in the Appendix).

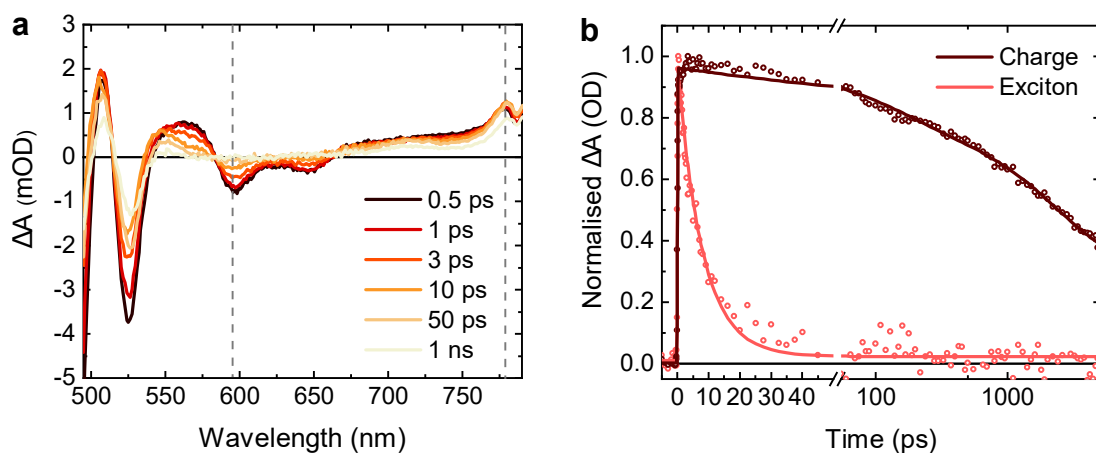


Figure 5.4 Transient absorption (TA) spectroscopy characterisation of an α -6T device. **a**, TA spectra as a function of pump-probe delay time and **b**, TA kinetics at 593 nm (orange dots) and 780 nm (brown dots) representing the kinetics for excitons and charges, respectively.

Turning to the α -6T based homojunction OSC with rubrene as the buffer layer, similar exciton decay lifetimes were observed as shown in Figure 5.4. Except for a slightly faster charge decay (brown dots in Figure 5.4b), all the spectral features are nearly identical with those in the pristine α -6T thin films on ITO substrates. The faster charge decay kinetics is likely to be affected by the measurement setup difference in TA, where the device was measured with a reflectance geometry due to the opaque Ag electrode, in contrast with the film measurement carried out in a transmittance geometry. Nevertheless, the resemblance between the film and device TA suggest that efficient free charge carrier generation is not only present in devices but also in α -6T thin films. This confirms the conclusion described above that device interfaces are not the origin of charge generation and indicates rather that this is a bulk phenomenon inherent to α -6T, one that is not usually observed in pristine organic materials devoid of D-A nature. This observation strengthens the hypothesis, suggested by the device study above, that charge generation takes place inside the α -6T layer.

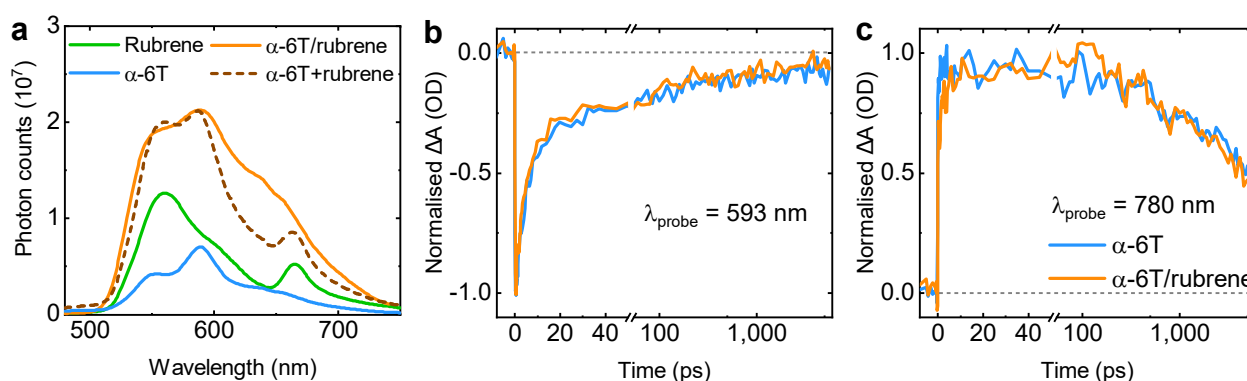


Figure 5.5 Steady-state absorption and photoluminescence characterisation comparing α -6T, rubrene, and α -6T/rubrene thin films. **a**, steady-state PL spectra for each film. The PL of α -6T/rubrene film resembles the sum of that in the pristine α -6T and pristine rubrene. **b** and **c**, Normalised TA kinetics probed at **b**, 593 nm and **c**, 780 nm representing the exciton and charge kinetics for α -6T and α -6T/rubrene thin films respectively.

It is clear now that charge generation occurs in the bulk of the α -6T layer as evidenced from the comparison of the TA measurements on α -6T thin films and devices. To further support this conclusion and eliminate the impact of the rubrene buffer layer on charge generation, PL and TA measurements were carried out on an α -6T/rubrene bilayer film. As shown in Figure 5.5a, it is observed that the PL intensity of the α -6T/rubrene bilayer is the sum of the PL of each individual layers, indicating negligible exciton quenching at the α -6T/rubrene interface. TA measurements on an α -6T/rubrene bilayer film also indicate the same exciton (probed at

593 nm) and charge (probed at 780 nm) kinetics as that in the pristine α -6T film (Figure 5.5b,c). In summary, the photon absorption and the subsequent charge generation both occur in the bulk of the α -6T layer and is not facilitated by the rubrene buffer layer.

Finally, TA measurements were extended into the near-infrared region to investigate if there are other excited-state species. As shown in Figure 5.6, a broad PIA signal centring at 990 nm was observed. Fitting the kinetics with a monoexponential decay, the lifetime was determined to be 58 ps, which is of the similar magnitude as the GSB (at 593 nm) in the visible region, suggesting that this signal is due to the photoninduced absorption (PIA) of excitons. The kinetics at different probe wavelengths ranging from 900 nm to 1200 nm all decay with the same rate, further indicating that there are no other excited-state species and the TA spectra in the NIR region are dominated by the PIA of excitons.

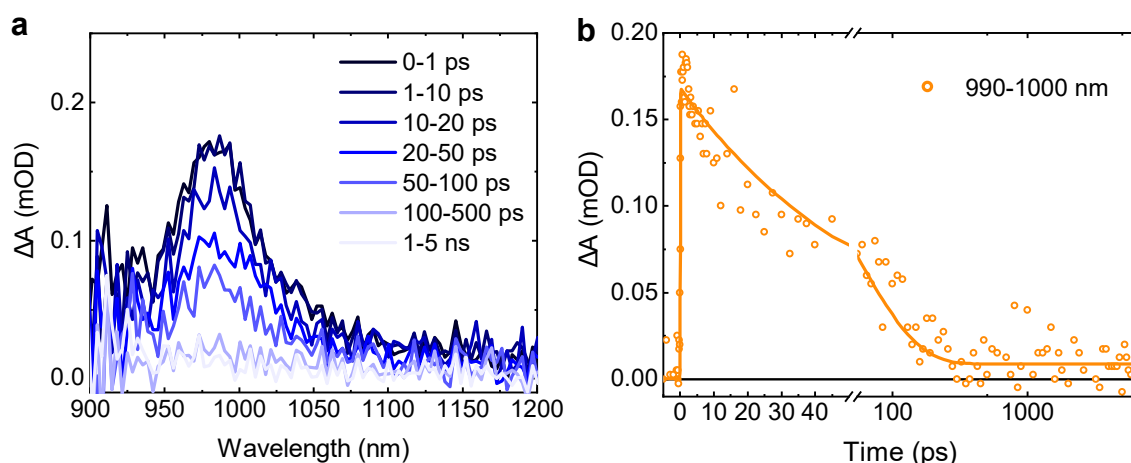


Figure 5.6 Transient absorption (TA) spectroscopy characterisation of a pristine α -6T thin film probed in the near-infrared region. **a**, TA spectra as a function of pump-probe delay time and **b**, TA kinetics probed at the wavelength from 990 nm to 1000 nm. The sample was excited at 450 nm with a fluence of $10 \mu\text{J cm}^{-2}$.

In summary, a combination of PL and TA measurements was employed to understand charge generation in pristine α -6T thin films and α -6T homojunction OSC devices. The agreement in features of the spectra and the kinetics suggest that charge generation occurs in both pristine α -6T thin films and α -6T homojunction OSC devices. Further measurements comparing the pristine α -6T thin film and α -6T/rubrene bilayer film indicate that the interfacial transport layer plays a negligible role in driving charge generation. As mentioned above, the pristine α -6T film and homojunction OSC discussed herein possess a mixed orientation of standing and lying,

which could potentially lead to such charge generation phenomenon. In the next section, the effect of orientation on charge generation will be explored.

5.3.3 The impact of orientation on energetics and kinetics

It is known that energetics in organic semiconductor devices is strongly intertwined with the molecular organisation in the solid state.^{43–46} For instance, Duhm et al. have reported a 0.4 eV difference in the ionisation potential of α -6T films as the orientation transitions from standing to lying.²² Indeed, the presence of a possible energy offset between domains characterised by different molecular orientations may determine the favourable conditions for charge separation. It is thus essential to unravel the relationship between electronic properties, the molecular organisation as well as the device processing conditions that confer the possibility to control the first two aspects, as addressed below. To understand the contribution from morphology and energetics, thin films with mainly standing and mainly lying molecules were fabricated alongside the film with mixed orientations following methods in the literature.^{26,27,47} GIWAXS measurements on these films confirm that the desired orientations were obtained following the well established processing methods in the literature (see Figure A.8 in the Appendix for details).^{26,27,47}

The schematic of different orientations is shown in Figure 5.7. In the standing oriented film (Figure 5.7a), molecules orientate with their long axis almost perpendicular to the substrate. Whereas in the lying oriented film (Figure 5.7c), molecules align parallel to the substrate. Finally, both standing and lying orientations described above are present in the mixed oriented film (Figure 5.7b).^{27,47,48} Absorption and PL measurements were carried out to confirm the orientation and elucidate the impact of orientation on their properties. As shown in Figure 5.7d, in the lying orientation, the absorbance is maximised due to the parallel alignment between the transition dipole moment of the molecule and the electric field vector of the incident light.⁴⁹ Since the amount of lying molecules is lower in the mixed and standing films, the absorbance decreases accordingly (Figure 5.7d). The mixed oriented film lies in between the two, indicating the co-existence of both orientations (see also Figure A.8). While the absorption spectra vary in shape and intensity for differently oriented films, the PL spectra retain the same shape

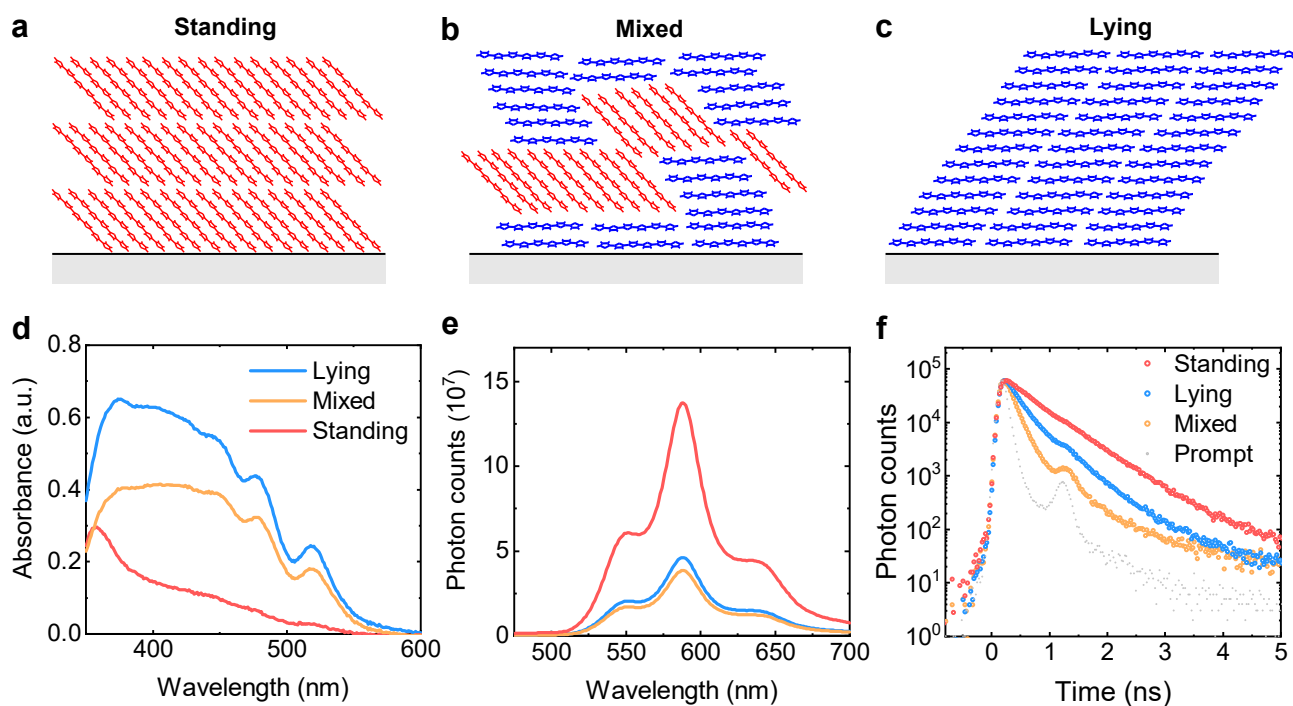


Figure 5.7 **a-c**, Schematic morphology for α -6T thin films with different molecular orientations (standing, mixed and lying). Optical characterisation for thin films with different orientations including mixed (orange), standing (red) and lying (blue). **d**, Absorption spectra; **e**, Photoluminescence spectra normalised to the absorbance at the excitation wavelength of 450 nm for α -6T thin films and **f**, Time-correlated single photon counting kinetics probed at 580 nm.

since they originate from the lowest excited state after the excitation undergoing a significant vibrational relaxation (Figure 5.7e). However, PL spectra and time-correlated single photon counting (TCSPC) kinetics show a quenching and a faster photoluminescence decay in the mixed film in comparison with the other two orientations (Figure 5.7e,f), implying that an enhanced exciton quenching mechanism is present in the mixed film containing both standing and lying α -6T domains.

Turning to the effect of orientation on the energetics, Ambient photoemission spectroscopy (APS) was employed to investigate the HOMO energy levels for thin films of standing and lying orientations prepared on ITO substrates. As shown in Figure 5.8a, a HOMO level of 4.8 eV was observed for the standing film, compared to a value of 5.2 eV for the lying film. These measurements confirmed the existence of an energy offset of ~ 0.4 eV between the HOMO levels of samples of lying and standing α -6T molecules, in agreement with that reported by Duhm et al.²²

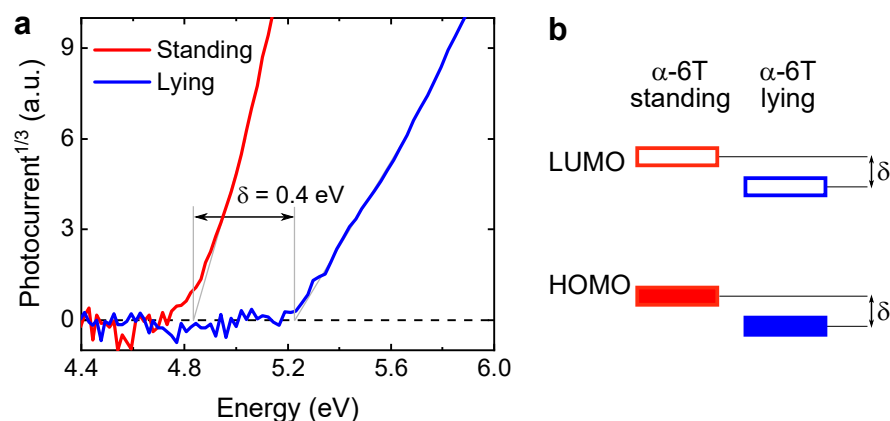


Figure 5.8 Energetics characterisation for α -6T thin films with standing and lying orientations respectively. **a**, Ambient photoemission spectroscopy and **b**, Schematic for the energy levels of the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) in two films. (Data measured and analysed by Yi-Chun Chin)

APS measurements determine the energetics of charge carriers at the surface of the two films of standing or lying molecules. However, the energy landscape at the boundary between two domains may also be affected by the different nature of the environment (bulk-like, without an interface to air). To complement APS measurements, embedded many-body GW calculations were carried out to reach quantitative accuracy in the determination of energy levels in α -6T. In embedded many-body GW calculations, a model interface between lying and standing molecules was explicitly considered to yield an inter-domain energy offset of ~ 0.4 eV, which is in good agreement with the one determined by APS for the two films with different molecular orientations. The calculations show that this energy offset is determined by the different orientations of the molecular quadrupoles in each side of the grain boundary, which dictate a step in the electrostatic potential across the interface that affects occupied and unoccupied levels. As illustrated in Figure 5.8b, standing and lying α -6T molecules behave therefore as the electron-donating and the accepting components of a conventional organic heterojunction, consistent with the efficient charge generation observed in the device performance and the TA data discussed above. In a working device consisting of such components, hole and electron transport takes place in the domains with standing and lying orientations, respectively, as a result of the ambipolar nature of α -6T,^{24,25} consistent with the reasonably slow bimolecular recombination observed for this system.

5.4 Discussion

Based on the observation that different orientations lead to an energy offset between α -6T domains, the best performing homojunction OSC was fabricated by inserting rubrene as a buffer layer between α -6T and BPhen, as discussed above. Furthermore, the device optimisation was extended to a wide range of buffer layers including C545T, TPBA, TCTA, DBzA, TPBI, and TPBE. The corresponding EQEs and current-voltage characteristics are shown in Figure 5.9a,b. In all cases, the buffer layer was inserted between α -6T and BPhen. Consistently high EQEs between 38% to 49% were observed, being between 40% to 45% for most of them. Turning to the current-voltage characteristics, both J_{SC} and V_{OC} show a relatively small variation. Specifically, the values of J_{SC} are between 3.0 mA cm^{-2} to 3.8 mA cm^{-2} and the values of V_{OC} are between 1.41 V to 1.61 V. The details on the photovoltaic parameters as well as voltage losses analysis can be found in Table A.2 and A.3 in the Appendix. Overall, the device performance exhibits little dependence on the type of buffer layers, which further suggests that the interface between α -6T and the buffer layer has a negligible effect on charge generation and recombination. Moreover, the absence of any subgap absorption in the sensitively measured EQEs (Figure 5.9c) further substantiates this point and indicates that there is no interfacial charge generation pathway, in agreement with the PL and TA characterisation for the α -6T/rubrene bilayer film.

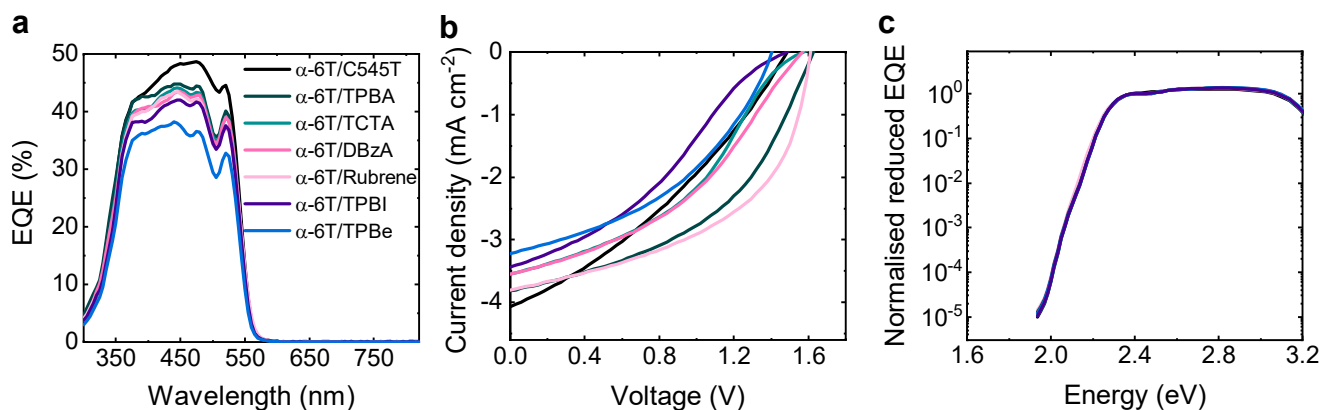


Figure 5.9 Device photovoltaic performance characterisation for α -6T (with mixed orientation) based homojunction organic solar cells with different buffer layers **a**, External quantum efficiency (EQE) spectra; **b**, Current-voltage characteristics and **c**, Sensitively measured EQE spectra employing C545T, TPBA, TCTA, DBzA, TPBI, TPBE and Rubrene respectively. (Data measured by Vasileios C. Nikolis, Johannes Benduhn and Jonas Kublitski)

Furthermore, TA results show that the same mechanism governs the photophysics in both α -6T films and devices based on similar spectral features and dynamics. Moreover, TA measurements

suggest that charge generation occurs in α -6T molecules with a mixed orientation—while excitons decay with a lifetime of 71 ps, charges are being generated with a similar rate. TCSPC kinetics reveal the quenching of excitons in such a mixed orientation and indicates that the interface between lying and standing α -6T domains plays an important role. These spectroscopic results are supported by the ambient photoemission spectroscopy which measures an energy offset of 0.4 eV at the standing:lying interface as well as theoretical calculations.

Efficient free charge generation in pristine organic semiconductors without intramolecular CT character has been rarely reported to date (unless very high photon energies are used⁵⁰) due to the strong binding energy of excitons in such materials (typically estimated as several hundreds of meV).^{51,52} Only a few spectroscopic studies have suggested ultrafast photogeneration of free charge carriers in pristine organic small molecule films, with these reporting only low EQEs of less than 10% and more often less than 1%.^{53–56} Keiderling et al. reported charge generation in pristine PCBM thin films.⁵⁷ This, however, results in rather low efficiency of photocurrent generation in PCBM homojunction OSCs, as also reported by Burkhard et al.⁵⁸ Other organic materials reported to exhibit charge or photocurrent generation include MEH-PPV, C₆₀ and ZnPc, to name a few.^{53,59,60} However, in those reports either the device performance was relatively poor or the mechanisms for the fairly limited intrinsic charge generation have remained unexplored. Herein, the interface between lying and standing domains is found to be the reason behind charge generation in α -6T molecules as presented in the TA results above.

Several studies have examined the impact of molecular electrostatics/orientation on OSC device performance for both planar and bulk heterojunction architectures.^{61–67} For example, Ray et al. have suggested photocurrent generation in Alq₃ could originate from a combination of its isomers.⁶⁸ In terms of organic planar heterojunction systems based on small molecules, for example, Ran et al, have reported that the face-on (similar to the ‘lying’) orientation of the donor molecules leads to a higher CT state energy (E_{CT}) and hence greatly suppresses the non-radiative voltage losses, whereas the edge-on (similar to the ‘standing’) orientation of the donor molecules enhances the charge generation.⁶⁹ Since OSCs benefit from both high radiative efficiencies and efficient charge generation yields, this work thus points out the importance of the fine balance between edge-on and face-on orientation. In other words, the optimal co-existence

of different orientations is crucial for efficient photovoltaic performance, which thus requires more research effort to understand how to best achieve such an optimal balance.

Apart from revealing the same mechanism for charge generation in α -6T films and devices, TA also shows the charge-induced EA signal at 525 nm, attributed to the fast formation of exciton-CT hybrid states as suggested by theoretical calculations targeting at the standing:lying α -6T interface (Figure A.9). The calculations illustrate the lowest energy excited-state possesses a CT nature, with hole and electron localised in the standing and lying domains, respectively. The identification of those excited states with a degree of charge-transfer act as the crucial gateway for charge splitting. This type of high-lying hybrid exciton/CT states have also recently been proposed to be responsible for the low voltage losses in the state-of-the-art polymer:non-fullerene OSCs.⁷⁰ It has also recently been suggested that CT separation may be assisted by the electrostatic interfacial fields in low energy offset, high performing OSCs based on a conventional D:A heterojunction.^{71,72} The population of the inter-domain CT excitations following light absorption appears to be the key for the unprecedented charge generation efficiency not only for a single component molecular film and device but also for D:A heterojunction OSCs.

5.5 Conclusions

This chapter demonstrates the origin and the mechanism for charge generation in an efficient homojunction organic solar cell employing only the organic donor material α -6T. By fabricating homojunction organic solar cells with identical α -6T crystallites but with a distribution of relative orientations including standing and lying, a high EQE of 44% and a high V_{OC} of 1.61 V were achieved. Transient absorption and photoluminescence measurements show that the buffer layer employed in the device plays a negligible role on charge generation, instead charge generation occurs only in the bulk of the α -6T molecules. Together with the ambient photoemission and theoretical calculations, time-resolved photoluminescence measurements show that the standing and lying interface provides an energy offset of 0.4 eV, forming hybridised exciton/charge-transfer states to allow the efficient quenching of excitons. A generalisation of this result is that the ordered morphology and the contact between different crystal facets are

crucial to dissociate excitons, and that grain boundaries in single component polycrystalline systems could be exploited as “heterojunctions”. Engineering morphology in the preferred way is the key to generate energy offsets in single materials and facilitate charge generation pathways. This chapter of the thesis reshapes the common understanding in the role of ‘donor’ and ‘acceptor’ in organic solar cells where this character is not only fixed by the primary chemical structure of the molecules but can also be modulated by interfacial packing and electrostatics. This further widens the broad potentiality in donor and acceptor materials in organic solar cells. Moreover, using a single material in the photoabsorbing layer presents the advantage of achieving high voltage and allows great potential for controlled and reproducible morphology as well as performance.

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Chapter 6

Field-assisted Charge Generation in Homojunction Organic Solar Cells

This chapter focuses on homojunction organic solar cells employing chloroboron subnaphthalocyanine (SubNc) as the only photoabsorber which exhibit an efficiency of 1%. To understand the origin of charge generation in this device, transient absorption, photoluminescence and electroabsorption spectroscopy were combined to investigate pristine SubNc thin films and SubNc devices. It was found that charge generation only occurs in the device whereas the thermal modulation signal dominates in the pristine SubNc film, suggesting charge generation only happens under the electric field. Further measurements on SubNc thin films deposited with various interfacial transport layers reveal that these interfacial layers have a negligible effect on charge generation. Finally, the role of field-assisted charge generation in SubNc on planar heterojunction devices employing α -6T as the electron donor and SubNc as the electron acceptor is discussed. Transient absorption and photoluminescence measurements show that the α -6T/SubNc planar heterojunction device does not function as a typical type II heterojunction when SubNc was selectively excited, but is rather governed by the field-assisted charge generation within SubNc. This previously unexplored mechanism can allow the suppression of energy offsets in the design and fabrication of planar heterojunction organic solar cells, whilst enabling high photocurrent generation efficiency.

The results of this chapter come from a collaborative work. My contribution involves the overall coordination of the project, performing the absorption and photoluminescence measurements, as well as TAS measurements and data analysis of those results. The T -dependent absorption measurements were performed together with Chengye Huang and the electroabsorption measurements were performed with the help of Xijia Zheng. Vasileios C. Nikolis fabricated all the samples and performed J-V and EQE measurements.

6.1 Introduction

As introduced in previous chapters, the low dielectric constants of organic semiconductors result in the formation of tightly bound electron-hole pairs under photoexcitation. A heterojunction architecture involving an electron donor (D) and an electron acceptor (A) can greatly assist the separation of excitons and lead to efficient charge generation.¹ However, as the field of organic solar cells (OSCs) moves towards efficient non-fullerene based D:A systems with low voltage losses, surprisingly high external quantum efficiencies (EQEs) have been achieved even in the absence of a significant driving force.^{2,3} For several such D:A systems, there is an increasing amount of evidence to suggest that the field can assist the charge generation.⁴⁻⁶ Employing field-dependent charge separation in single organic semiconductors thus remains appealing and is worth further exploration. Homojunction OSCs employ a single organic semiconductor as the photoactive layer and promise a simpler device fabrication and a potential solution to the morphological instability of many bulk heterojunction OSCs.^{7,8} Homojunction OSCs do not rely on charge separation at a heterojunction and research has been performed to enhance the efficiency of those systems by for example increasing their dielectric constants,^{9,10} or exploiting block copolymers that combine electron-donating and electron-accepting moieties to facilitate the exciton dissociation.^{11,12} Among others, Chandran et al. have reported direct free carrier generation in a homojunction OSC employing the small molecule chloroboron subnaphthalocyanine (SubNc), which reached an EQE of 22% despite the absence of an acceptor molecule.¹³

In this chapter, homojunction OSCs employing only SubNc as the photoactive layer have been studied. With a 12 nm SubNc layer, the device reaches a high peak EQE of over 35%, together with a V_{OC} of 1.1 V, a J_{SC} of 3 mA cm^{-2} . However, the relatively low fill factor (FF) leads the overall PCE to be only around 1%. By performing transient absorption (TA) spectroscopy on pristine SubNc films as well as SubNc based homojunction OSCs, the origin for charge generation is elucidated. Specifically, charge generation is only observed in SubNc homojunction OSC devices, suggesting that the electric field plays an important role in driving charge separation. In contrast, the long-lived signal in pristine SubNc films is dominated by thermal modulation, as evidenced by in-situ temperature-dependent UV-Vis absorption measurements. Based on the

field-dependent charge generation within SubNc, this chapter further discusses the impact of this phenomenon on the excited-state carrier dynamics in a planar heterojunction (PHJ) OSC employing α -6T as D and SubNc as A. It is shown with the aid of transient absorption and photoluminescence (PL) measurements that the dissociation of SubNc excitons is not facilitated by the energy offset at the α -6T/SubNc interface, but rather the device performance is driven by the individual charge generation channels within each layer. This unexplored mechanism can be utilised to design and fabricate other non-fullerene OSCs, where the field-assisted charge generation within single photoabsorbers dominates the charge generation pathway and avoids energy losses associated with D/A heterojunctions without sacrificing photocurrents. The findings are also of relevance to non-fullerene based bulk heterojunction OSCs where high charge generation yields have been observed even at a low driving force.²

6.2 Experimental details

Sample preparation, device characterisation measurements including current-voltage and EQEs, in this chapter were carried out by Vasileios C. Nikolis at TU Dresden. Other experimental details can be found in Chapter 2.

6.2.1 Sample fabrication

All the used materials were purified twice in-house by vacuum gradient sublimation.

Film and device fabrication

Following the processing methods discussed in Section 2.1.2, the solar cell devices were encapsulated in a nitrogen atmosphere with transparent encapsulation glass substrates, fixed by UV hardened epoxy glue. During the processing run, the hole transporting layer (HTL) material BPAPF (Lumtec, Taiwan) was p-doped before a layer of 30 nm was deposited on top of the anode, ITO. In addition, an intrinsic layer of 5 nm of BPAPF was used as the exciton blocking layer, avoiding also the contact between the active layer and the p-dopant. In the active layer,

12 nm of SubNc (Lumtec, Taiwan) were used as the donor. A 8 nm layer of BPhen (ABCR, Germany) was used as the exciton blocking and electron transporting layer (ETL). Each organic material layer was evaporated at a rate of $0.3 \text{ \AA s}^{-1}$, apart from the SubNc layer which was deposited at $0.5 \text{ \AA s}^{-1}$. The Ag electrodes were deposited at $1 \text{ \AA s}^{-1}$. All layer thicknesses were precisely monitored with calibrated quartz crystal microbalances. All thin film samples on glass or ITO shown in this work reproduce the layers in the solar cells as described above, regarding deposition conditions and layer thicknesses.

6.2.2 Device characterisation

Current-voltage measurements

Current-voltage measurements were carried out in ambient conditions using a source measurement unit (SMU 2400 Keithley, USA) and a simulated AM1.5G illumination (16S-003-300-AM1.5G sunlight simulator, Solar Light Co., USA). A silicon photodiode (Hamamatsu S1337) was used as a reference and the spectral mismatch was taken into account during the measurement.

EQE measurements

External quantum efficiency measurements were performed using a Xenon lamp (Oriel Xe Arch-lamp Apex, Newport, USA), a monochromator (Cornerstone 260 1/4m, Newport, USA), an optical chopper, and a lock-in amplifier (SR 7265, Signal Recovery, USA). The EQE of the OSCs was measured with an aperture mask (2.78 mm^2) and without bias light. A calibrated silicon photodiode (Hamamatsu S1337, Japan) was used as a reference.

6.3 Results

6.3.1 Material properties and device performance

Phthalocyanine materials such as CuPc, ZnPc have been thoroughly investigated in terms of their chemical properties and photovoltaic performance, for example.^{14–16} However less attention has

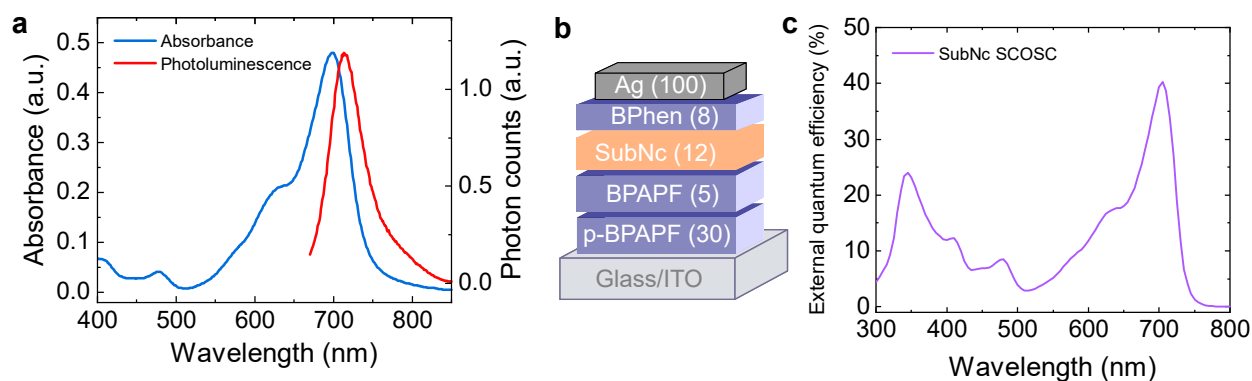


Figure 6.1 Characterisation for a pristine SubNc film and a SubNc based homojunction organic solar cell (OSC). **a**, Absorption and photoluminescence (PL) spectra for a pristine SubNc thin film. In the PL measurement, an excitation wavelength of 600 nm was used. **b**, Device architecture of a SubNc based homojunction OSC and **c**, External quantum efficiency (EQE) for a SubNc based homojunction OSC (EQE Data measured by Vasileios C. Nikolis).

been paid to naphthalocyanines, which typically show red-shifted absorption and can potentially harvest more of the solar spectrum.¹⁷ Figure 6.1a presents the steady-state absorption and PL spectra for a pristine SubNc thin film. The absorption spectrum exhibits a sharp absorbance peak centring at 690 nm, while the PL peak exhibits a small Stoke's shift of 20 nm and centres at 710 nm. The optical band gap of SubNc was determined to be 1.73 eV from the crossing point between absorption and PL spectra. When incorporating SubNc molecules into a homojunction OSC device following the architecture of ITO/p-BPAPF/BPAPF/SubNc/BPhen/Ag (Figure 6.1b,c), the device reached a relatively high peak EQE of over 35%, together with a V_{OC} of 1.1 V and a J_{SC} of around 3 mA cm^{-2} . However, the low FF leads to an overall PCE of only 1%, though it is still relatively high for a 12 nm-thick homojunction OSC device employing only a single photoabsorbing organic small molecule material.

6.3.2 Charge generation vs heating effect

To elucidate the charge generation mechanism in SubNc homojunction OSCs, TA spectroscopy was carried out on both pristine SubNc films as well as SubNc devices. Figure 6.2a shows these spectra for the pristine SubNc film, where two negative bands at 624 nm and 700 nm are apparent, along with two positive absorption bands in the region between 730 nm to 800 nm as well as between 500 nm to 570 nm immediately after photoexcitation. Similarly, a strong bleaching band at 700 nm was also observed in the device spectra in Figure 6.2b, together with

a positive band above 730 nm. However, the bleaching band in the device is narrower than that in the film, which is most likely related to the different light propagation through an opaque device compared to a transparent film during the TA measurements (see further discussions below). Comparison with the steady-state absorption and PL spectra (see Figure 6.1a and Figure A.10 in the Appendix) allow the assignment of this strong bleaching peak at 700 nm to be the ground state bleach (GSB), together with some contribution from the stimulated emission (SE). Interestingly, the GSB peak shifts to shorter wavelengths in the film (Figure 6.2a) whereas it shifts to a longer wavelength in the device (Figure 6.2b) with increasing pump-probe delay times. In particular, the peak of the GSB shifts from 700 nm to 690 nm in the film, whereas it shifts to 710 nm in the device at a pump-probe delay time of 1 ns to 5 ns. The opposite trends in peak shifts is observed for the film and the device indicate that the photoinduced species at long times (1 ns to 5 ns) differ in the film from that in the device, albeit the initially photoinduced species are the same. Besides being related to the conversion of excitons into charges, the peak shift can have several other origins including thermal modulation.^{18–20}

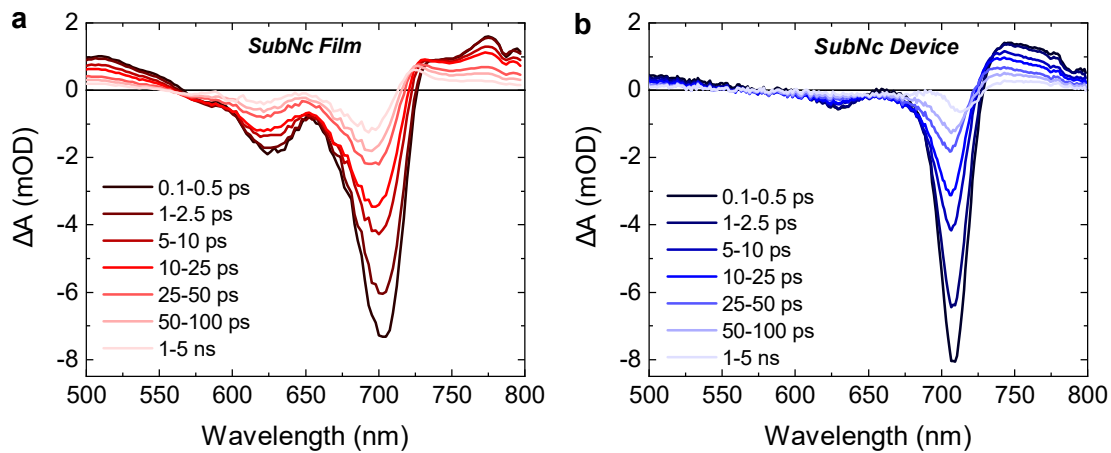


Figure 6.2 Transient absorption spectra for **a**, a pristine SubNc film and **b**, a SubNc homojunction organic solar cell device. The SubNc thin film was measured with a transmittance mode, while the SubNc device was measured with a reflectance mode due to the opaque Ag electrode.

To thoroughly understand the origin of the GSB peak shift, pristine SubNc films were heated to various temperatures and the in-situ change in its absorbance was characterised by UV-Vis absorption spectroscopy. As shown in Figure 6.3a, the absorbance at 690 nm decreases as T increases from 293 K to 333 K. The thermal modulation signal is determined by subtracting the absorption spectrum at 293 K from the absorption spectra at higher T (Figure 6.3b). Comparing the thermal modulation signal with the TA spectra for the long-lived species in the film (averaged

between 1-5 ns) shows a well-matched resemblance, as shown in Figure 6.3c. Hence, the GSB peak shift in the film is attributed to the slow arousal of the thermal modulation signal, but not due to charge generation. The origin of thermal modulation signals in organic semiconductors has usually been attributed to the reduction in the effective conjugation length as a result of the thermally induced dynamic disorder,^{18,19} but it can also be related to the thermally assisted population of subgap states.²¹ In either case, it is not suggesting any charge generation in the film.

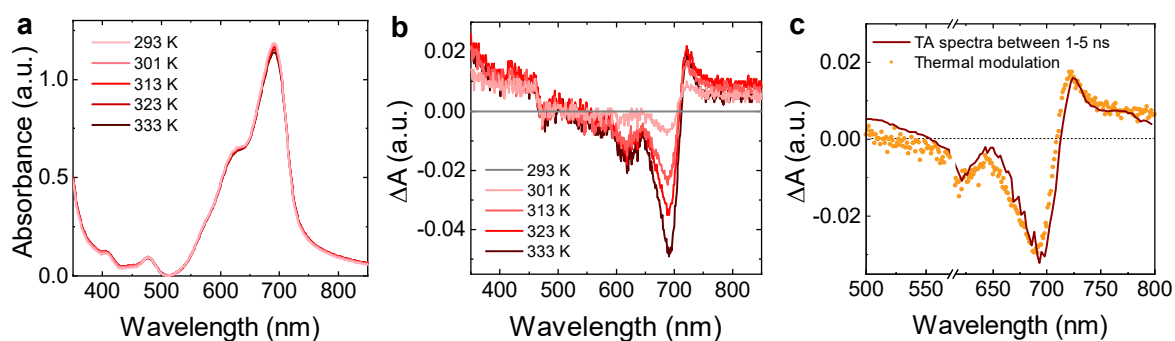


Figure 6.3 Thermal modulation characterisation for a pristine SubNc film. **a**, Absorption spectra measured in-situ while heating the SubNc thin film to various temperatures, and **b**, The differential absorption spectra by subtracting the absorption spectra at the high T from the absorption spectrum at 293 K. **c**, Comparing the thermal modulation signal and the transient absorption spectra (1-5 ns) for the SubNc film.

Now turning to SubNc homojunction OSC devices, as aforementioned, the GSB peak within the device shifts in the opposite wavelength direction in contrast with the film, even if the early-time spectra between the two resemble each other. Further comparison shows that the TA spectra for the device averaged between 1 ns to 5 ns differ considerably from the thermal modulation signal (see Figure A.10 in the Appendix), ruling out the possibility of any contribution from the thermal signal. In order to understand what governs the charge generation in the device, genetic algorithm (GA) was employed to decouple overlapping features in the TA spectra of SubNc homojunction OSCs. In GA, one or more reference spectra can be fixed while letting other species evolve. In this case, the spectra at early times (< 200 ps) and the spectra at long time (1 ns to 5 ns) were fixed as reference spectra. Other combinations of reference spectra have also been carried out to ensure the reproducibility of the GA results. Figure 6.4 shows the decoupled spectra for each excited-state species generated by the pump, alongside their corresponding kinetics. As shown in Figure 6.4a, three species are present including photogenerated excitons

and charges as well as a derivative-shape intermediate species (see further discussions below). The kinetics in Figure 6.4b shows that excitons are immediately generated after the pump excitation, which subsequently decay with lifetimes of 4.6 ± 0.2 ps and 178 ± 15 ps (purple circles in Figure 6.4b). The fast decay component is likely due to the exciton-exciton annihilation as a result of the slightly high excitation fluence employed and the slow component is attributed to the monomolecular exciton decay to the ground state as often observed in organic semiconductors. The intermediate species (brown line in Figure 6.4b), however, are slowly generated with a lifetime of 2.7 ± 0.2 ps, followed by a decay with a half-life of 250 ps. Further fitting yields the charge formation lifetime to be 302 ± 54 ps. As such, the decay lifetime of the intermediate species is on the same order as the charge formation lifetime, implying that the decay of intermediate species correlates with the formation of charges. In contrast with the GA results for SubNc homojunction OSCs, GA for the SubNc film can only give rise to two components regardless of the input reference spectra (as shown in Figure A.11 of the Appendix).

To explore the nature of this intermediate species, electroabsorption (EA) spectroscopy measurements were carried out on a SubNc homojunction OSC device under different biases as indicated in Figure 6.4c. In fact, the EA spectrum resembles the spectrum of the intermediate species derived from the GA shown in Figure 6.4d. Hence, this intermediate species is assigned to the EA signal. GA results in Figure 6.4b show that both exciton and the EA gradually decay followed by simultaneous charge generation. Moreover, the instantaneous rise of the kinetics for both charge and EA suggest that a portion of charges has already been generated within sub-picosecond. This confirms that charge generation is occurring much more efficiently in the SubNc homojunction OSC device than in the pristine SubNc film. That is, the majority of excitons undergo relaxation and dissipate to heat in SubNc thin films, without the presence of electrodes. On the contrary, the thermal modulation signal disappears in SubNc homojunction OSC devices as a result of the efficient conversion from excitons to charges due to the built-in electric field.

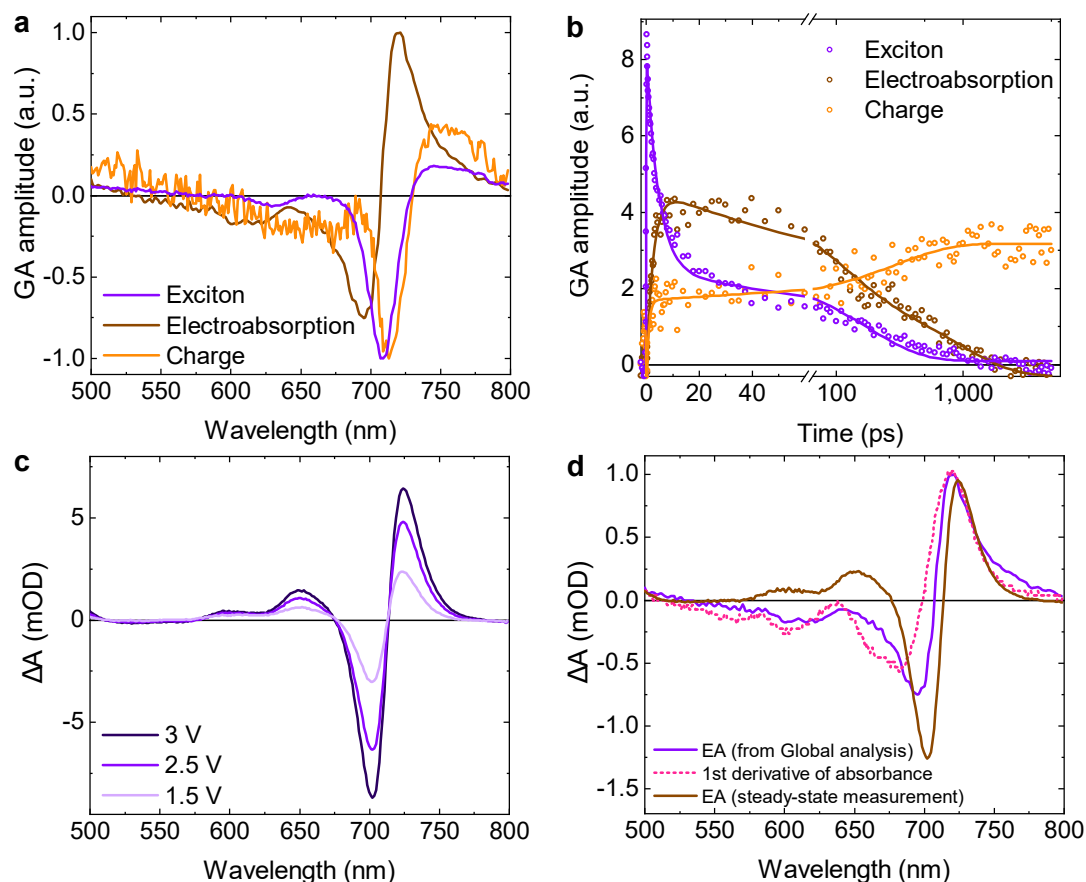


Figure 6.4 Genetic algorithm (GA) analysis for a SubNc based homojunction organic solar cell (OSC): **a**, Spectra and **b**, Kinetics for excitons, electroabsorption and charges, respectively. Electroabsorption (EA) spectroscopy characterisation for a SubNc homojunction OSC: **c**, Steady-state EA measurements at different biases; **d**, Comparing the steady-state EA with the EA extracted from GA as well as the first derivative of its absorption spectrum.

6.3.3 The impact of interfacial layers on charge generation

As mentioned in Section 6.3.1, the complete device architecture of a SubNc homojunction OSC employs hole transport layers (p-doped BPAPF and BPAPF) as well as the electron transport layer BPhen to facilitate charge transport and collection. While TA measurements on a full SubNc homojunction OSC device in Figure 6.2b shows features of charge generation, the impact of the interface between the SubNc layer and those charge transport layers on charge generation remains unclear. Therefore, PL and TA measurements were further utilised to study the impact of interfacial layers on charge generation in those devices. Following the same processing methods, a series of bilayer films on glass with SubNc and every other layer existing in the device (ITO, p-doped BPAPF, BPAPF, BPhen) were prepared and characterised, as further discussed below.

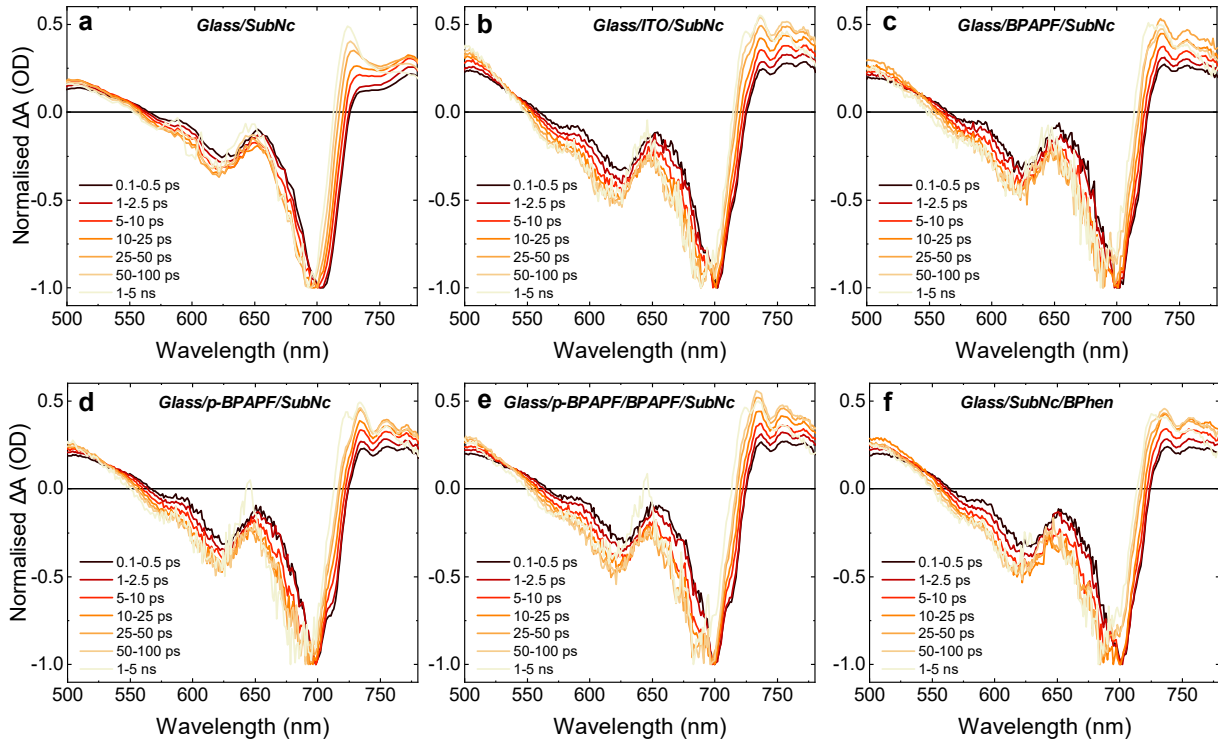


Figure 6.5 Normalised transient absorption spectra for SubNc films with different interlayers: **a**, SubNc; **b**, ITO/SubNc; **c**, BPAPF/SubNc; **d**, p-BPAPF/SubNc; **e**, p-BPAPF/BPAPF/SubNc; **f**, SubNc/BPhen. The ground state bleach peak consistently shifts from 700 nm to a higher wavelength as the pump-probe delay time increases in all the samples. Thicknesses for p-BPAPF, BPAPF, SubNc and BPhen were 35, 5, 80 and 8 nm respectively.

Figure 6.5 presents the TA spectra for all the bilayer films. Firstly, at the pump-probe delay time between 0.1 ps to 0.5 ps, same spectral features were observed in all the bilayer films when compared with the pristine SubNc film on glass substrates, including negative bands at 624 nm and 700 nm as well as two positive absorption bands in the region between 730 nm to 800 nm and between 500 nm to 570 nm. As previously discussed in Section 6.3.2, the strong bleaching peak has been assigned to the GSB. Interestingly, in all the bilayer films, the GSB peak shifts from 700 nm to 690 nm regardless of the type of interfacial layers or substrates. The blue-shift of the GSB peak is associated with the thermal modulation as previously discussed. Herein, it can therefore be concluded that all the long-time (1 ns to 5 ns) signals in the bilayer thin films are dominated by the thermal modulation signal instead of charge generation, implying that interfacial layers have a negligible impact on exciton dissociation. Moreover, the same exciton decay lifetime (as shown in Figure 6.6b) is observed in all the samples and thus further substantiates this point.

PL measurements on those films are shown in Figure 6.6a. When SubNc molecules were evaporated on to the ITO substrate, it gives the highest PL yield. When SubNc molecules were deposited on either the glass substrate or other HTLs, the PL yield is reduced slightly, varying from 16% to 33%. The minor quenching of the PL yields might be related to some interfacial surface traps or moderate morphological changes. In either way, the PL quenching yield is still negligible, especially when compared with that in scenarios where the interface can assist with charge separation such as in polymer:non-fullerene bulk heterojunctions, which typically reach at least 80%. This again suggests that the transport layer has no contribution towards dissociating SubNc excitons. Together with the same TA exciton lifetimes, it can be concluded that these interfacial charge transport layers do not assist in the exciton quenching.

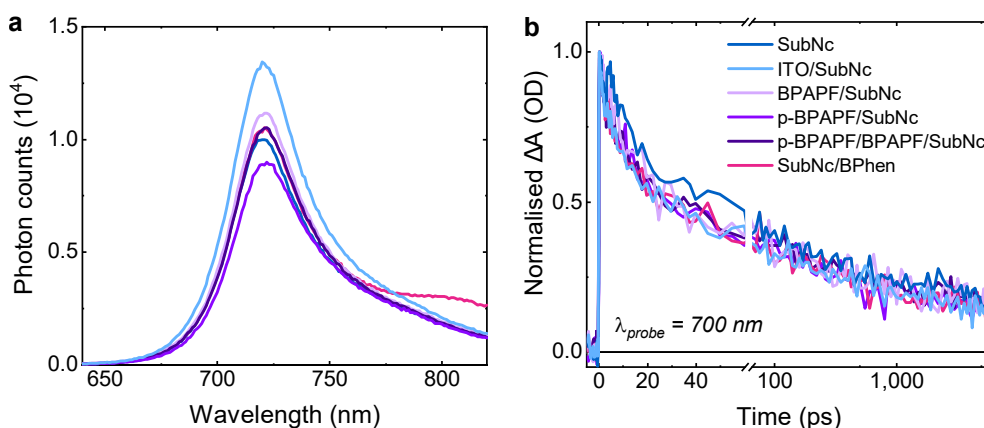


Figure 6.6 Characterisation for thin films of SubNc with different interfacial layers. **a**, Steady-state photoluminescence spectra and **b**, Normalised transient absorption kinetics at the probe wavelength of 700 nm for SubNc thin films with different interlayers where p-BPAPF and BPAPF were used as the hole transport layers in the device and BPhen was used as the electron transport layer.

6.3.4 The impact of field-assisted charge generation on the carrier dynamics in planar heterojunction devices

Having shown that charge generation in SubNc can be efficient in the presence of an electric field, this section moves on to investigate how the field-assisted charge generation in SubNc impacts on the characteristics of planar heterojunction (PHJ) devices, with a focus on the carrier dynamics. Specifically, the excited-state carrier dynamics in a PHJ OSC employing α -6T as donor and SubNc as acceptor were studied (See Figure A.12 in the Appendix for the device

architecture), which have both been shown to be able to generate charges when assisted with interfacial molecular electrostatics for the former (see Chapter 5) and with an electric field for the latter.²²

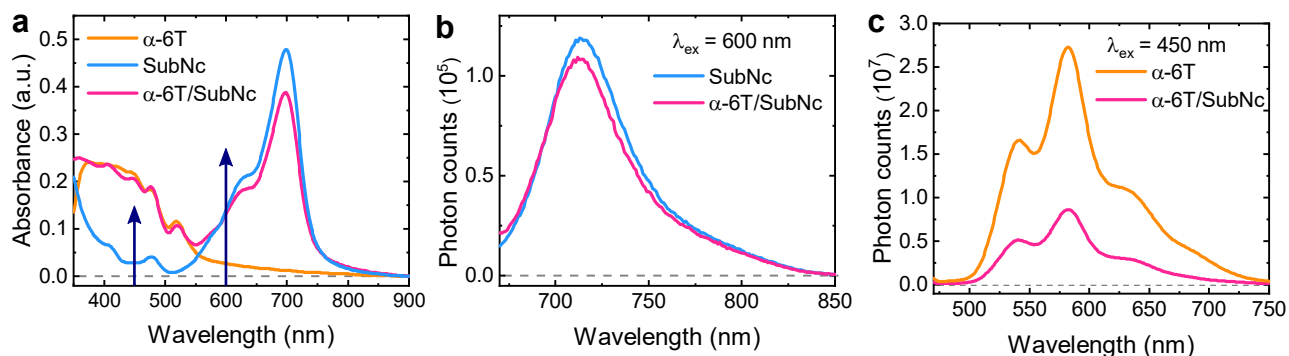


Figure 6.7 Steady-state characterisation: **a**, Absorption spectra for a pristine α -6T film, a pristine SubNc film and an α -6T/SubNc bilayer film deposited on glass substrates. **b** and **c**, Photoluminescence spectra for these thin films under an excitation wavelength of **b**, 450 nm and **c**, 650 nm, respectively and the α -6T/SubNc film was excited from the α -6T side.

Figure 6.7a compares the absorption spectra for a pristine α -6T film (with mixed orientation), a pristine SubNc film and an α -6T/SubNc bilayer film. In the α -6T/SubNc film, the absorption features of α -6T (ranging between 350 nm to 600 nm) resembles that in the pristine α -6T film, implying that α -6T molecules in the bilayer film retain the same orientations (a mixed orientation of standing and lying) as in the pristine film. The same absorption peaks were also observed for SubNc in the pristine film and the bilayer film, indicating that its morphology remains the same after evaporating SubNc molecules onto the α -6T layer. To understand the exciton dissociation efficiency at the α -6T/SubNc interface, PL measurements were carried out on all three samples. As shown in Figure 6.7b, when SubNc in the bilayer α -6T/SubNc film was selectively excited at 600 nm, the PL yield of the bilayer film is only quenched by 9% relative to the pristine SubNc film. The extremely low PL quenching yield thus suggests an inefficient SubNc exciton dissociation at the interface. However, when the α -6T/SubNc film was excited at 450 nm which excites α -6T, the PL quenching yield increases to 68% as shown in Figure 6.7c, suggesting that α -6T excitons are more efficiently quenched at the interface. It can also be noted herein that energy transfer from α -6T to SubNc is not dominating the quenching of α -6T emission, despite the overlap between α -6T emission and SubNc absorption, which is likely due to the small Förster radius and the sharp boundary between α -6T and SubNc layers.^{23,24} The PL quenching yield of 68% in the bilayer α -6T/SubNc film is only moderate compared to what

has been commonly observed in bulk heterojunction blends, which is most likely related to the reduced interfacial areas in a planar heterojunction (PHJ) morphology. In spite of that, the PL quenching yield results indicate that α -6T excitons can be relatively effectively quenched, at the α -6T/SubNc interface, but not SubNc excitons. To further explore the exciton dissociation kinetics, TA spectroscopy was employed on α -6T/SubNc PHJ devices, as further discussed below.

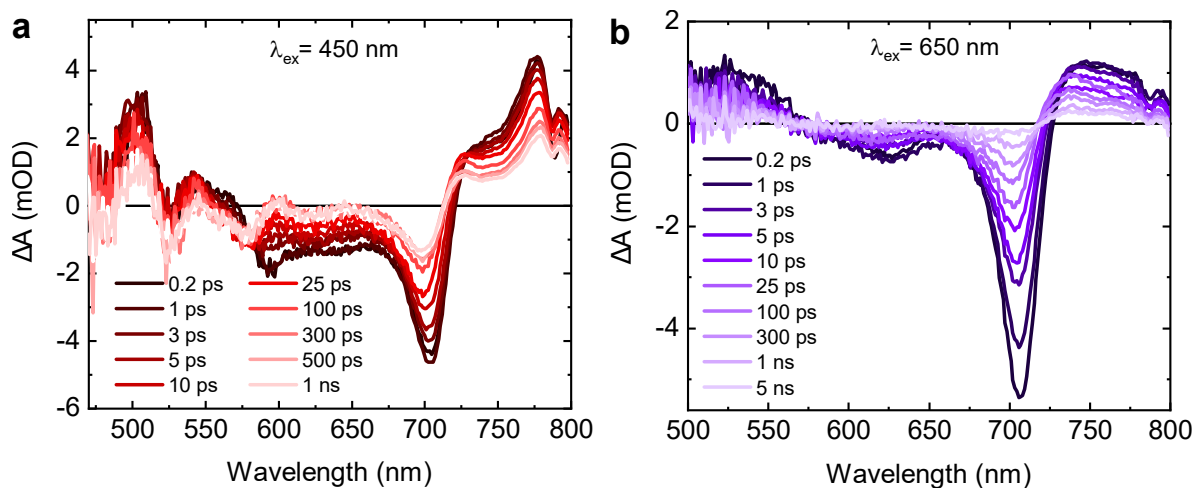


Figure 6.8 Transient absorption spectra as a function of pump-probe delay time for an α -6T/SubNc planar heterojunction device excited at **a**, 450 nm and **b**, 600 nm.

Figure 6.8 shows the TA spectra for an α -6T/SubNc PHJ device by selectively exciting either the donor α -6T at 450 nm or the acceptor SubNc at 650 nm. As shown in Figure 6.8a, following the excitation of α -6T, positive bands at 500 nm and above 730 nm, together with a negative band at around 600 nm are apparent, which have been individually assigned to the electroabsorption, polaron absorption and stimulated emission respectively in α -6T (see Section 5.3.2 for details). Additionally, a strong GSB peak at 700 nm can be observed immediately after photoexcitation. Since the pump at 450 nm mainly excites α -6T, the prompt bleaching signal at 700 nm therefore suggests an ultrafast electron transfer from α -6T to SubNc and a rapid relaxation to the ground state, consistent with the PL quenching yield observed in Figure 6.3.2c. However, when SubNc was selectively excited, the spectra footprints including PIA peaks at 525 nm and above 730 nm, as well as GSB peaks spanning from 570 nm to 725 nm, completely overlap with the pristine SubNc homojunction OSC devices as shown in Figure 6.2b. This includes a red-shifted GSB peak as the pump-probe delay time increases, representative of the electroabsorption features and charge generation as previously discussed in Section 6.3.2. TA results further substantiate

steady-state PL characterisation and indicate an inefficient dissociation of SubNc excitons at the α -6T/SubNc interface. The fact that no charge transfer occurring from SubNc to α -6T is rather striking since the energetics between these two materials are aligned for a typical type II heterojunction (with a staggered band alignment) as widely reported in the literature, where one would normally expect charge transfer to happen.^{25,26} Moreover, the region in the EQE spectrum of the α -6T/SubNc PHJ device associated with SubNc absorption has a similar magnitude to that in the SubNc homojunction OSC device, implying that the charge generation in α -6T/SubNc is governed by the field-assisted charge generation within SubNc itself rather than charge transfer across the heterojunction (see Figure A.12c in the Appendix). Finally, Figure 6.9 summarises the photophysics of the α -6T/SubNc type II heterojunction device, illustrating that SubNc excitons are not dissociated by the energy offset at this junction.

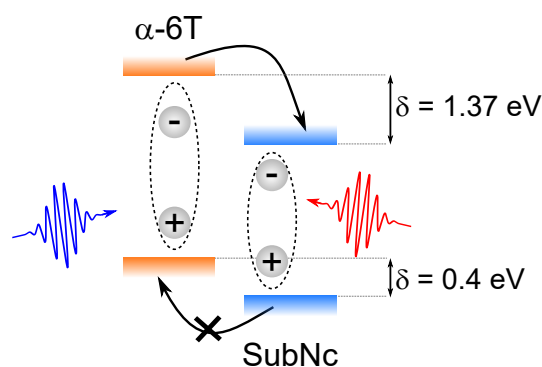


Figure 6.9 Schematic depicting the exciton dissociation in a planar heterojunction α -6T/SubNc device, where the energetics were taken from the reference.²⁵

To date, no transient absorption studies have been reported on either the SubNc homojunction OSC or the α -6T/SubNc PHJ OSC, while a few have focused on a similar planar heterojunction system employing α -6T and chloroboron subphthalocyanine (SubPc). For example, Takahashi et al. examined the carrier dynamics in both α -6T/SubPc and SubPc/ C_{60} thin films where SubPc can either act as an electron acceptor or an electron donor, revealing the charge injection mechanism into SubPc from electron donors or electron acceptors.²⁷ Herein, in addition to exploring the carrier injection dynamics into SubNc, this chapter also examines the hole transfer dynamics from SubNc to electron donors, α -6T. Bringing the results together within this section, it suggests that charge generation from SubNc is not assisted by the other electron donor materials (α -6T) even in the presence of a type II heterojunction when SubNc is incorporated

in a planar heterojunction device, but rather it is dominated by field-assisted charge generation within SubNc.

6.4 Discussion

The drastically different transient absorption (TA) spectra and dynamics for pristine SubNc films and SubNc homojunction OSC devices suggest that the long-lived TA features are dominated by different species depending on whether the electric field is present. Together with in-situ temperature-dependent UV-Vis absorption, the long-lived signal in the film is attributed to the thermal modulation signal. In contrast, genetic algorithm (GA) reveals efficient charge generation in the SubNc homojunction OSC device, which correlates with the decay in electroabsorption signal and a rise in charge absorption signal. While the device exhibits narrower GSB features than the film (most likely due to the different experimental set up), the main conclusion drawn herein is based on the relative shift of the GSB peak and the kinetics of charge generation, which are not influenced by the spectral shape. It needs to be noted herein that the presence of charges in devices may be able to quench SubNc excitons, however, it would seem unlikely to show a rise in kinetics of charge generation in that case. Furthermore, PL and TA characterisation demonstrate the negligible role of interfacial transport layers on exciton dissociation and charge generation. These observations lead to the conclusion that the built-in field in the device is the origin behind charge generation in SubNc homojunction OSCs. Furthermore, field-assisted charge generation within SubNc also plays an important role in planar heterojunction devices with SubNc as the acceptor, in which case the dissociation of SubNc excitons is driven by the field rather than by the energetic offset at the D/A interface.

Chandran et al. also reported direct free charge generation in a single-layer SubNc device, with an architecture similar to the SubNc homojunction OSCs discussed herein, yet they attributed the origin for charge generation to the high dielectric constant ($\epsilon_r = 5.8$) in SubNc.¹³ If this was the case, one would expect to observe features of charge generation not only in the device but also in the thin film, which contradicts with the TA results reported above. In addition, several studies have reported that increasing the dielectric constant has a minor effect on device performance

unless the dielectric constant reaches a value of around 10.^{9,28} Nevertheless, it would still be interesting to examine the impact of dielectric constants on the charge generation mechanism in SubNc. Furthermore, a recent study pointed out that SubNc has the potential to reduce device energy losses when used in PHJ devices, as a result of the strong hybridisation between SubNc exciton and CT states.²⁹ The observation that SubNc can lead to low energy losses is indeed correct—this is because similarly when SubNc was paired with a range of chlorinated SubPc derivatives with various driving forces, it was found out that efficient photocurrent generation occurs independent of the D/A interfacial energetics (See Figure A.13 in the Appendix for details).

Subnaphthalocyanine based materials continue to attract extensive research interests due to their strong absorption.^{30–37} OSC devices based on SubNc have been reported to be resilient towards oxygen and water, showing excellent thermal and chemical stability.^{38,39} Moreover, recent studies have also suggested that such ambipolar molecules including SubNc, its analogue SubPc as well as their derivatives have great potential to replace fullerenes.^{13,27,33,40} Together with the low energetic disorder nature of SubNc,⁴¹ and the field-assisted charge separation in SubNc without relying on a driving force, SubNc based OSC devices present a promising potential for future applications such as integration into a device stack for tandem devices.

6.5 Conclusions

This chapter rationalises the origin for charge generation in SubNc homojunction organic solar cells, which exhibits a power conversion efficiency of 1%. Using a combination of transient absorption and photoluminescence spectroscopy, it is shown that charge generation only occurs in SubNc homojunction organic solar cells as a result of the field but not in SubNc thin films. Further temperature-dependent in-situ UV-Vis absorption measurements indicate that photogenerated excitons in the SubNc film dissipate to heat instead of converting to charges. The study then goes further to explore the impact of field-assisted charge generation in SubNc on the carrier dynamics in a planar heterojunction α -6T/SubNc OSC device, where the dissociation of SubNc excitons was found to occur within itself rather than at the D/A interface. A key point

learnt from these observations is that charge generation across a type II heterojunction can proceed without the aid of an energy offset at the D/A interface when the field-assisted charge generation can occur in either D or A. As mentioned in Chapter 3 and 4, suppressing the energy offset at the D:A interface is key to minimising voltage losses in OSCs in order to boost their efficiency. As such, utilising materials like SubNc which show field-assisted charge generation is particularly of interest in OSCs with low energy offsets, in which both efficient charge generation and low voltage losses can be expected to be achieved simultaneously under careful design. While planar heterojunction devices present several advantages over the bulk heterojunction devices, their efficiencies are still far behind bulk heterojunction analogues, limiting their further development. More research effort is needed to realise the full potential of planar heterojunction organic solar cells.^{42,43}

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Chapter 7

Conclusions and Outlook

7.1 Conclusions

Using a combination of steady-state and transient spectroscopic tools, this thesis describes a study of the carrier dynamics in state-of-the-art organic solar cells (OSCs) and provides insight into the origin of charge generation as well as elucidates various factors dictating the recombination processes. Chapter 3 and 4 investigate the photophysics of bulk heterojunction devices whilst Chapter 5 and 6 shift the focus to homojunction devices.

Chapter 3 shows that the performance in a non-fullerene based Donor:Acceptor (D:A) bulk heterojunction OSC with a low driving force (PffBT4T-2OD:EH-IDTBR) is limited by a significant amount of geminate recombination from charge-transfer (CT) states, which is in contrast to a ‘conventional’ larger driving force system employing PC₇₀BM as the acceptor. Furthermore, transient absorption (TA) spectroscopy on PffBT4T-2OD:EH-IDTBR films shows that charge transfer in this blend is relatively slow, attributed to the combined effect of the phase segregated morphology and the small driving force. In-depth *T*-dependent pump push photocurrent (PPPC) spectroscopy measures a value of 100 meV for the binding energy of CT states in PffBT4T-2OD:EH-IDTBR devices, which interestingly is on the same order as that reported for fullerene-based devices, yet the CT states in the non-fullerene blend suffers severe geminate recombination.¹ In this case, a simple rationale behind these observations is that the recombination characteristics in non-fullerene OSCs are largely governed by the driving force for charge separation, where a low driving force induces more geminate recombination. In addition, other factors such as disorder may facilitate the CT state dissociation even in the presence of a large binding energy and can be further explored.^{2,3}

Chapter 4 continues to examine the unique photophysics of CT states in D:A bulk heterojunction OSCs using TA spectroscopy. By screening seven non-fullerene OSC blends which all suffer from significant CT recombination losses, the present findings suggest that the CT state lifetime strongly correlates with voltage losses and hence the driving force. That is, the lower the driving force, the faster the CT decay, implying an inverted energy gap law relationship between the CT state lifetime and its energetics. While all seven systems examined within this chapter show CT geminate decay, not every OSC system with small driving forces shows such geminate recombination. The results presented in Chapter 4 are indeed exciting, yet are still far away

from a comprehensive study. While addressing this unexplored CT state behaviour, Chapter 4 also raises more open questions, for example, what governs the extent of geminate recombination in contemporary small driving force OSCs and how to design material systems with a small driving force without causing any geminate recombination.

Chapter 5 investigates small molecule based homojunction OSCs employing polycrystalline alpha-sexithiophene (α -6T) as the photoactive layer, showing that the energy landscape can be controlled via carefully tailoring the orientation of α -6T molecules. TA spectroscopy carried out on pristine α -6T films shows strong evidence of charge generation, resembling the TA characteristics for α -6T homojunction OSCs. This efficient charge generation in α -6T films is attributed to the molecular electrostatics arising from the interface between standing and lying domains of α -6T molecules. This is further supported by the time-correlated single photon counting kinetics measurements, in which the excitons in the mixed oriented α -6T molecules were found to be efficiently quenched. These results aid the understanding of molecular electrostatics on charge generation, which is not only applicable to α -6T homojunction OSCs, but has also been recently reported to be the decisive factor leading to the high efficiency in PM6:Y6 OSCs.^{4,5}

Chapter 6 extends the research scheme on homojunction OSCs and explores the charge generation in chloroboron subnaphthalocyanine (SubNc) based homojunction OSCs with SubNc as the main photoabsorber. By examining both pristine films and devices, it has been shown with TA spectroscopy that only devices exhibit features of efficient charge generation, instead the TA characteristics in films are dominated by the thermal modulation, supported by in-situ T -dependent absorption spectroscopy. One of the main conclusions from this study is that the built-in field plays a vital role in driving charge generation in SubNc homojunction OSCs. Additionally, the contribution of thermal modulation signal in pulsed laser measurements may be substantial in certain materials, which should not be overlooked when interpreting those data. Finally, this chapter also touches upon the dynamics and device performance of planar heterojunction α -6T/SubNc OSCs, showing that the external quantum efficiency of this device is mostly governed by the charge generation pathways within each photoactive layer, rather than the charge transfer across this type II junction.⁶

7.2 Outlook

This thesis has addressed several aspects on the photophysics of excited-state carriers in OSCs with a wide range of material systems, from exciton dissociation to CT state recombination as well as free carrier recombination, spanning across the timescale from sub-picosecond to nanosecond. Transient spectroscopic studies on OSCs are certainly useful and interesting to rationalise those unique photophysics, especially given the rapid surge in the OSC device efficiencies, yet there is still a long way to go before this technology can be fully exploited. Moving forward, this section presents my perspectives on the future fundamental research directions that would be beneficial to push the field forward, covering aspects including material design and property, as well as ultrafast spectroscopy. Nonetheless, all of these research directions must be accompanied by industrial efforts to realise the full commercialisation of low-cost, environmentally friendly OSCs.

7.2.1 Material design and properties

During the past few years, a vast range of organic materials have been synthesised and employed in OSCs, among which the non-fullerene acceptors (NFAs) are of particular interest.^{7–9} Following some recent works studying the role of NFAs in OSCs by Qian et al. and Classen et al.,^{10,11} more research is still needed to relate the optoelectronic properties of NFAs to device photophysics. Firstly, research efforts must be spent on understanding what optoelectronic properties of NFAs can govern the high efficiency in OSCs, for example, whether molecular rigidity,⁵ electron wavefunction delocalisation,¹² or long exciton lifetime¹¹ is universally important to achieve highly efficient OSCs remains intriguing. Secondly, correlating the structure-property relationship to identify the structural origins for preferred properties of NFAs, which currently still remains an open question in the field. For instance, the impact of intermolecular interaction strength and molecular aggregation on the exciton kinetics are continued to be studied following this thesis. Thirdly, as it is apparent that the state-of-the-art efficiency in OSCs is achieved by combining NFAs with polymer donors,¹³ the rapid development in NFAs needs to be balanced with the search for suitable polymers with matching properties such as mobility, crystallinity etc.

Recognising a clear structure-property correlation for NFAs and pairing with suitable polymers would pave the way for future material design and enhancement in efficiency.

Furthermore, a deeper understanding of the charge generation mechanism in D:A bulk heterojunction systems is still needed. Moving from a single material to a blend of two means that the interaction between the two would introduce more states, such as CT states investigated within this thesis, making the whole system more complicated to study. On top of understanding material properties within NFAs, it thus becomes clear that understanding the role of these states and their relationship between each other is equally important. For example, it remains unclear whether the hybridisation between the lowest exciton and CT states is beneficial for OSCs, to the best of my knowledge, which certainly merits more research. While this thesis has explored the impact of a few factors influencing charge separation and recombination including molecular electrostatics, electric field and driving force, other factors could be playing a vital role as well. Among those factors, many are largely determined by specific material properties, hence understanding the aforementioned structure-property relation in NFAs is essential towards this. Firstly, as pointed out by several modelling studies already,^{14–16} entropy can increase the escape probability of excitons, yet this remains unexplored experimentally. This is mostly due to the challenges in controlling and varying the entropy in a given material system. Nevertheless, the entropic contribution on charge separation is worth looking into and it is hoped that controlling the entropy and evaluating its role to be possible in the near future. Secondly, investigating the field-effect on charge generation dynamics in devices remains appealing, based on the observation that films sometimes may not fully represent what happens in devices. As such, it is proposed that comparing the transient characteristics of both films and devices should become a standard experimental approach for future research.

7.2.2 Ultrafast spectroscopy

From the work presented here, it is apparent that TA and PPPc spectroscopy (in visible and near-IR regions) offer extensive information on the fate of electronically excited states and the subsequent charge transfer and/or energy transfer events in OSC devices. However, the structural inhomogeneities within OSC blends should not be overlooked. Combining time-

resolved spectroscopy with optical imaging, such as transient absorption microscopy can provide spatial information of these excited states together with the temporal information.^{17–19} In addition, the electronic properties of organic semiconductors are also largely affected by vibronic coupling, being able to access information on such vibrational motions would enrich current understandings.²⁰ Extending the probe wavelength to mid-IR to monitor those vibrational models, coupled with femtosecond lasers would be interesting. For example, techniques such as femtosecond resonance or stimulated Raman spectroscopy can therefore be of use to identify the spectral footprints of interest.^{21–23}

Lastly, while significant progress has been made on OSC fabrication not only in small research lab scales but also in large modules, material discovery and deployment are still rather slow. More specifically, it can take many years to develop a novel material, not to mention the lengthy time taken to optimise morphology and devices. It is apparent that accelerating the translation from a material property into a product property is what would drive the further development of this technology. One way to realise this is to couple machine learning with solution deposition and morphology imaging to speed up the material screening processes and eventually the organic photovoltaics technology as a whole.²⁴

7.3 Concluding remarks

The last decade has definitely been an enlightening period for the field of organic solar cells. It may not seem clear to one whether organic photovoltaics technology is hope or just hype. Nevertheless, the ‘soft’ nature of organic semiconductors governs their unique properties and has stimulated intense research in order to best utilise these materials. As such, fundamental research is still driving their development, which at the same time also has the potential to provide transferable knowledge to the field of organic electronics as a whole. As human beings strive for a greener environment, more fundamental research on solar energy conversion devices is still of great importance.

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Appendix A

A.1 Calculation of excitation fluence and density

The following notes and equations detail the calculation methods for the excitation fluences and densities reported within this thesis. Excitation fluence F is calculated by dividing the incident excitation energy E by the area of the equipped pinhole (with a radius r), where the excitation energy E is determined by dividing the power P (measured with an energy meter VEGA P/N 7Z01560, OPHIR Photonics) against the frequency f of the excitation laser:

$$F(\text{J cm}^{-2}) = \frac{E}{\pi r^2} = \frac{P}{f \times \pi r^2} \quad (\text{A.1})$$

The number of incident photons per unit area is calculated via dividing the incident excitation fluence F by the photon energy E_p at the excitation wavelength λ :

$$n_i(\text{cm}^{-2}) = \frac{F}{E_p} = \frac{F}{hc/\lambda} \quad (\text{A.2})$$

The number of photons absorbed by the material is calculated by taking into account the sample absorbance A at the excitation wavelength λ :

$$n_a(\text{cm}^{-2}) = 10^{-A} \times n_i \quad (\text{A.3})$$

Finally, the excitation density is calculated by dividing the thickness d of the sample from the number of photons absorbed:

$$n(\text{cm}^{-3}) = \frac{n_a}{d} \quad (\text{A.4})$$

A.2 Supporting data for Chapter 3

A.2.1 Linearity in TA amplitudes

Figure A.1 shows that the yield of photogenerated charge carriers varies linearly with the pump fluence. The values were taken from the maxima of the kinetics for charges (or CT states) from Figure 3.7.

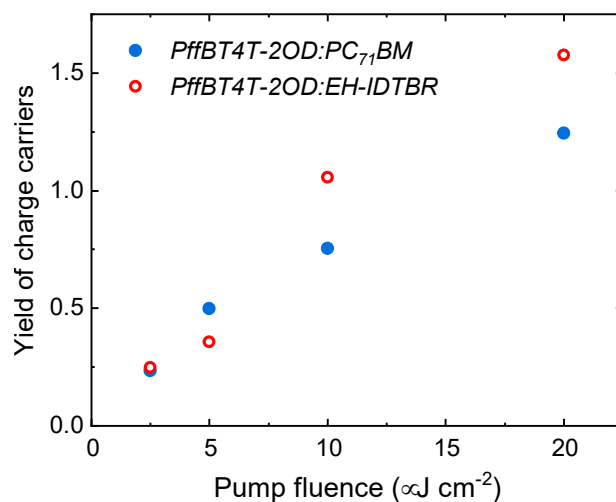


Figure A.1 Yield of photogenerated charge carriers for a *PfBT4T-2OD:EH-IDTBR* blend film and a *PfBT4T-2OD:PC₇₁BM* blend film determined from transient absorption spectroscopy.

A.3 Supporting data for Chapter 4

A.3.1 Device performance

The device performance for the blend systems investigated in Chapter 4 is summarised in Table A.1.

Table A.1 Photovoltaic parameters of bulk heterojunction D:A organic solar cells

D:A systems	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PfBT4T-2OD:IDFBR	1.12	9.06	0.45	4.52
PfBT4T-2OD:FBR	1.11	13.8	0.5	7.83
PfBT4T-2OD:EH-IDTBR	1.08	14.7	0.6	9.53
PfBT4T-2OD:ITIC	0.85	12.1	0.51	5.52
PBDB-T:EH-IDTBR	1.00	15.0	0.58	9.3
PBDB-T:IT-4F	0.84	19.3	0.71	11.54
PTQ10:IDIC	0.97	20.2	0.63	12.4

A.3.2 TA and TCSPC kinetics for pristine EH-IDTBR films

Figure A.2 summarises the EH-IDTBR exciton kinetics measured by transient absorption spectroscopy and time-correlated single photon counting (TCSPC) respectively, which both yielded an exciton lifetime of 328 ps, showing good agreement. Figure A.2a presents the kinetics as the one shown in Figure 3.4d in Chapter 3.

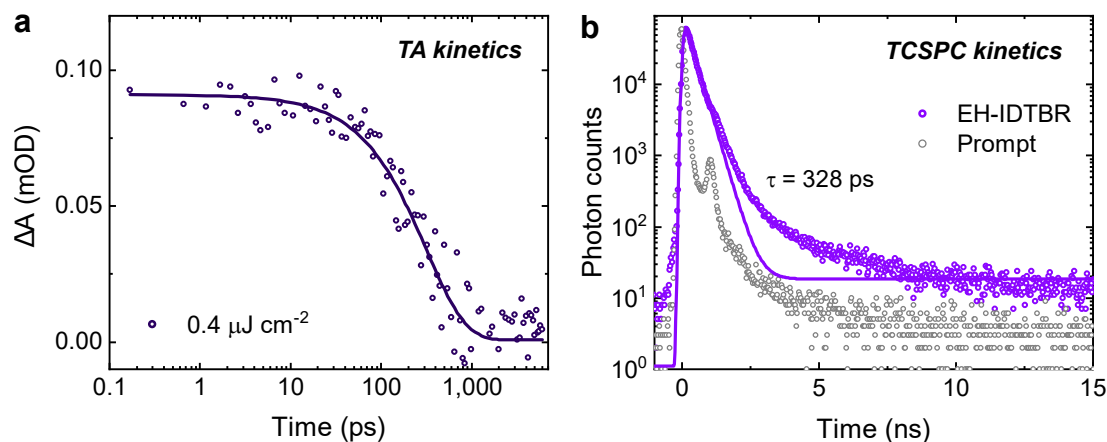


Figure A.2 Exciton decay kinetics for pristine EH-IDTBR films, measured by **a**, Transient absorption spectroscopy, and **b**, Time-correlated single photon counting.

A.3.3 TA spectra for Y6 solutions and films

Figure A.3 shows the TA spectra for a pristine Y6 film and a pristine Y6 solution. In both Y6 solutions and films, pronounced photoinduced absorption peaks can be observed, situating at 906 nm and 878 nm individually, assigned to Y6 excitons.

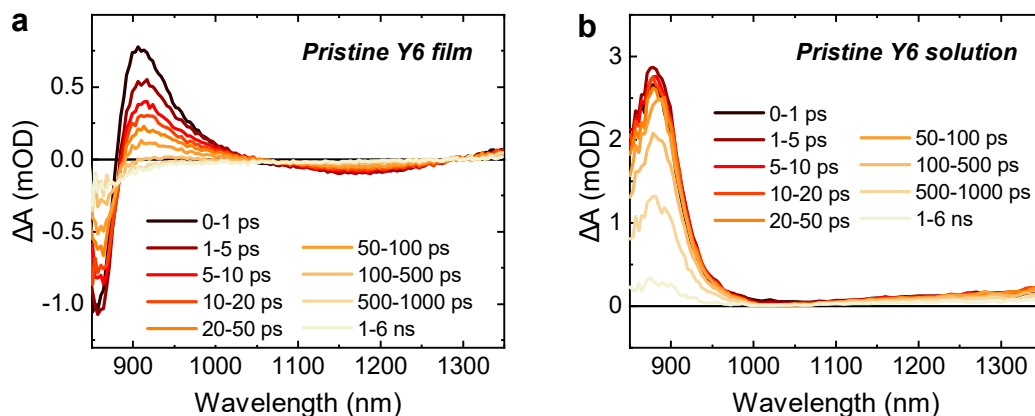


Figure A.3 Transient absorption spectra at various pump-probe delay times for **a**, a pristine Y6 film and **b**, a pristine Y6 solution, which was excited at 650 nm and 700 nm, respectively.

A.3.4 Characterisation for Y6 solutions, films and devices

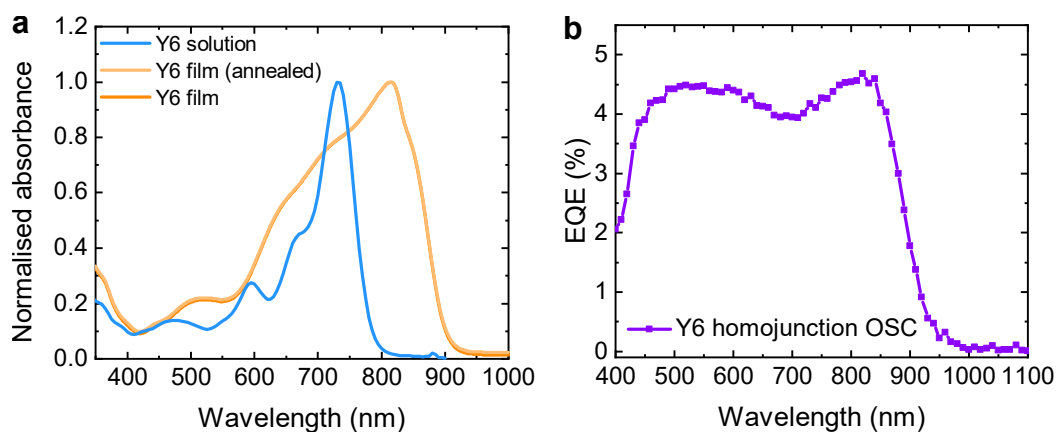


Figure A.4 **a**, Absorption spectra for a pristine Y6 solution, a pristine Y6 film and a thermally annealed pristine Y6 film. **b**, External quantum efficiency spectra for a single-component Y6 homojunction organic solar cell device.

Figure A.4a presents the absorption spectra for a pristine Y6 film, a thermally annealed Y6 film as well as a Y6 solution. The absorption maximum in the Y6 film red-shifts to 816 nm compared to the Y6 solution (at 730 nm), indicating a significant amount of molecular aggregation in the solid film. However, thermal annealing has a negligible effect on its absorption features, and

hence morphology. In addition, Figure A.4b shows that charge photogeneration can occur in Y6 homojunction OSCs.

A.3.5 Absorption and PL characterisation for the lower gap components

Figure A.5 presents the reduced absorption and photoluminescence spectra for the lower gap materials in the blend systems. The optical band gaps of these materials were determined from the intersection point between the reduced absorption and photoluminescence spectra following the literature method.¹

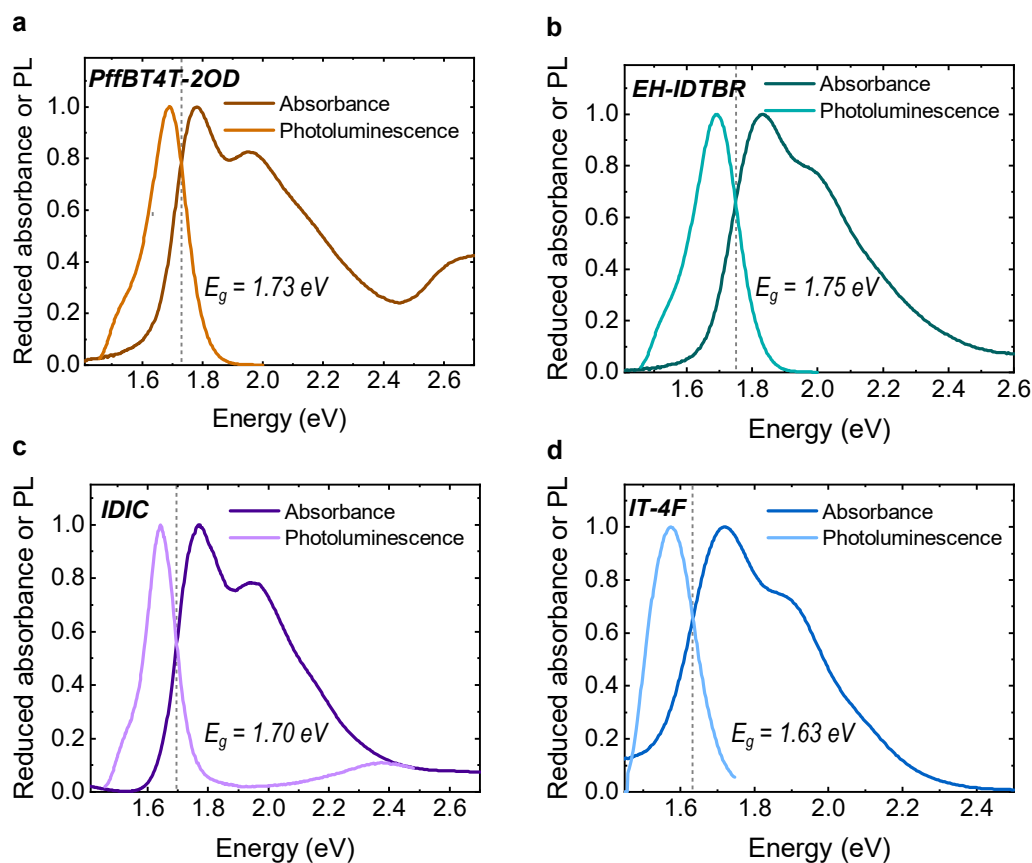


Figure A.5 Reduced absorption and photoluminescence spectra for the lower band gap component in the blends investigated including **a**, PffBT4T-2OD, **b**, EH-IDTBR, **c**, IDIC, **d**, IT-4F, where their optical gaps were determined from the crossing point between the reduced absorption and reduced photoluminescence spectra.

A.4 Supporting data for Chapter 5

A.4.1 Absorption and PL characterisation

Figure A.6a shows the reduced absorption and photoluminescence spectra for an α -6T film with mixed orientations. The optical band gap was determined to be 2.33 eV from the crossing point between the two curves following the literature method.¹ Shown in Figure A.6b is the in-situ absorption spectra measured at different temperatures from 293 K to 353 K for an α -6T film with mixed orientations, where no change in the amplitude of absorbance was observed. The T -independent absorbance thus indicates that the transient absorption data in the visible probe region is not influenced by any thermal modulation/artefacts.

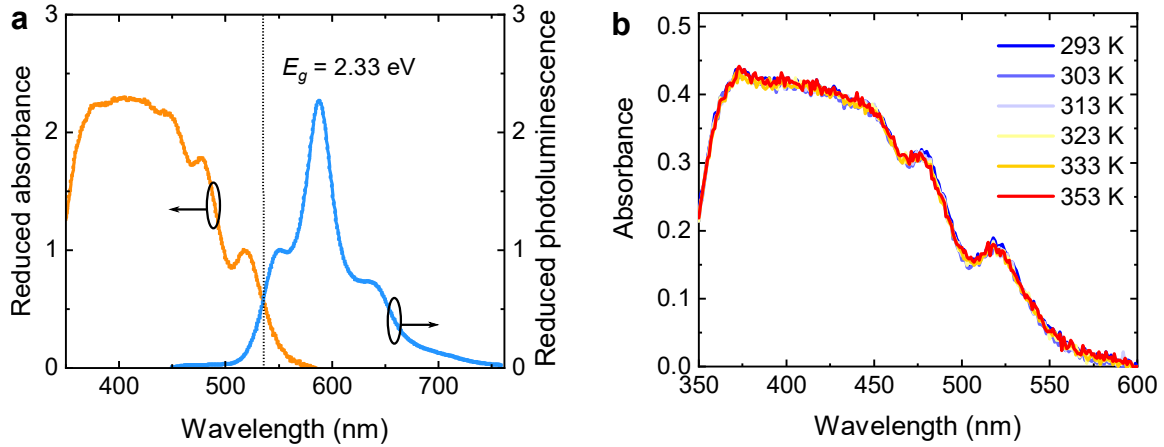


Figure A.6 Optical band gap determination and T -dependent absorption characterisation. **a**, Reduced absorption and photoluminescence spectra for an α -6T film with mixed orientations; **b**, In-situ absorption spectra measured at different T between 293 and 353 K.

A.4.2 EA spectroscopy for 6T homojunction solar cell devices

Figure A.7 compares the electroabsorption (EA) spectrum with the 1st derivative of the α -6T absorption spectrum in Figure A.6a, showing a good resemblance, as well as the normalised transient absorption spectra presented in Figure 5.2a.

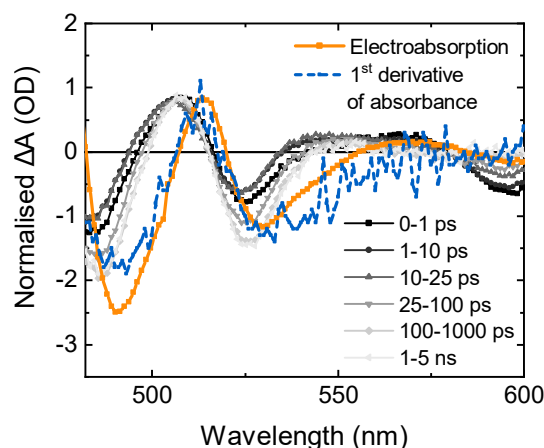


Figure A.7 Comparing the normalised transient absorption spectra with the electroabsorption measured independently for a device and the first derivative of the absorbance of an α -6T thin film.

A.4.3 Morphology characterisation for 6T orientations

Grazing-incidence wide-angle X-ray scattering diffraction images in Figure A.8 show that the desired molecular orientations of α -6T thin films were successfully fabricated by tuning the specific processing conditions.

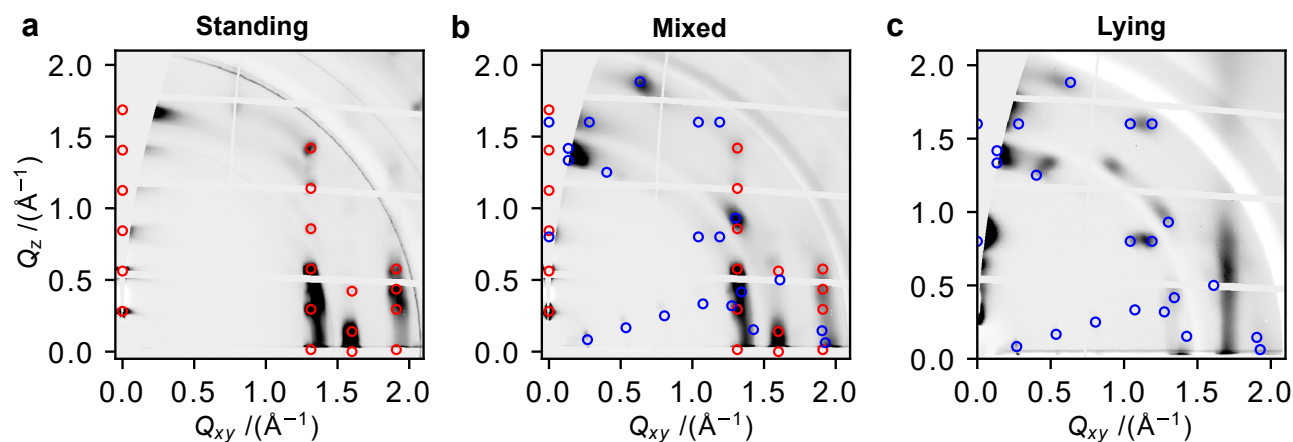


Figure A.8 Grazing-incidence wide-angle x-ray scattering (GIWAXS) diffraction images for α -6T thin films with different orientations including **a**, Standing, **b**, Mixed, and **c**, Lying. The peaks indicated by red and blue circles originate from crystallites with standing and lying molecules, respectively.

A.4.4 Device photovoltaic parameters and voltage losses analysis

Table A.2 Photovoltaic parameters of α -6T based homojunction organic solar cells with different buffer layers. The current-voltage characteristics for these devices are presented in Figure 5.9.

Device architecture	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
ITO/ α -6T/Rubrene/BPhen/Ag	1.61	3.6	50.2	2.9
ITO/ α -6T/C545T/BPhen/Ag	1.46	3.8	34.7	1.9
ITO/ α -6T/DBzA/BPhen/Ag	1.57	3.3	39.9	2.1
ITO/ α -6T/TCTA/BPhen/Ag	1.57	3.3	39.4	2.1
ITO/ α -6T/TPBA/BPhen/Ag	1.61	3.6	47.0	2.8
ITO/ α -6T/TBPe/BPhen/Ag	1.41	3.0	42.5	1.8
ITO/ α -6T/TPBI/BPhen/Ag	1.50	3.2	33.3	1.6

Table A.3 Voltage losses analysis for homojunction organic solar cells based on α -6T with different buffer layers. The radiative limits of the voltage (V_{rad}) were calculated from the EQE spectra in Figure 5.9 following the literature method.¹ The non-radiative voltage losses ($\Delta V_{non-rad}$) were calculated by subtracting the open-circuit voltage (V_{OC}) from V_{rad} . The total voltage losses were estimated by subtracting V_{OC} from the optical bandgap of α -6T determined from Figure A.6.

Device architecture	V_{OC} (V)	V_{rad} (V)	$\Delta V_{non-rad}$ (V)	$E_g/q - V_{OC}$ (V)
ITO/ α -6T/Rubrene/BPhen/Ag	1.61	1.87	0.26	0.72
ITO/ α -6T/C545T/BPhen/Ag	1.46	1.89	0.40	0.87
ITO/ α -6T/DBzA/BPhen/Ag	1.57	1.88	0.31	0.76
ITO/ α -6T/TCTA/BPhen/Ag	1.57	1.88	0.31	0.76
ITO/ α -6T/TPBA/BPhen/Ag	1.61	1.88	0.27	0.72
ITO/ α -6T/TBPe/BPhen/Ag	1.41	1.88	0.47	0.92
ITO/ α -6T/TPBI/BPhen/Ag	1.50	1.88	0.38	0.83

A.4.5 Theoretical calculations

Theoretical calculations were performed for a 2D-infinite interface between standing and lying α -6T domains. The interface morphology has been built from the experimental crystal structure² and relaxed with classical simulations based on a validated force field³ performed with the NAMD code⁴. Hybrid quantum/classical (QM/MM) GW⁵ and Bethe-Salpeter⁶ many-body electronic structure calculations were performed with the FIESTA package. These calculations considered up to six molecules in the QM region, embedded into the MM electrostatic and polarisable crystalline environment described with the charge response model in the MESCal code implementation.⁷ The starting Kohn-Sham orbitals were obtained with the gap-tuned density functional ω B97X ($\omega = 0.141$ Bohr⁻¹) and the cc-pVTZ basis, which ensures accurate energy levels with single-iteration G0W0 calculations. Bethe-Salpeter calculations were performed beyond the Tamm-Dancoff approximation, including all electron-hole transitions up to 10 eV.

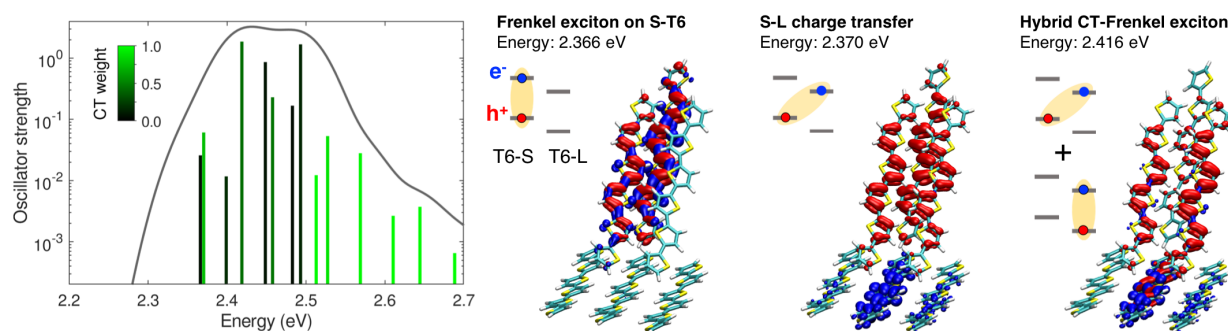


Figure A.9 Theoretical calculations for the optical excitation. **a**, Absorption spectrum of the standing-lying α -6T interface. Bar colours indicate the weight of inter-layer CT states of each excitation, showing that the lowest-energy region of the spectrum presents states that have a pronounced charge separation, with hole and electron localised in the standing and lying domains, respectively. The energy of these states with spatially separated charges is determined by the interfacial energy offset and can act as a gateway for an efficient charge splitting. **b-d**, Electron-hole density plots and the corresponding simplified energy-level sketches of representative low-energy excitation.

A.5 Supporting data for Chapter 6

A.5.1 TA assignment for SubNc films and devices

Figure A.10 compares the TA spectra at short pump-probe delay times (0.1 to 0.5 ps) and long pump-probe delay times (1 to 5 ns) for the SubNc pristine film and SubNc SCOSC device with the absorption, PL as well as the thermal modulation signals. As can be seen from Figure A.10a, TA spectra for both film and device at short delay times is mostly dominated by the ground state bleaching, with some contribution from the stimulated emission. In terms of the TA spectra at long delay time, the film spectrum is in good agreement with the thermal modulation signal (see discussions about Figure 6.3), whereas the device spectrum deviates significantly from the thermal modulation signal, suggesting the presence of other excited-state species.

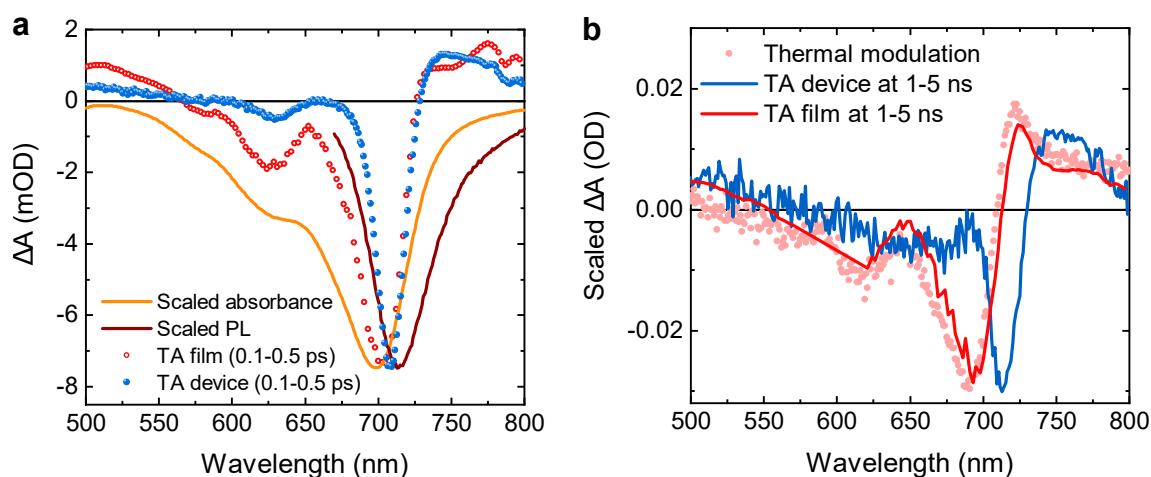


Figure A.10 Transient absorption (TA) spectra assignment for SubNc films and devices. **a**, Comparing the TA spectra at 0.1 to 0.5 ps for SubNc films and devices with the scaled steady-state absorbance and photoluminescence spectra. **b**, Comparing the TA spectra at 1 to 5 ns for SubNc films and devices with the thermal modulation signal.

A.5.2 Genetic algorithm analysis for a pristine SubNc film

Figure A.11 presents the genetic algorithm analysis results for a pristine SubNc film, in which only two components can be resolved including the exciton and the thermal modulation signals.

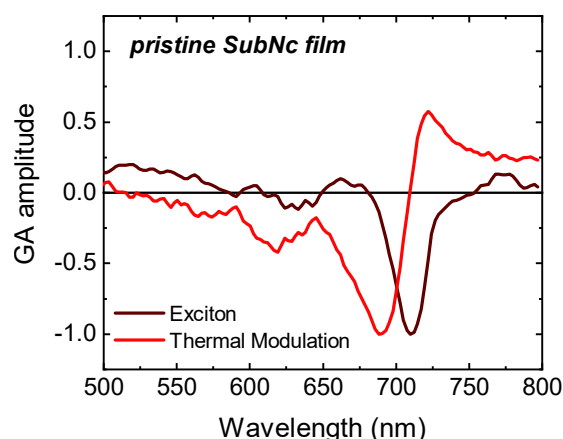


Figure A.11 Genetic algorithm analysis for the transient absorption data for a pristine SubNc film, showing only two components.

A.5.3 External quantum efficiency spectra for a 6T/SubNc planar heterojunction device

Figure A.12b compares the external quantum efficiency (EQE) spectrum for a α -6T/SubNc planar heterojunction (PHJ) OSC with that in a SubNc homojunction OSC and an α -6T homojunction OSC. One obvious feature that can be observed from this figure is that the EQE amplitude at around 700 nm is similar in the SubNc homojunction OSC and the α -6T/SubNc device, suggesting that charge generation from SubNc in the PHJ α -6T/SubNc is driven by the charge generation from SubNc itself, rather than by the hole transfer at the heterojunction.

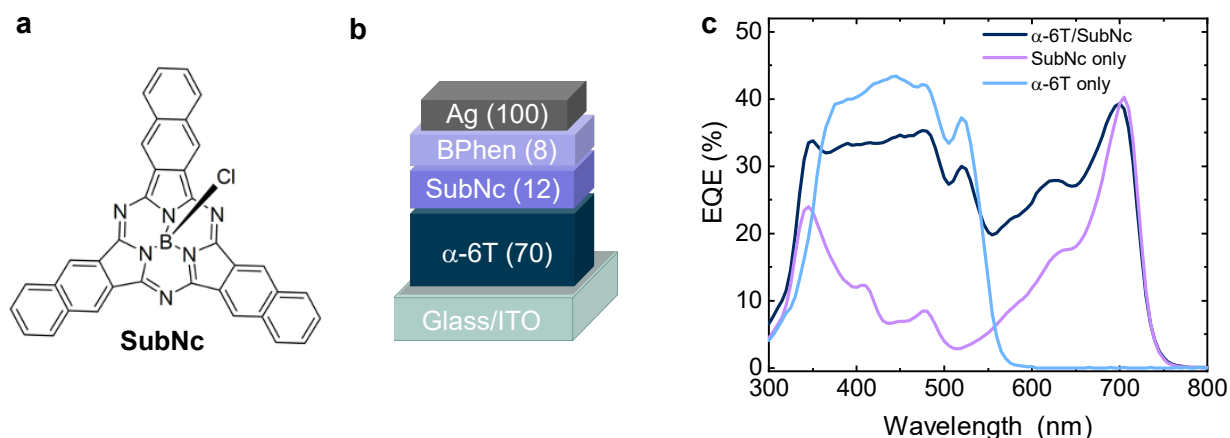


Figure A.12 **a**, Chemical structure of SubNc. **b**, Device architecture of an α -6T/SubNc planar heterojunction organic solar cell (OSC) device. Numbers inside the parentheses denote the thickness of each layer in nanometers. **c**, External quantum efficiency spectra for an α -6T/SubNc planar heterojunction OSC as well as a SubNc homojunction OSC and an α -6T homojunction OSC.

A.5.4 Current-voltage characteristics for SubNc/SubPc based derivatives planar heterojunction devices

Figure A.13 shows the current-voltage characteristics for planar heterojunction devices employing SubNc as the donor with a range of SubPc derivatives as acceptors, showing that high photocurrent can be achieved regardless of the magnitude of driving forces.

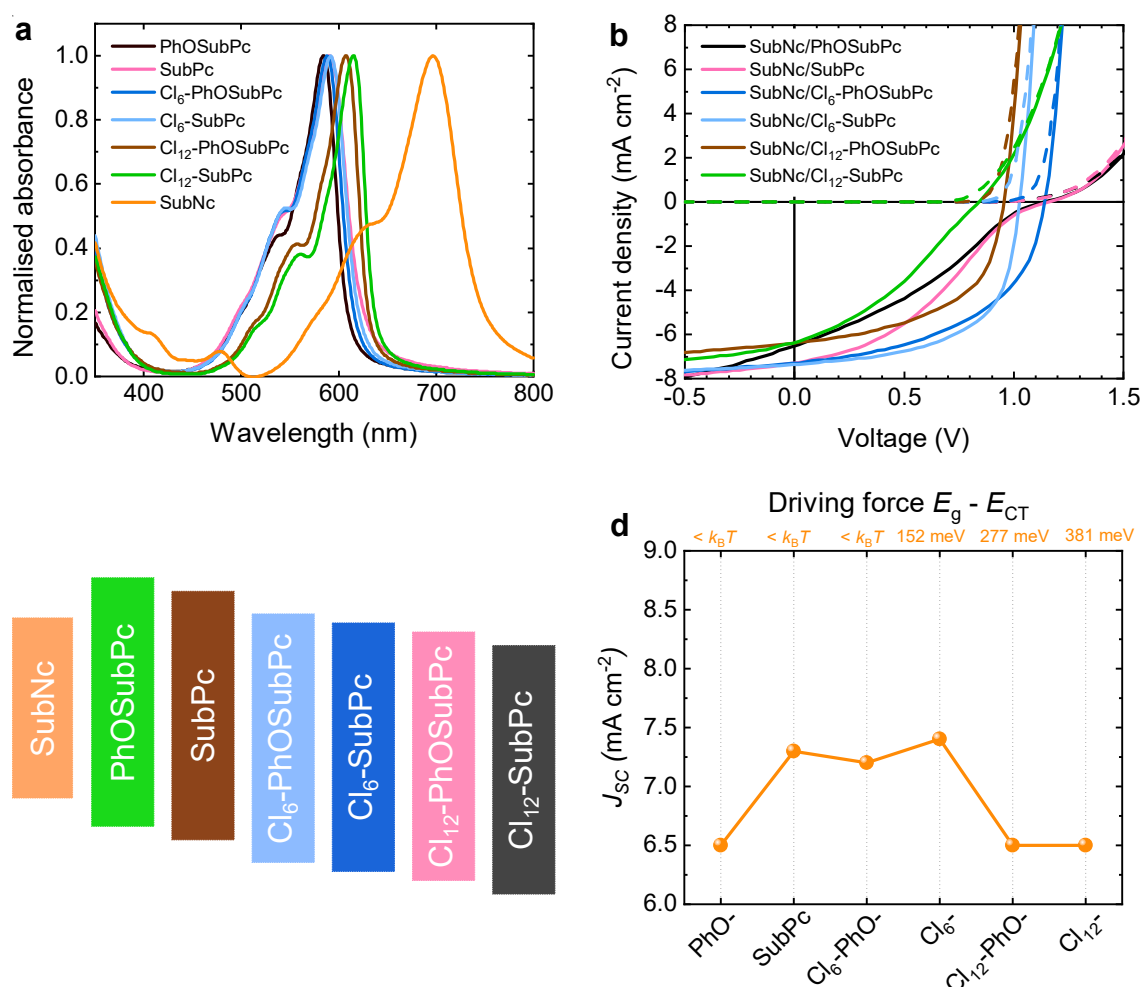


Figure A.13 **a**, Normalised absorption spectra for pristine films of SubNc (of 12 nm) and SubPc derivatives (of 15 nm) including PhOSubPc, Cl₆-PhOSubPc, Cl₆-SubPc, Cl₁₂-PhOSubPc, and Cl₁₂-SubPc. **b**, Current-voltage curves for the investigated devices under 1 sun illumination (solid lines) and in dark (dashed lines). **c**, Band alignments of the investigated materials. **d**, Short-circuit current density (J_{SC}) plotted as a function of driving force for the investigated devices.

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