

Competition between Charge Collection and Non-Geminate Recombination in Bulk Heterojunction Solar Cells

by

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We have found it of paramount importance that in order to progress, we must recognise our ignorance and leave room for doubt.

- Richard Feynman.

Chaque flot est un ondin qui nage dans le courant, chaque courant est un sentier qui serpente vers mon palais, et mon palais est bâti fluide, au fond du lac, dans le triangle du feu, de la terre et de l'air.

- Aloysius Bertrand.

Abstract:

This thesis is concerned with quantification of non-geminate recombination losses in organic bulk heterojunction solar cells. After description of the context of this work, the theoretical background and the methodology employed are presented. In this thesis, many different polymer:fullerene systems are investigated.

In the next chapter, we show that the study of non-geminate losses using charge extraction/transient photovoltage analysis can be applied to many different systems away from P3HT/P3HS blends. We see to what extent ideality factors can give a more precise description of the exact recombination mechanism.

Then, the change of optoelectronic properties of a high performance polymer:fullerene blend upon a blend ratio perturbation is investigated. The resulting shifts in energetics and dynamics of the blends are quantified. A quantitative agreement between two methods (charge extraction and electroluminescence) probing the shifts in the energetics at the heterojunction is presented.

In the next two chapters, two limits of the common vision of polymer:fullerene systems are explored by combining experiment and 1D drift-diffusion modelling. First, the impact of the variations of the spatial distribution of carriers on the apparent reaction order is experimentally investigated. The study reconciles the apparent contradictions currently in the literature regarding the meaning of high reaction orders. In the following chapter, the often underestimated effects of unintentional doping in polymer blends are addressed experimentally. In particular, its effect on device optimisation, understanding of carrier collection and recombination dynamics are explored. This study suggests that many donor/acceptor blends are not, contrary to common belief, intrinsic semiconductors.

Finally, an analysis of the Langevin and non-Langevin behaviour of some efficient systems is presented. The different interpretations of regular observations disproving non-geminate recombination following the Langevin type mechanism are reviewed. We suggest the ratio 'recombination over collision' is often overlooked and question the underlying assumption that it should be unity.

Keywords: disordered semiconductors, charge transport, non-geminate recombination

Statement of own work

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1. H. Zhong, Z. Li, F. Deledalle, E. C. Fregoso, M. Shahid, Z. Fei, C. B. Nielsen, N. Yaacobi-Gross, S. Rossbauer, T. D. Anthopoulos, Fused Dithienogermolodithiophene Low Band Gap Polymers for High-Performance Organic Solar Cells without Processing Additives. *J. Am. Chem. Soc.* 2013, 135, 2040-2043.
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- Submitted or in preparation:
7. F. Deledalle, T. Kirchartz, M.S. Vezie, M. Campoy-Quiles, P. Shakya Tuladhar, J. Nelson, J.R. Durrant, Understanding the Effect of Unintentional Doping on Transport Optimisation and Analysis in Efficient Organic Bulk Heterojunction Solar Cells. submitted to *Adv. Energy Mater.* 2014.
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List of Abbreviations

IEA	International Energy Agency
OECD	Organisation for Economic Co-operation and Development
RDD&D	Research development demonstration and deployment
EDI	Energy Development Index
PV	Photovoltaic
W_p	Peak Watt
OLED	Organic Light Emitting Diode
FET	Field Effect Transistor
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
ASA	Advanced Semiconductor Analysis
AM	Air Mass
IP	Ionisation Potential
EA	Electron Affinity
BHJ	Bulk Heterojunction
ITO	Indium Tin Oxide
Al	Aluminium
LiF	Lithium Fluoride
ZnO	Zinc Oxide
PEDOT:PSS	Poly(3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid)
MoO_x	Molybden Oxides
PCBM	[6,6]-phenyl $C_{71/61}$ -butyric acid methyl ester
FF	Fill Factor
PCE	Power Conversion Efficiency
MPP	Maximum Power Point
IQE	Internal Quantum Efficiency
EQE	External Quantum Efficiency
CT	Charge Transfer
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
DoS	Density of States
CE	Charge Extraction
TPV	Transient Photovoltage
TPC	Transient Photocurrent
UIPAC	International Union Pure and Applied Chemistry

SCLC	Space Charge Limited Current
CELIV	Charge Extraction by Linearly Increasing Voltage
OSC	Organic semiconductors
TDCF	Time-Delayed Collection Field
TCO	Transparent Conducting Oxide
CF	Chloroform
ODCB	O-dichlorobenzene
MMT	Matrix Modelling Technique
CGS	Centimetre gram second system of units

List of Symbols

p_z	P-type orbital
$N_{0CBtail}$	Densities of intra bandgap tail states at the conduction band edge
$N_{0VBtail}$	Densities of intra bandgap tail states at the valence band edge
E_{chC}	Slope of the tail states for electrons
E_{chV}	Slope of the tail states for holes
E_C	Conduction band edge
E_V	Valence band edge
λ	Wavelength
k_B	Boltzmann constant
T	Temperature
E_{Fn}	Quasi-Fermi level for electrons
E_{Fp}	Quasi-Fermi level for holes
E_g	Band gap
ϕ_c	Workfunction of the cathode
ϕ_a	Workfunction of the anode
n_i	Refractive index of media i
d	Thickness
$\tilde{n}$	Real part of refraction index measured by ellipsometry
$\tilde{k}$	Imaginary part of refraction index measured by ellipsometry
J_{sc}	Short-circuit current density
ψ	Electric potential
ρ	Space charge density
ϵ_0	Permittivity of vacuum
ϵ_r	Relative permittivity
n	Density of electrons
p	Density of holes
t	Time
e	Elementary charge
J_n	Current density of electrons
J_p	Current density of holes
R	Recombination rate per unit of volume
G	Generation rate per unit of volume

V_{BI}	Built-in voltage
n_0	Intrinsic density of electrons
p_0	Intrinsic density of holes
ϕ_{fc}	Contact barrier at front contact
ϕ_{bc}	Contact barrier at back contact
V_{oc}	Open-circuit voltage
R_{ext}	External load
E_{net}	Net electric field
R_{shunt}	Shunt resistance
J_{mpp}	Short-circuit current density at maximum power point
V_{mpp}	Voltage at maximum power point
η_{PCE}	Power conversion efficiency
P_{light}	Power of incident light
R_{series}	Series resistance
S	Total spin or surface velocity
S^n	Singlet state
T^n	Triplet state
D_n	Diffusion coefficient
μ_n	Mobility
λ_{free}	Mean free path
r_c	Capture radius
v_h	Velocity of a hole
i_h	Current of holes through elementary surface
γ_{eh}	Langevin recombination rate
μ_{chem}	Chemical potential
τ	Carrier lifetime
L_D	Drift length
J_{ph}	Corrected photocurrent
G	Spatially averaged generation rate
S_{min}	Surface recombination velocity
E_F	Fermi energy
k	Recombination rate
Z_{input}	Input impedance
$\Delta n, \Delta p$	Excess electrons, holes
A	Pixel area
C	Capacitance
N_A	Apparent doping density (p-type)
w	Space charge width
ϑ	Dimensionless parameter for TPV fitting
β	With dimension parameter for TPV fitting
$\tau_{\Delta n}$	Small perturbation lifetime
m	Dimensionless parameter for charge extraction at open-circuit fitting
γ	With dimension parameter for charge extraction at open-circuit fitting

τ_n	Macroscopic carrier lifetime
J_{gen}	Generation flux
J_{loss}	Loss flux
Φ	Illumination level
n_{id}	Ideality factor
δ	Reaction order
n_{free}	Density of free electrons
n_{tot}	Density of total electrons
μ^*	Effective mobility
n_0, p_0	Intrinsic density of electrons and holes
G_{SCR}	Average generation rate within the space charge region
J_{light}	Light current density
J_{dark}	Dark current density
$N_{\text{A}}^{\text{max}}$	Maximum doping density allowed to have fully depleted device at the second interference maximum
ζ	reduction Langevin factor
ε	Recombination efficiency

Context

More than sixty years after WWII, the world has shifted into a multi polar pattern of international relations. Developed countries exchange and deal with extremely dynamic developing countries on an increasingly equal basis. The International Energy Agency (IEA) predicts world primary energy demand increasing by thirty six percent between 2008 and 2035,(IEA, 2010) driven by an increasing world population and economic development. This prediction assumes a new policy scenario in which the international community manages to agree on stronger commitments in modulating the energy demand and boosting the energy efficiencies of the current energy intensive processes. Ninety-three percent of this increase in energy demand was predicted to come from non-OECD countries in this study. A more sustainable development is internationally recognised to be necessary,(N.Stern, 2006; Pachauri and Reisinger, 2007) and will require deep social and technological changes.

The electric power sector has a paramount role to play in reducing the impact of more homogeneous economic development on the environment across the globe. This is even more important if others sectors such as transport shift towards electric power. Even though it is widely acknowledged that fossil fuels will remain the main source of energy in the next decades, renewable energies such as wind, solar and hydro are increasingly important as 'green alternatives' to fossil fuels and nuclear power (by complementing the latter). Indeed, despite the large efforts to exploit non-conventional fossil fuels, peak oil is predicted to occur between 2020 to 2050 depending on the scenario.(Sorrel, 2009) A further advantage of renewable energy technologies is to enable more delocalised energy production. Solar power will be particularly suitable for remote (off-grid) areas as long as the solar insulation is strong enough. The access to 'green' energy must remain affordable and therefore, substantial efforts are still needed to decrease the cost per Watt produced (including production, installation and maintenance costs) over the lifetime of the module. Strong international cooperations are needed between policy makers, researchers and industries to push forward these renewable technologies along the RDD&D axis.

The advantages brought by renewable energy technologies, including solar, are

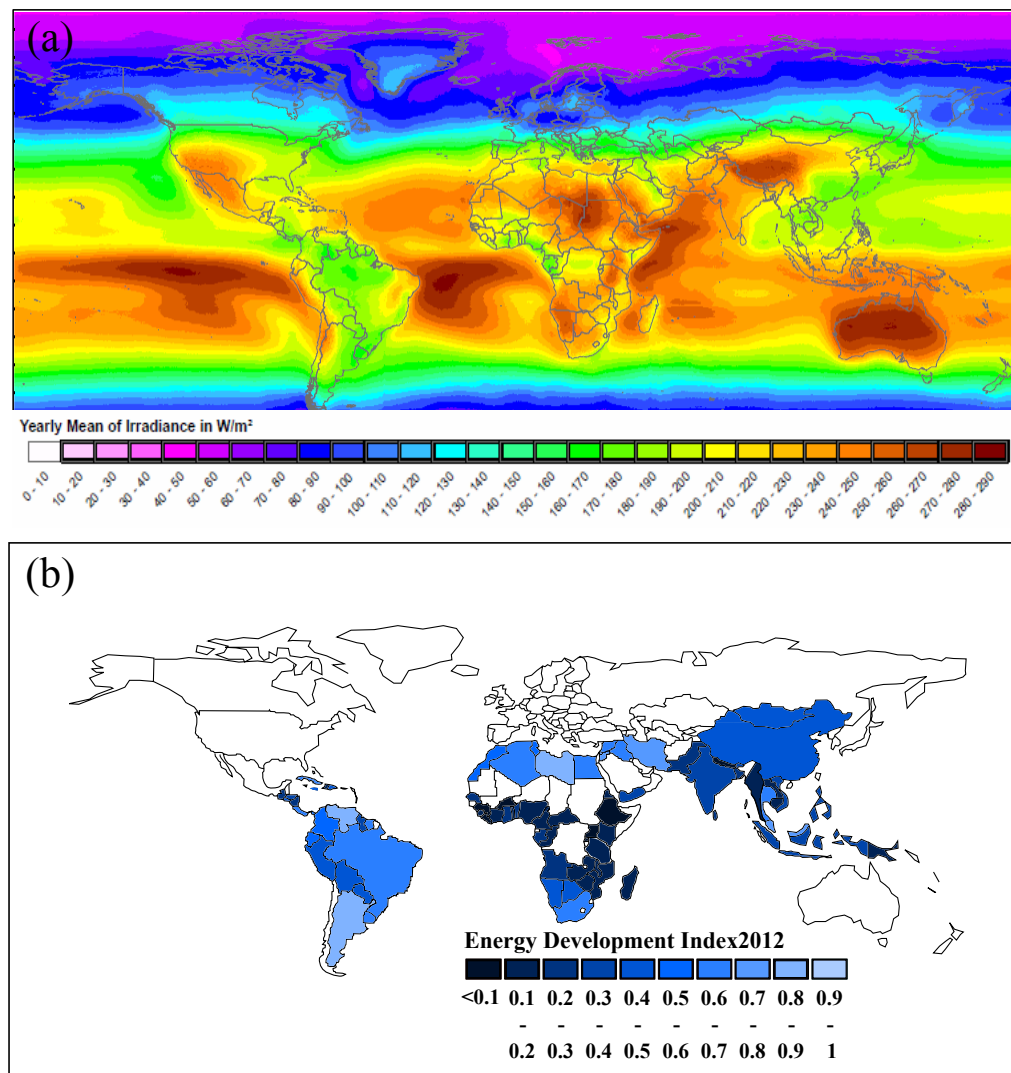


Figure 1.1: a) Yearly mean solar Irradiance [W.m^{-2}] across the globe (HelioClim server). Map copyright Ecoles des Mines de Paris/Armines 2006.(CEP Centre of Energy and Processes, 2012) b) 2012 Energy Development Index of a pool of 80 monitored countries worldwide. The index was developed by the IEA and part of the World Energy Outlook 2012 as a measure of the transition of a country towards modern fuels and modern energy services.(IEA, 2012) In many cases, solar energy has great potential in energy poor countries.

diverse and vary given the region of the world. In the developed countries, solar energy is a way to diversify the energy mix and therefore participate in the construction of a more secure and robust energy market. The state of this power market in Europe is crucially dependent on potential, although unconfirmed, investments in further infrastructure in a few super oil/gas fields, which are mainly located at the gate of eastern Europe (around the Caspian sea) and building projects for nuclear power plants, which will proceed if licencing and sufficient funds to meet the initial investment are approved rapidly. In developing nations, where the solar irradiation is often higher than the world average, photovoltaics could help to achieve the energy equity in a sustainable manner. Figure 1.1 a) shows the mean yearly solar irradiance across the globe and illustrates in particular how heterogeneous the distribution of solar power is. As a comparison, Figure 1.1 b) represents the 2012 Energy Development Index (EDI) created by the International Energy Agency (UN) for a pool of 80 monitored countries within the developing nations. This composite index takes into account different parameters such as electricity access (percentage of population who have access to electricity and per capita residential electricity consumption), access to clean cooking facilities, energy public services and energy for productive use (share of economic purposes like industry, transport, services, agriculture, fishery, in the total final consumption). More details about this index can be found in IEA (2012). The higher the index, the more advanced the energy development. It seems striking that the countries which most need to improve energy access for health and economic development are predominantly the countries with the highest resources in solar energy in the world.

Energy equity is a core issue in this century, as many developing countries are copying the model of developed countries in developing their power infrastructure. Although, this could lead to climate, environment and health degradations, it is difficult for developed nations to object, since they have already benefited from this approach. Indeed, despite the high population growth in these regions of the world, the energy per capita consumption is still very low compared with countries such as the US. For example, the Indian per capita energy consumption is currently 17 percent of the US. (Clarke and Graczyk, 2010) It is clear that strong interactions between different regions of the world is needed to put the different countries in a win-win situation concerning energy issues, sharing the state of the art technology to ensure that international targets to tackle climate change and energy equity are reached.

Until now, the solar market has mainly been driven by the production of silicon based photovoltaics. The capacity is growing rapidly (in 2011, half of the world cumulated PV capacity was installed), in particular since China and Taiwan

entered mass production. In 2011, around 40% of global photovoltaic (PV) production came from mono-crystalline silicon modules (9114 MW_p), whilst $\approx 45\%$ (10336 MW_p) came from multi-crystalline silicon. (Fraunhofer Institute for Solar Energy Systems ISE, 2012) The lowest reported retail price for a multi-crystalline Silicon module is at $\text{€}0.78/\text{W}_p$ and $\text{€}0.81/\text{W}_p$ for a mono-crystalline silicon module.¹ In 2013, Chinese manufacturers alone fabricated 12 GW_p worth of PV products. (Bloomberg New Energy Finance, 2014) In 2009, QuantaSol reported a 28.3% efficient single junction solar lab-scale cell, quantifying the current state of the art. Nevertheless, ultimately to achieve the grid parity in many power markets, it is necessary to reduce the cost per kWh of photovoltaic systems. To try to address this, thin film technologies have been introduced and since 2006, the production has ramped up to represent a $\approx 14\%$ share (3204 MW_p) in the total global production in 2011 (more than half of which is CdTe, and the rest a-Si and CuIn(G)S). The reduction of the total cost could also be achieved by developing alternative PV technologies such as excitonic solar cells. Indeed, the use of rare earth elements and/or very pure silicon remains the main barriers preventing a further reduction in the cost of current PV technologies for mid to long term development. To address this, there are two main routes for photovoltaics, namely either producing very expensive, efficient technology in small quantity (such as those used in solar concentrators) or less efficient, substantially cheaper materials such as excitonic solar cells including molecular semiconductors, conjugated polymers and dye-sensitised solar cells.

The study of some of these alternative excitonic solar cells dates back as far as the 1950's including work by Tollin et al. (1960), Fox et al. (1963) and Kallmann and Pope (1960). A growing interest in organic semiconductors has arisen in the field of plastic electronics and new display technologies such as Organic Light Emitting Diodes (OLEDs) and Field Effect Transistors (FET)s, along with an increasing price of oil on the market, have favored more intensive studies of organic solar cells. Progress in the understanding and development of polymer based photovoltaics has been conducted by achieving different milestones such as the use of semiconducting polymers, (Shirakawa et al., 1977; Heeger, 2010) the improvement of the architecture of the solar device involving a bulk heterojunction to ease the exciton separation, (Yu et al., 1995) and the synthesis of lower band gap polymers to match better the solar spectrum. (Brabec et al., 2011) Today, it is increasingly thought that the key issues to be tackled have been discerned. This would enable the development of devices at the laboratory scale whose efficiency would pass the current confirmed record of 9.2% by He et al. (2012b) to join the range of 10-15

¹the module cost represents here approximately 35-40 % of the total installation cost

percent, which would be sufficient to attract the attention of investors.(IDTechEx, 2013)

One characteristic of these polymer:fullerene cells is that at the optimal thickness, only a certain percentage of the incoming light is absorbed. Generally the active layer is thin (in the range of 100 nm). The molar extinction coefficient of these materials is such that it appears obvious to enhance the absorption by increasing the thickness of the blend donor/acceptor. Moreover, increasing the thickness would ease the production of such devices and consequently would reduce their cost. However, in spite of the increased absorption, the overall efficiency of thicker device, for most polymers, does not improve. This issue is the core question addressed in this thesis. I aim to develop an understanding of the parameters which control the loss of device performance with increasing thickness, and ultimately to suggest routes to fabricate polymer:fullerene devices with thicker active layers.

Background

2.1 Origin of semiconductivity in π -conjugated systems

At the core of the organic semiconducting behaviour is the existence of π -conjugation which makes some electrons weakly bound to their nuclei, such that they tend to be delocalised, as illustrated in Figure 2.1. In this configuration, the carbons are sp^2 hybridised. Each of the carbon atoms in this conjugation has 3 sp^2 orbitals constituting the backbone of the molecule (with strongly bound electrons involved in σ -bonds with the neighbors atoms) and one p_z orbital perpendicular to the plane of the sp^2 orbitals. When the p_z orbitals of two neighbors overlap, there is a π -conjugation (bonding character when they overlap in phase and anti-bonding character when in opposition of phase). Using the approximation of Hückel, the molecular orbitals ψ are a linear combination of the related atomic orbitals ϕ_i , as pictured in Figure 2.1. Increasing the length of the conjugation therefore increases the number of the linear combinations of all the atomic p_z orbitals. In the ideal case of an infinite and linear π -conjugated chain, the number of molecular orbitals would be such that the energy difference between two consecutive levels would be very small, thus by extrapolation, the system would start to present a character of metallic conduction. However, in such a conjugated system, the electronic states are substantially affected by the electron/phonon interaction. These π -conjugated systems present what was discovered earlier in 1D metals: the Peierls distortions, which is a consequence of an instability of the Fermi level states breaking spontaneously the symmetry of distribution over the chain to lower the total energy of the system. (Peierls, 1955) This leads to the opening of a band gap at the Fermi level and the creation of all the optoelectronic properties of the π -conjugated organic semiconductors. This is generally represented by the standard Highest Occupied Molecular Orbital (HOMO)/ Lowest Unoccupied Molecular Orbitals (LUMO) chemistry. Moreover, the organic semiconductors are not straight chains. On the contrary, disorder interrupts the wave functions over the chain, transforming the polymer into a succession of segments, each having a specific energy gap. In consequence, the HOMO/LUMO gap of each organic semiconducting material shows some Gaussian widening of typically ≈ 0.1 eV. (Koster

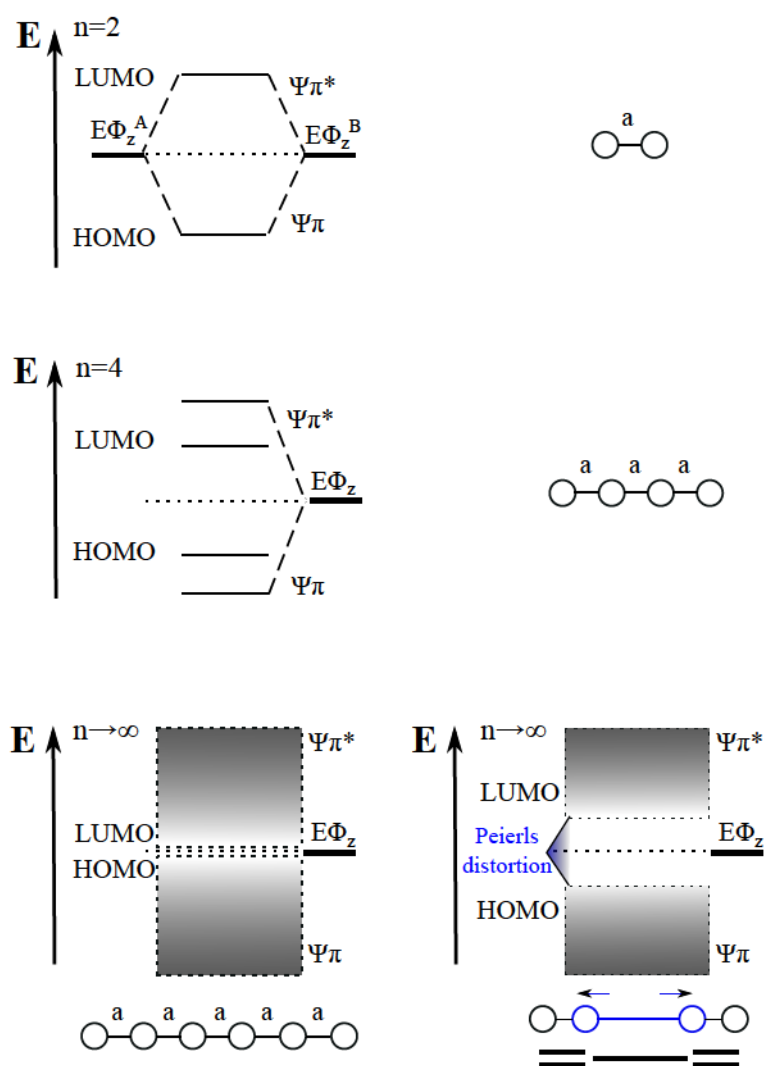


Figure 2.1: Formation of semiconductivity in organic π -conjugated systems. a is the distance between carbon atoms, Φ_z^A , Φ_z^B the atomic p_z orbitals of atoms A and B, Ψ_π , Ψ_{π^*} are the bonding and antibonding π molecular orbitals respectively.

et al., 2005b; Bäessler, 1993) The disorder also increases the overall bandgap.

The population of carriers is represented by the product of the density of states (number of available states per unit of energy and volume) and the probability of occupation of this state. Polymer:fullerene solar cells are usually disordered. The inhomogeneity of structures (local orientations of the polymer chains, conformations) and compositions (donor, acceptor, charged or neutral impurities) at the nanoscale in materials of low relative permittivity affect the energy landscape in which the polarons¹ spatially evolve and can lead to low lying states that act as charge traps. The exact shape of the density of states in the band gap is generally not known. In the modelling using advanced semiconductor analysis (ASA) here in this thesis, it is assumed that the sub bandgap tails can be represented by an exponential as follows:

$$N_{\text{CBtail}} = N_{0\text{CBtail}} \exp\left(\frac{E - E_C}{E_{\text{chC}}}\right) \quad (2.1)$$

$$N_{\text{VBtail}} = N_{0\text{VBtail}} \exp\left(\frac{E - E_V}{E_{\text{chV}}}\right) \quad (2.2)$$

where $N_{0\text{CBtail}}$, $N_{0\text{VBtail}}$ are the densities of tail states at the conduction and valence band edges (respectively E_C and E_V) and E_{chC} , E_{chV} are the slope of the tail states within the band gap, usually expressed in [meV]. This representation of density of states has recently provided good approximations supported by experiments. (Nelson, 2003; Street et al., 2011; Street, 2011) Figure 2.2 represents the distribution of localised states within the band gap assumed in the simulations of transport and recombinations presented in this thesis.

2.2 Solar spectrum on Earth

At the basis of the solar potential is a light source with a specific spectral irradiance which can be approximated by the emission of a black body with a temperature of ≈ 5777 K. (NASA, 2013) This is a similar temperature to the surface of the sun, whose emission maximum (when expressed in per unit of wavelength [$\text{W}\cdot\text{cm}^{-2}\cdot\text{nm}^{-1}$]) coincides with the visible region for the human eye.

This spectrum is only extraterrestrial and after traveling through the atmosphere, has been truncated due to the absorption/scattering of different elements within the atmosphere such as atoms and molecules (size $d \ll \lambda$, Rayleigh scattering), particles ($d \approx \lambda$, Mie scattering) or bigger droplets ($d \gg \lambda$, geometric optics).

¹free electron or hole in interaction with the distortions of the neighboring lattice.

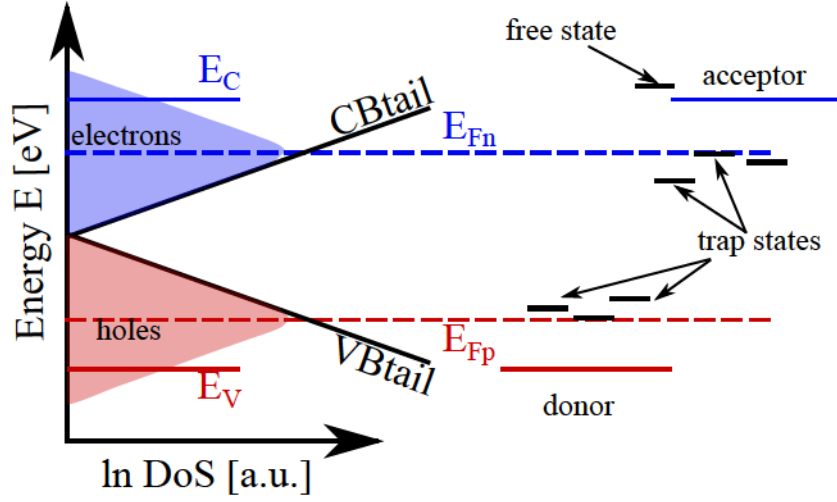


Figure 2.2: Schematics of the density of states in disordered semiconductors. On the left, exponential tails states are present within the band gap. On the right, if the slope of the tail states are higher than $k_B T$, the traps states are just below the quasi-Fermi levels. The figure was adapted from Kirchartz and Nelson (2012).

We note in particular the truncation due to water vapor absorption in the regions [600;720] nm, ≈ 850 nm, ≈ 950 nm, Ozone [450;750]nm and Oxygen [630;760] nm.

The exact density of photons over the entire spectrum depends on many parameters including the region of the globe, the inclination on the ground relative to the sun and the altitude. For comparison purposes, standardization is required. In this thesis, according to the tradition in solar photovoltaics, the evaluation of solar cell performance is given under 1 sun equivalent illumination, which corresponds to standard test conditions: 1000 W.m^{-2} with a Global AM (Air Mass) of 1.5, corresponding to a solar zenith angle of 48.19° (0° would mean that the sun rays are directly facing the ground surface).

Finally as single junction solar cells can only absorb photons equal or greater in energy to the material bandgap and since any excess energy of the photon is lost as heat, PV single junction solar cells under AM1.5 spectrum have a maximum power conversion efficiency of $\approx 31\%$ for a 1.1 eV band gap, known as the Shockley-Queisser limit.(Shockley and Queisser, 1961)

2.3 Macroscopic description of organic solar cells

2.3.1 Structures

The most basic model of an organic semiconductor device is usually the Metal–Insulator–Metal architecture, which involves two metal electrodes of different workfunctions, one of them being semi-transparent.(Brabec et al., 2001b). In this architecture, the process of charge generation in conjugated polymers is very poor (though a PV effect using one pure conjugated polymer with typical power conversion efficiencies of $[10^{-3};10^{-1}]%$ was observed by Karg et al. (1993); Antoniadis et al. (1994); Yu et al. (1994)), for reasons which are developed just below in the subsection on charge generation. Instead, the active layer of the organic single junction solar cells is typically composed of two semiconductors with different electron affinities (EA), typically one electron donor (e.g. conjugated polymer) and one electron acceptor (often molecules such as fullerene,(Yu et al., 1995) perylene Imides/diimides,(Tang, 1986) or another conjugated polymer with deeper LUMO (Halls et al., 1995)). Either the two semiconductors are

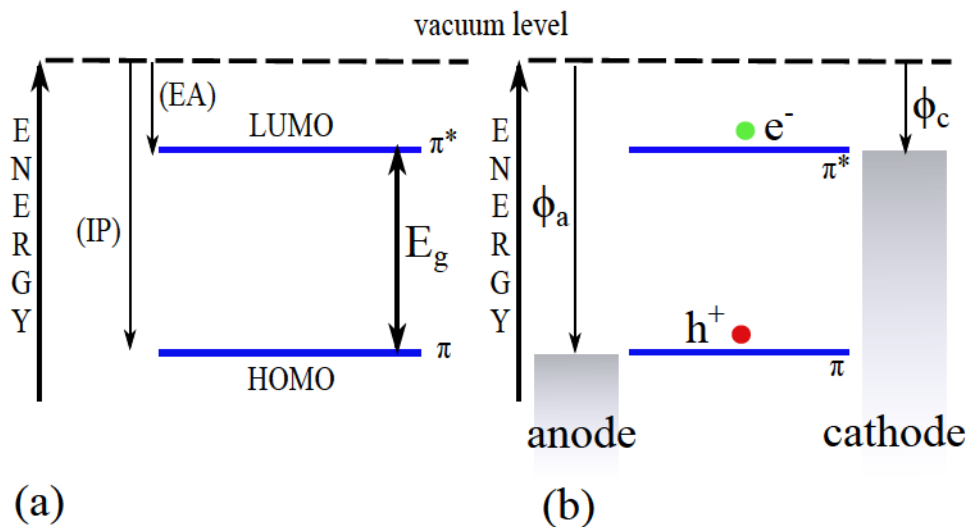


Figure 2.3: a) Energy levels of a conjugated polymer semiconductor showing Electron Affinity (EA), Ionisation potential (IP), intrinsic band gap (E_g). b) Typical Metal–Insulator–Metal device energy level using a pure conjugated polymer with two electrodes with asymmetric workfunctions ϕ_a , ϕ_c . The latter are chosen to match the energy levels of the semiconductor.

deposited layer by layer, in which case the active layer is a bilayer ², or the two semiconductors are blended to form an intimate mixing, in which case the active layer is referred to a bulk heterojunction (BHJ). (Yu et al., 1995) In this thesis, all the devices used for study are bulk heterojunction organic solar cells.

With bulk heterojunctions, the active layer is usually considered as an effective single semiconductor with the LUMO of the acceptor (sometimes called effective conduction band to mirror the band diagrams of mono-semiconductor solar cells like in silicon solar cells) and the HOMO of the donor (sometimes called the effective valence band). To add selectivity to the relevant carriers at the contacts between the active layer and electrodes, thin blocking layers are very often added, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulphonic acid) (PEDOT:PSS). These interlayers also help reducing the extraction barriers Φ_{bc} , Φ_{fc} between the active layer to the relative electrode workfunction to obtain quasi-ohmic contacts as discussed just below. (Park et al., 2010) The overall architecture of a typical polymer:fullerene solar cell is shown in Figure 2.4. The semitransparent electrode typically used is Indium Tin Oxide (ITO) as the hole collecting electrode and a low workfunction metal back electrode such as Aluminium used as the electron collecting electrode. However, these low workfunction metals are particularly sensitive to oxidation in the presence of moisture. (Chen et al., 2009b) Consequently, higher workfunctions metals such as Silver or Gold are sometimes chosen and in that case, the ITO is used as electron collecting electrode in an inverted architecture as shown in Figure 2.5. While the conventional architecture has been traditionally preferred, some inverted structures have been recently shown to perform equally well as their conventional counterpart. (Sun et al., 2011) This has some important implications, in particular from the perspective of device stability.

Metal/organic semiconductor interfaces were shown to be a major challenge if high efficiencies solar cells are targeted. (Liu et al., 2010) By putting into contact a metal electrode and an organic semiconductor without interlayer, the equalisation of the Fermi level of the semiconductor to the electrode workfunction (Fermi level pinning) will result in the creation of an interface dipole whose magnitude will depend on the metal only and will therefore always adapt to the organic counterpart. Many different mechanisms of Fermi level pinning at a metal/organic interface exist (charge transfer, covalent bonding, permanent molecular dipole, image force and exchange/Pauli repulsion) but they will all participate in the creation of the interface dipole. Consequently, the pinning occurs usually in the middle of

²obtaining a proper bilayer is in practice difficult as the two phases usually blend to some extent over a certain depth. (Ayzner et al., 2012; Tang, 1986)

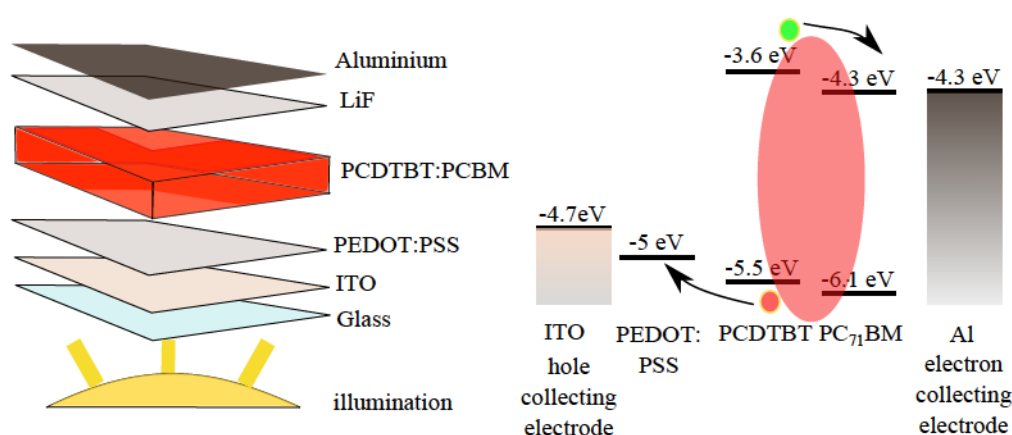


Figure 2.4: Device structure of a typical PCDTBT:PCBM in conventional architecture (left) and equivalent energy level diagram of the different materials stacks (right). In this architecture, the holes are collected by ITO. The molecular structures of the organic materials are detailed in the Chapter 4. The energy levels were extracted from Heeger (2010).

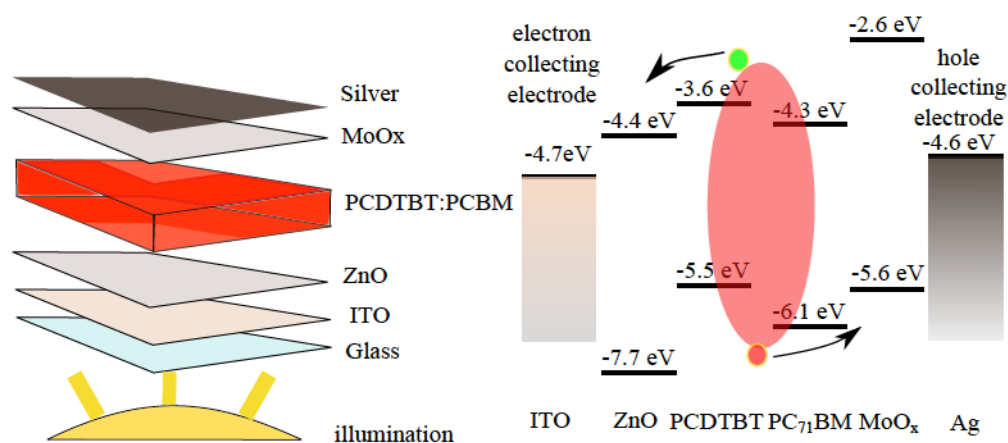


Figure 2.5: Device structure of a typical PCDTBT:PCBM in inverted architecture (left) and equivalent energy level diagram of the different materials stacks (right). In this architecture, the electrons are collected by ITO.

the band gap of the organic semiconductor, away from the transport energy level (or mobility edge), giving rise to the back and front contact barriers ϕ_{bc} and ϕ_{fc} as shown in Figure 2.6.

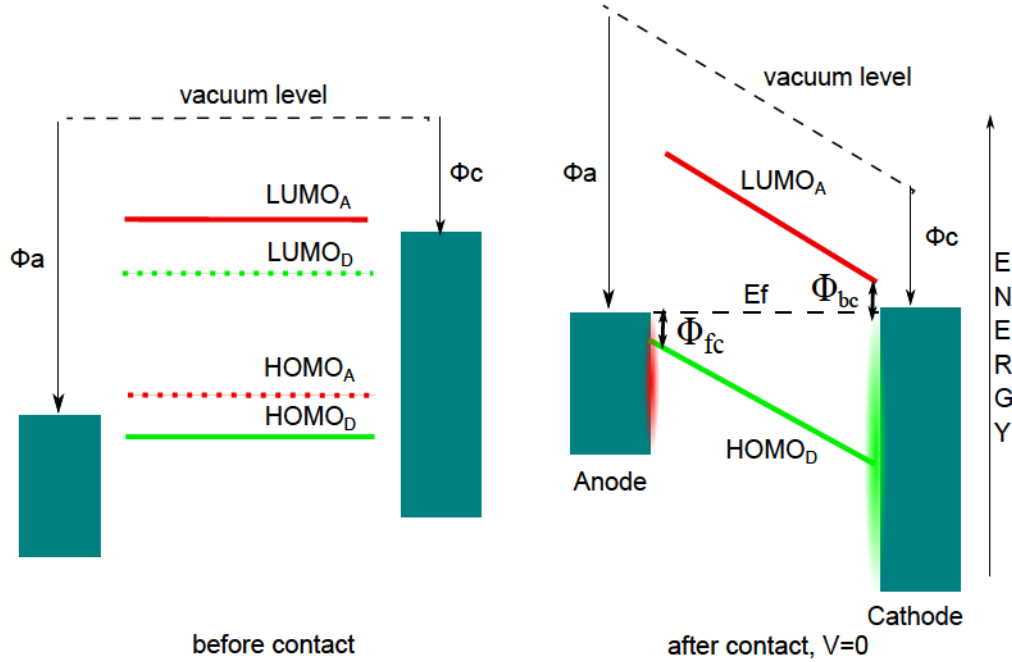


Figure 2.6: Energy diagram in the dark at zero bias of the different components of the device before being in contact(left). After contact, in the dark under no external applied bias, the overall system reaches thermal equilibrium and the Fermi levels of the different components match. Illumination in this system will push the system into non-equilibrium. To demonstrate, front and back contact energy barriers (ϕ_{fc} , ϕ_{bc}) at the interfaces with the electrodes have also been drawn.

2.3.2 Light harvesting and interference effects

As presented just above, the typical polymer:fullerene solar cell is made of a multistacks of materials each with a different refractive index $\tilde{n}$ and extinction coefficient $\tilde{k}$. The light comes into the active layer through the semitransparent electrode and at the other extreme side of the stack, there is a metal electrode with a high reflection coefficient, which depends on the exact thickness and deposition technique. Consequently, the fraction of the light which makes it all the way through the active layer is mainly reflected at the back metal electrode.

The typical thickness the photoactive layer of polymer:fullerene solar cells d is of the order of 100 nm, which is the same order as the wavelengths absorbed by the blend, typically [350;850] nm.(Bronstein et al., 2011) As a result, at each wave-

length of the spectrum, the light coming back and forth within the multistack will interfere. Thus, the standard Beer-Lambert law for absorption in the blend cannot be used rigorously. The profile of light distribution within the active layer will be the result of the complex sum over the entire spectrum of the light source of the interference patterns of the different wavelengths. The situation is similar to coherent propagation in multilayer structures:(Harbecke, 1986) The main conse-

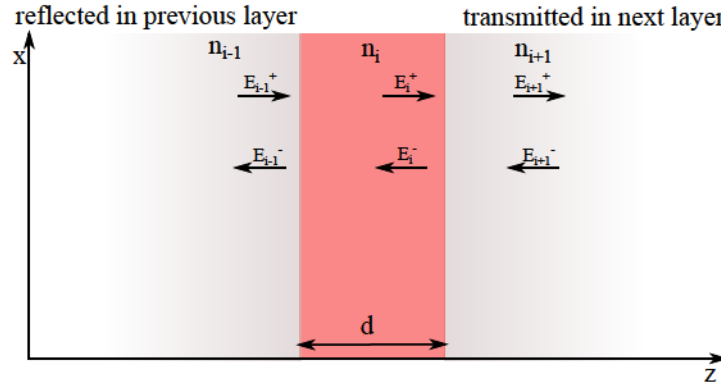


Figure 2.7: Schematics of reflection and transmission of a single transverse optical wave into a multistack of materials with different complex refractive index $\tilde{n}$. The difference in optical path between forward and backward waves of the same wavelength and same polarisation is in the same order than that of the wavelength. Consequently, these will interfere, making the overall intensity within each layer i different from the geometric sum of the two waves E_i^+ and E_i^- .

quence of this phenomenon is that at fixed architecture and interlayers, when the thickness of the active material is increased, the overall photon supply harvested into the active layer does not necessarily increase in the same way. The theoretical short-circuit current J_{sc} obtained assuming 100% collection at all thicknesses is oscillating and is not increasing linearly with the thickness of the absorber. The so called first interference maximum occurs at a position that depends on the exact blend and architecture, but is usually around $100 \pm 30\text{nm}$), (Burkhard et al., 2010; Albrecht et al., 2012a; Hadipour et al., 2011; Dennler et al., 2009) with a second interference maximum around 200-250 nm. Typical profiles of interference will be presented in the thickness studies presented in this thesis.

In order to calculate the distribution of optical intensity throughout the active layer (position dependent in consequence), a model was proposed for bilayer organic solar cells by Pettersson et al. (1999), refined by Hoppe et al. (2004) and further adapted to Bulk Heterojunction solar cells by the Transfer Matrix formalism by Harbecke (1986). To be applicable, the optical constants ($\tilde{n}; \tilde{k}$, such that $\tilde{n} = \tilde{n} + i\tilde{k}$) of all the layers constituting the solar cell are required. These latter are

measured by ellipsometry.(Hoppe et al., 2002)

2.3.3 Workfunctions of electrodes, built-in field and space charge

We saw previously that the typical bulk heterojunction solar cell is composed of two asymmetric workfunction electrodes, the anode (with high work function) and the metal back electrode (with a low workfunction). These electrodes sandwich an intimate blend of two organic semiconductors: one donor (for instance polymer) and one acceptor (for instance [6,6]-phenyl C₇₁/61-butyrac acid methyl ester: PCBM). Each has a defined HOMO, LUMO and band gap. The overall description of the intimate mixing of the two semiconductors can be assimilated to an effective one composed of the LUMO of the acceptor and the HOMO of the donor.

The distribution of electric field in steady-state within the active layer of a device can be calculated using the Poisson equation, linking the Laplacian of the electric potential ψ to the space charge density ρ inside the active layer. The presence of charges in one point of the active layer will create a gap between the value of the electric potential in this point and its average value around this point according to the following:

$$\nabla^2 \psi = -\frac{\rho}{\epsilon_0 \epsilon_r} \quad (2.3)$$

On the other hand, the continuity equations will express the conservation of charges in any point of the active layer, in 1D:

$$\frac{dn}{dt} = G - R + \frac{1}{e} \frac{dJ_n}{dx} \quad (2.4)$$

$$\frac{dp}{dt} = G - R - \frac{1}{e} \frac{dJ_p}{dx} \quad (2.5)$$

where R and G are the charge recombination and generation rates, e the elementary charge. In steady state, $dp/dt = dn/dt = 0$. Solving the equations in particular in the dark under no applied bias requires knowing the boundary conditions which are:

- The difference of electric potential at the two contacts at short circuit is fixed by the built-in potential:

$$\psi(d) - \psi(0) = V_{BI} \quad (2.6)$$

- The equilibrium concentrations in the dark in the bulk are given by:

$$n_0 p_0 = n_i^2 = N_C N_V \exp\left(-\frac{E_g^*}{k_B T}\right) \quad (2.7)$$

where the gap between the valence and conduction band edge $E_g^* = E_C - E_V$

$$E_g^* = IP_{\text{donor}} - EA_{\text{acceptor}} \quad (2.8)$$

- At the contacts (the anode is assumed here to be at $x = 0$ and the cathode at $x = d$), the concentrations of electrons at the cathode (respectively holes at the anode) injected from the contacts is fixed by the contact barriers Φ_C (Φ_A respectively) which are the energetic gaps between the conduction band edge and the cathode workfunction (respectively the valence band edge and the anode workfunction), following:

$$n_0(x = d) = N_C \exp\left(-\frac{\Phi_C}{k_B T}\right) \quad (2.9)$$

$$p_0(x = 0) = N_V \exp\left(-\frac{\Phi_V}{k_B T}\right) \quad (2.10)$$

Under illumination at the contacts, while the majority carrier concentration is still close to the one at equilibrium, the minority carrier concentration can change significantly. When a minority carrier (for instance a hole) is diffusing at the vicinity of the cathode, it may recombine with an electron from the cathode. This is usually described by surface recombination currents which fix the boundary condition for J_n and J_p at the contacts ($x = 0$ and $x = d$) in Equations 2.4 and 2.5. In the undoped case, the potential is found to be linear in the bulk with a constant electric field throughout the whole active layer. Assuming no surface dipole at the interface active layer/electrodes (over a typical thickness of $d \approx 100$ nm) and a difference in electrode workfunctions of 700 mV, the macroscopic field at zero bias is $E \approx \frac{\phi_{\text{anode}} - \phi_{\text{cathode}}}{d} \approx 7 \times 10^6 \text{ V.m}^{-1}$.

However, the presence of dopants will modify the space charge ρ in the Poisson equation. As a result, the electric potential can change depending on the doping level and its type in the active layer. Eventually, when the doping level is sufficiently high ($N_A \geq 7 \times 10^{15} \text{ cm}^{-3}$), a neutral region is created in which the electric field is low and a space charge region in which the electric field is strong, as discussed further in Chapter 7.

2.4 Device current-voltage response

Independent of the exact technology, photovoltaic cells are designed to deliver electrical power produced from photon absorption to an external load. The stan-

standard way of testing the performance of the solar cell is the current density-voltage response as represented in Figure 2.8. The fourth quadrant ($V \geq 0; J \leq 0$) is generating power to the external load. The inset pictures the basic electronic circuit equivalent of a solar cell under normal operation. The sweep from short circuit ($V = 0$) to open circuit ($V = V_{oc}$) enables the probing of the different operating points that the solar cell would work on with a varying external load (if $V = 0$, R_{ext} would be 0 and if $V = V_{oc}$, and $J = 0$, the external load would be infinite). The power produced $P_{photovoltaic}$ (dashed-dot line) peaks at the maximum power point.

We saw previously in equation 2.6 that the sweep from far reverse bias to beyond the built-in field changes the net electric field $E_{net} \approx \frac{(V - V_{BI})}{d}$ substantially. Figure 2.9 represents key band diagram regimes in the fourth quadrant in the dark. As a result of the changes in internal electric field, the current density-voltage response in the dark (dashed line Figure 2.8) can be described by the sequence of three regimes:(Dyakonov, 2004b)

- at reverse bias ($V < 0$) and at low forward bias ($0 < V < V_{oc}$) the dark curve is governed by the leakage of charges, i.e. extraction of the minority carriers (R_{shunt}). Ideally for high performance devices, $R_{shunt} \rightarrow \infty$ and the current density in the dark is very low in this regime. In this region, the energy barrier to injection is too high, the contacts do not inject carriers in the active layer. When photogeneration will occur in this regime, the carriers will have a strong drift component under the net electric field for good collection.
- close to the flat band condition (around bias where V_{oc} in the light will be), injection from the contacts initiates and diode rectification can be observed. When photogeneration occurs, the drift component will decrease and will be equal to zero when the bias exactly compensates the built-in potential.
- beyond the zero net electric field ($V \geq V_{BI}$), the net electric field is reversed and the injection of carriers from the contacts is strong. The current is therefore entirely governed by the injection of carriers into the active layer.

In the light, the thermal equilibrium described just above is perturbed and the photovoltaic effect takes place. A few operating points can be distinguished throughout the current density-voltage response. At zero bias, the current density is the short-circuit current J_{sc} ; closer to the flat band condition, the rectification can be observed up to the point where the current density is cancelled, at open circuit V_{oc} . The squareness of the rectification will define the fill factor:

$$FF = \frac{J_{mpp} V_{mpp}}{J_{sc} V_{oc}} \quad (2.11)$$

The power conversion efficiency η_{PCE} is defined as:

$$\eta_{\text{PCE}} = \frac{P_{\text{photovoltaic}}^{\text{max}}}{P_{\text{light}}} = \frac{V_{\text{oc}} J_{\text{sc}} FF}{P_{\text{light}}} \quad (2.12)$$

where $P_{\text{photovoltaic}}^{\text{max}}$ is the power at the maximum power point ($V_{\text{mpp}}; J_{\text{mpp}}$) and P_{light} corresponds to the incident power under 1 sun.

Overall, for efficient solar cells, the light curve will be a translation of the dark curve by superimposing a generation term. (Shuttle et al., 2010b) We note that the phenomenon of carrier injection at the contacts in forward bias can be affected by the photogenerated population close to the contacts. Finally, to describe the conversion of photons into charges to conduct current into an external load, two quantum efficiencies are regularly used:

- the internal quantum efficiency (IQE), which describes the ratio of current density J obtained over the highest possible current if all the photons absorbed create free charges that are collected to the electrodes.
- the external quantum efficiency (EQE), which represents on the other hand the ratio current density obtained J over the current density of incident photons, independently of the quality of absorption of the blend.

These two parameters are usually assessed at zero bias and monochromatically.

2.5 Device operation

Four key steps in polymer:fullerene bulk heterojunction solar cells operations can be identified:

- photon absorption within the active layer, formation of the exciton
- polaron formation
- polaron transport
- carrier extraction at the contacts of active layer/electrodes

2.5.1 Charge generation

Charge generation in organic solar cells differs substantially from the charge generation in inorganic silicon solar cells due to the existence of a strongly bound intermediate excited state upon light absorption, the exciton, prior to the generation of free polarons. Typical blends of donor/acceptors in organic solar cells

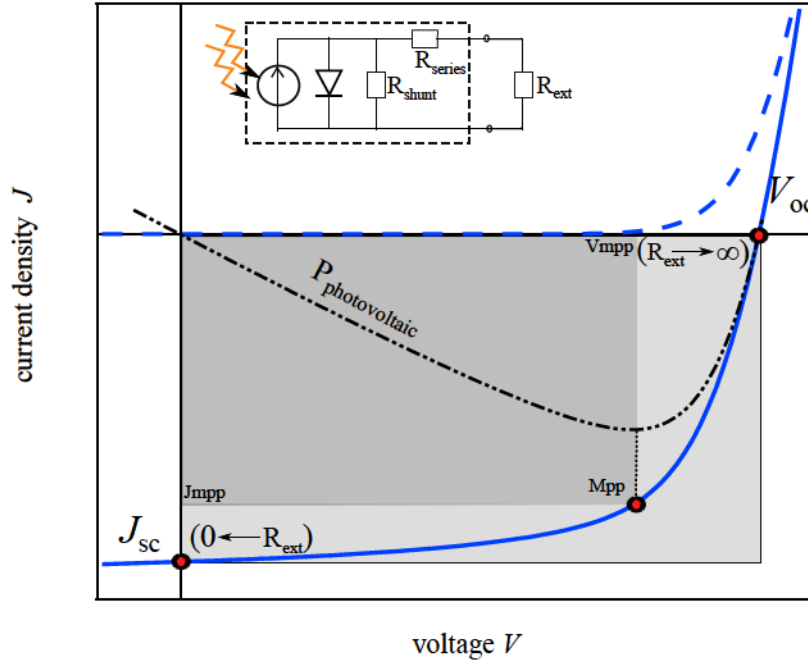


Figure 2.8: Schematics of the current density-voltage response of a typical high efficiency polymer:fullerene solar cell (at room temperature) under AM1.5 equivalent illumination (solid line) and in the dark (dashed line) as well as the power produced by the device (dashed-dots line) (note this is negative when producing power available to an external load). A few specific points are drawn, namely the open-circuit voltage V_{oc} (low net field), short-circuit current J_{sc} and maximum power point M_{pp} ; operating point where the product $J_{mpp} \times V_{mpp}$ is the highest in the power generating quadrant. The sweep from short circuit to open circuit represents the continuity of operating points the solar cell would work on if it had to deliver a hypothetical external load with a resistance $R_{ext} \in [0; \infty[$. In inset on top in the dashed rectangle, a basic electronic circuit equivalent of the solar cell with series resistance R_{series} and the shunt resistance R_{shunt} , the whole powering an external load R_{ext} .

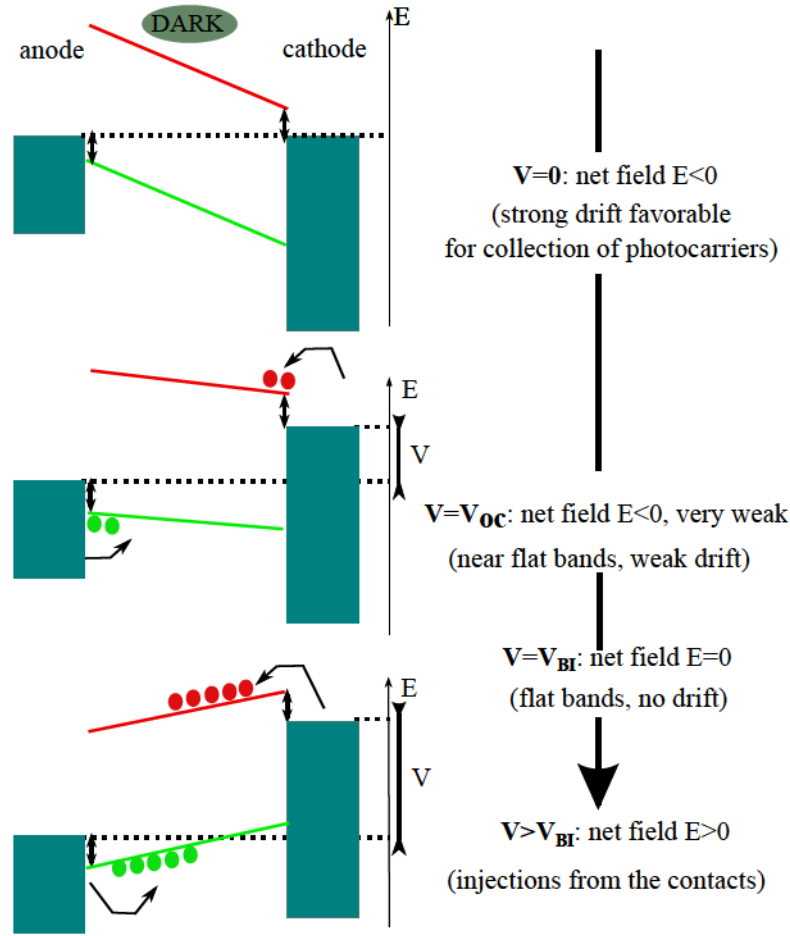


Figure 2.9: Band diagram in the dark showing the conduction and valence band edges at different biases. From top to bottom, at short circuit ($V=0$) to $V \approx V_{oc}$, $V = V_{BI}$ and forward bias $V > V_{BI}$. For general purposes, front and back contact energy barriers are drawn at the interface of blend/electrodes. The active layer is here assumed to be fully depleted. The net electric field within the device is strong at short circuit (the injection barrier is strong and the contacts do not inject), decreases towards forward bias (the injection barrier is smaller than short circuit, the contacts start to inject carriers) to equal zero at the flat band potential $V = V_{BI}$. Beyond this bias, the net electric field is reversed, strong injections from the contacts are occurring. When under illumination, the same trends are observed. The injection barriers can potentially be modified due to the population photogenerated within the bulk.

have a rather low electric permittivity ($\epsilon_r < 10$, typically 3-4).(Müller et al., 2008) As a result, directly following the absorption of a photon in one of the semiconductors and the promotion of an electron into the conduction band and leaving a hole in the valence band, the Coulomb interaction is still strong enough so that the generated charges are not, in most cases, free. Indeed, this binding energy is so high that in normal conditions, it cannot be overcome by thermal agitation. This is contrary to the exciton formed in higher permittivity media like in silicon solar cells (these low binding energy excitons are called Wannier-Mott excitons, typically $< 0.1\text{eV}$). What is formed instead is an overall neutral electron/hole pair with a typical coulomb binding energy of $\approx 0.1 - 0.3\text{ eV}$, also called a Frenkel exciton.(Clarke and Durrant, 2010)

Directly following photon absorption, the newly formed excited state must have the same symmetry as the initial ground state (total spin $S = 0$). However, after this event, an intersystem crossing can occur, potentially resulting in a change of spin state from 0 to 1. There are therefore two possible types of excited states: singlet state (S^1 , total spin $S=0$) and triplet state (T^1 , total spin $S = 1$). In terms of energy, due to symmetry considerations, the triplet state is lower than its equivalent singlet state $E(T^n) < E(S^n)$. Due to the difference in symmetry between the singlet excited state and the triplet state relative to the ground state, the lifetime of the two types of excited state are different. Triplets states are longer lived due to the spin forbidden aspect of the decay to the ground state from the triplet state, although it is debated whether the diffusion coefficient of the triplet state is lower or not compared with the one of the singlet state.(Heremans et al., 2009; Lunt et al., 2009) The singlet exciton typically has a lifetime ranging from 100 ps to 1 ns during which it may reach by diffusion (intra or inter molecular) an interface with a favorable energetic offset before decaying radiatively or non radiatively.(Clarke and Durrant, 2010; Deibel and Dyakonov, 2010) Consequently, to enhance charge generation, the nanomorphology needs to be tuned to allow a maximum of excitons to reach a heterojunction within their lifetime; hence the substantial increase in the performance of polymer solar cells with the use of the bulk heterojunction solar cell.(Yu et al., 1995) This counteracts the issue that occurred in bilayers, which were only able to generate within a finite depth around the heterojunction, whose extent was dictated by the finite exciton diffusion length (typically 10 nm).

The exciton diffusion is strongly influenced by the neighboring lattices distortions. As a result, if the exciton stays long enough at the heterojunction, the quenching (transfer of the electron across the interface) of the exciton may occur either while the exciton is still in a "hot state" (Franck-Condon exciton)(Arkhipov et al., 1999; Basko and Conwell, 2002; Gregg, 2003) (not thermalised with its en-

vironment) or in a cold state, if molecular vibrational relaxation was able to take place (typically within ≈ 100 fs). (Clarke and Durrant, 2010) In most cases, the electron is transferred to the acceptor.³

Charge transfer between two molecules in organic semiconductor can be described by Marcus theory, which considers the variations in potential surface energy of the two systems D^*/A (photoexcited donor+acceptor) and D^+/A^- (electron transferred to the acceptor and leaving the hole on the donor). It links the rate constant for electron transfer to the potential activation energy barrier and the reorganisational energy necessary to reach the energy level which allows transfer of the electron to the acceptor, assuming that at that stage, the rapid electron transfer does not require nuclear reorganisation (the Franck-Condon principle). Furthermore, this transfer rate depends on the overlap of the wavefunctions of the initial (D^*/A) and final state (D^+/A^-). (Marcus, 1956) However, the use of the Marcus theory in organic thin films is limited and fails in general to predict the generation yield when going away from solution or diluted molecules for instance in very low PCBM loading. (Coffey et al., 2012; Zhao and Liang, 2012; Clarke and Durrant, 2010)

Due to the low permittivity and the relative short initial distance between the two opposite charges, once the electron transfer has occurred, sometimes an intermediary interfacial bound state is formed, called a 'charge transfer' or 'bound polaron pair' state. In such states, although separated physically onto two phases, the hole and electron are still coulombically linked. There is currently a strong debate as to whether hot charge transfer (CT) state is important for efficient charge generation. (Vandewal et al., 2014; Dimitrov and Durrant, 2013) This charge-transfer state (CT-state) can decay before total separation of the charges radiatively (useful for Electroluminescence) or non radiatively. The theory addressing geminate recombination (recombination of electron and holes originally from the same exciton) has been suggested to originate from Onsager theory of recombination of electron and holes in weak electrolytes by Onsager (1938), adapted later for use on semiconductors by Braun (1984) and gradually modified. (Tachiya, 1988; Wojcik and Tachiya, 2005)

It has been suggested recently that efficient charge generation occurs via "resonance charge transfer" which populates highly delocalised bound polaron states. (Rao et al., 2013) To occur, it has been proposed that a high driving energy (Dimitrov and Durrant, 2013) or high crystallinity of the acceptor domain (Rao et al., 2013) were required. These two criteria are not independent as the PCBM

³although it is not uncommon to observe the acceptor injecting the hole into the donor as shown for instance by Dimitrov et al. (2011).

LUMO for instance has been shown to shift down with the crystallinity of domains, as will be discussed further in Chapter 5.

2.5.2 Charge transport

Concerning the transport of carriers through the active layer, the substantial difference between organic and inorganic materials is the importance of localised states due to structural and energetic disorder, as mentioned at the start of this chapter. Carriers are transported along one conjugated segment of the polymer chain, tunnelling from one conjugated segment to another through an energy barrier, or hopping from one polymer chain to another by thermal excitation over the local energy barrier. Moreover, this motion is coupled with the structural relaxation of the local molecular environment, hence the term polaron instead of simply electron/holes. As a result, the mobilities of these polarons are usually measured to be low, ranging from 10^{-6} to $1 \text{ cm}^2/\text{Vs}$ depending on the material and the experimental method involved. (Liang et al., 2010; Walker et al., 2009; Subramaniyan et al., 2011; Sakamoto et al., 2004; Park et al., 2006; Morana et al., 2008; Kumar et al., 2009; Kettle et al., 2011; Heremans et al., 2009; Heeney et al., 2007; Heeger, 2010; Cowan et al., 2011a; Chen et al., 2011; Bronstein et al., 2011; Ballantyne et al., 2010).

Overall, within the active layer, the transport of polarons is governed by the continuity equation. As presented in Figure 2.10, assuming an elementary volume (V) of the active layer, whose typical distance is greater than the distance between polymer chains but small enough at the scale of the active layer:

$$\frac{dn}{dt} = \frac{1}{q} \text{div}(\vec{J}_n) + G_n - R_n \quad (2.13)$$

where q is the elementary charge, G_n is the generation and R_n is the loss of polarons in the elementary volume V . The electrons flux J_n is defined by the following relation:

$$\vec{J}_n = nq\mu_n\vec{E} + qD_n\text{grad}(n) \quad (2.14)$$

where n is the concentration of free electrons, q the elementary charge, $\vec{E}$ is the local electric field and D_n is the coefficient of diffusion given by Einstein's relation: $D_n = \frac{k_B T}{e} \mu_n$. The definition for holes is analogous. In steady-state, the first term in Equation 2.13 $\frac{dn}{dt} = 0$.

As shown in the previous equation, the transport of carriers can present two components: drift (under electric field, directional) and diffusion. In operating polymer:fullerene devices, the active material is usually at least partly depleted

and the electric field (and consequently the drift component) is thought to play an important role in the transport of carriers, at least at low bias. The dominance of the drift component will depend on the net electric field within the bulk; in other words, it will depend on the built-in potential, the applied bias and potentially dipoles present at the interface with the electrodes.(Bisquert et al., 2008) Furthermore, the phase segregation of donor and acceptor materials creates large variations of carrier concentrations within the bulk. The drift component is usually assumed to be dominant during the collection of charges, although this assumption is quite debated, in particular in the fourth quadrant.(Nenashev et al., 2010). While the charges are being transported through the material, each carrier can re-

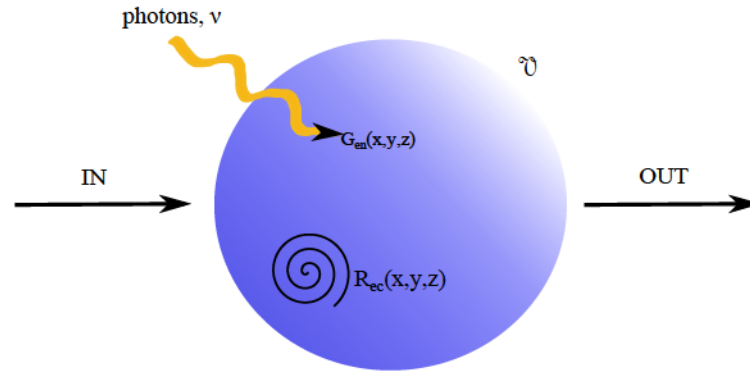


Figure 2.10: Continuity equation in the elementary volume v . At equilibrium, $\frac{dn}{dt} = 0$ and the divergence of the flux of charges through the sphere S delimiting v is compensated by the difference between local generation and local recombination events.

combine with one opposite carrier. This is a non-geminate recombination event if the two carriers do not originate from the same electron/hole pair produced upon light absorption.

The standard way of understanding the recombination of free charge carriers is by Langevin bimolecular recombination.(Pope and Swenberg, 1982) This recombination mechanism uses the work of P. Langevin on recombination of ions in gas phase dating from 1903.(Langevin, 1903) Assuming that the free carriers are generated independently (geminate recombination is therefore excluded here), their recombination is random and ideally of second order from a kinetic point of view. Moreover, if the mean free path λ_{free} of the charge carrier is smaller than the ra-

dius of coulomb capture r_c , then the Langevin requirement is met.⁴ The capture radius is defined by matching the potential energy of one charge in the electric potential of the other to the thermal agitation energy:

$$k_B T = e \times \frac{e}{4\pi\epsilon_0\epsilon_r r_c} \quad (2.15)$$

In this context, the recombination can be viewed as the drift of two charges under the coulombic field they create. For ease of explanation, the negative charge is assumed to be fixed in space and the positive charges are arriving at the radius capture of the negative charge as presented in Figure 2.11. At $r = r_c$, the average current of holes i_h entering the sphere S is:

$$J_h \approx n_h e v_h = n_h e \mu_h E = n_h e \mu_h \times \frac{e}{4\pi\epsilon_0\epsilon_r r_c^2} \quad (2.16)$$

Therefore, $i_h = \oint_S \vec{J}_h \cdot d\vec{S} = \frac{n_h \mu e^2}{\epsilon_0 \epsilon_r}$. In this example, all the flux would actually be a recombination flux as it is assumed implicitly that the ratio $\frac{\text{recombination}}{\text{collision}}$ tends to 1. This recombination current can be expressed as a function of the Langevin recombination rate γ_{eh} such that $I_{rec} = n_h \gamma_{eh} e$. Equating the two currents leads to the expression of the standard Langevin recombination rate:

$$\gamma_{eh} = \frac{e\mu}{\epsilon_0\epsilon_r} \quad (2.17)$$

This common approach assumes that when an external charge (here represented by the red dot) moves within the radius of non escape ($r = r_c$), the charge is assumed to drift within the electric field created by the opposite central charge, leading to an approximation of the capture radius $r_c \approx 15$ nm. However, at that scale, the gradient in species represented by the red dot (so the entropy aspect) is completely neglected. Equation 2.13 can be rewritten using the thermodynamic chemical potential $\mu_{\text{chem}} = \mu_{\text{chem}}^0 + k_B T \ln(n)$ as suggested by Gregg and Hanna (2003). The latter explains that the flux of charges J_n can be rewritten in two components: due to the electrical potential energy gradient (still the drift) and the other due to the chemical potential energy gradient. However, given the intimate mixing of donor and acceptor in polymer:fullerene solar cells, it might be difficult to quantify or even to visualise the force applied due to the step of chemical energy at the heterojunction donor/acceptor (extended segments nearby, charge rich zone). Nevertheless, referring to the work on the influence of entropy in charge generation, (Gregg and Hanna, 2003; Gregg, 2011; Vithanage et al., 2013) where

⁴not obvious in organic disordered material

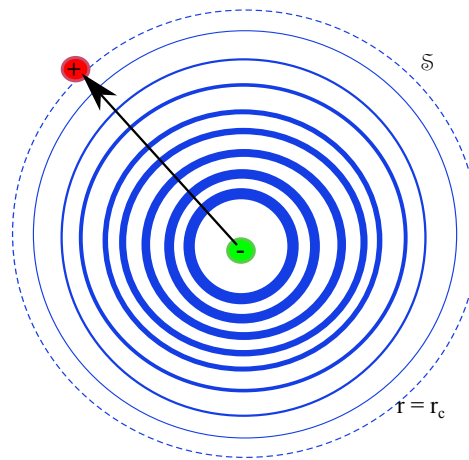


Figure 2.11: The circles correspond to fixed values of the electric potential created by the central fixed charge, decreasing with $1/r$. At $r = r_c$, any external charge (red spot) will be under the influence of both the thermal agitation ($kT \approx 25\text{meV}$ at room temperature) and the electric interaction due to the presence of the opposite central charge (green spot). The interpretation of Langevin recombination applied to bimolecular recombination assumes that the ratio $\frac{\text{recombination}}{\text{collision}}$ correspond to the extreme case and equals to unity.

in more than 1D, the entropy favors further charge separation, the impact of entropy is inverse during bimolecular recombination, which logically decreases the effective capture radius r_c .

Further details on the effect of non-geminate recombination on the performance of polymer:fullerene solar cells will be developed in the next chapter.

2.5.3 Analytical description of photocurrent: $\mu\tau$ product

The photocurrent is generally voltage dependent in our system (even if field dependent generation and dark leakages are neglected) due to a finite lifetime τ of the carriers during collection in systems which are usually assumed to be fully depleted. A useful indicator of the quality of the field driven collection is the drift length $L_D = \mu E * \tau$ which represents the typical distance a carrier will travel under an electric field $\vec{E}$ with a mobility μ . A common approach to describe the photocurrent in organic solar cells is based on the $\mu\tau$ product. The higher the product $\mu\tau$ relative to the thickness of the active layer, the better the collection of carriers. Li et al. (2012); Street et al. (2012); Tumbleston et al. (2012) applied the analytical description of the photocurrent in organic solar cells using the Hecht equation, which gives the voltage dependence of the current based on the finite mobility-lifetime product:(Hecht, 1932)

$$J_{ph} = 2q\bar{G}\mu\tau \frac{V_{BI} - V}{d} \left[1 - \exp\left(-\frac{d^2}{2\mu\tau(V_{BI} - V)}\right) \right] \quad (2.18)$$

where $\bar{G}$ is the space averaged generation of carriers. This expression is completely drift driven and diffusion is neglected. The lifetime τ here can be ambiguous as it represents the lifetime of a charge carrier before it cannot participate to the photocurrent any longer, without specific precision on the mechanism responsible for its loss. τ can refer to the typical time before the charge carrier is lost to a trap (given that with time this trap charge carrier can recombine with another free carrier in a first order mechanism) or if the materials is trap free, τ corresponds to the typical time before it is lost in direct (free) recombination (second order). Furthermore, in this model the mobility and lifetime are assumed to be intrinsic of the blend and not depending on the operating point, nor in carrier concentration. Consequently its application is limited. Nevertheless under the following set of assumptions:

- homogeneous electric field is assumed, only the fully depleted devices are therefore considered.
- spatially constant generation rate.

- balanced transport: $\mu_{\text{holes}}\tau_{\text{holes}} \approx \mu_{\text{electrons}}\tau_{\text{electrons}}$. If a space charge region is created due to imbalance of transport, the expression above is not valid anymore.
- no drop in the series resistance are accounted for.

this expression can be very useful to describe in particular the photocurrent around short circuit and understand the degradation of charge carrier transport in a fully depleted thickness series, as will be more developed in particular in Chapter 7.

2.5.4 Contacts

Previously, we saw that the bulk heterojunction could be assimilated to an effective semiconductor with the LUMO of the acceptor and the HOMO of the donor. Usually, the workfunction of the electrode is assumed to be pinned to the relevant energy level of the semiconductor as by Brabec et al. (2001a), independent of the actual Fermi level of the electrode compared with the Fermi level of the semiconductor. This phenomenon, usually induced via charge surface states, is called Fermi level pinning.(Brillson, 1982) The n-type semiconductor/metal electrode interface will show an upward band bending while the p-type semiconductor/counterelectrode will show a downward band bending at equilibrium. However, to be selective, each electrode needs to be blocking the minority carrier, in other words the workfunctions must be chosen so that they do not offer quasi-ohmic contacts to both the acceptor-LUMO and the donor-HOMO. Since the surface states behave as a transition from the Fermi level of the semiconductor and the relevant workfunction of the electrode, it is usually understood that some surface dipoles, as mentioned earlier with Liu et al. (2010), can exist and offer a quasi-pinning of the energy levels at the interface. However, the energetics at the contacts is a complex topic which is not in the scope of this work. To stay general, a small energy barrier at the contacts is usually used in the schematics and simulations in this thesis. Another consequence of the adjustment of the Fermi level at the contacts is that, depending how selective these are, minority carriers can recombine with the infinite reservoir of opposite carrier at the interface of active layer/electrode. This is surface recombination. This type of recombination is governed by the concentration of minority carriers at their counter electrode and the surface recombination velocity S_{min} which will be used in some simulations in this thesis.

$$J_S = qS_{\text{min}}\Delta n_{\text{min}} \quad (2.19)$$

The concentration of minority carrier $\Delta n_{\min}$ depends on the net field and the capacity of the minority carrier to diffuse against the net field towards the counter electrode. (Kirchartz and Nelson, 2012)

2.6 Maximum V_{oc} and losses

We saw previously that at thermal equilibrium (in the dark under no applied bias), intrinsic populations of electrons and holes are at equilibrium within conduction and valence bands respectively as well as relative to each other. As a result of this equilibrium, the Fermi energy E_F (level at which the probability of electron occupation at a level E given by Fermi-Dirac distribution $P(E) = 1/(1 + \exp((E - E_F)/k_B T))$ equals 0.5) of the intrinsic holes and electrons is the same and usually located in the middle of the band gap if no doping level is considered. However, under illumination triggering photogeneration or external applied bias, the system is pushed away from equilibrium. Since the thermalisation of the carriers within their band is usually much faster than the return to equilibrium in between the bands (through recombination for instance), each band can be at local equilibrium and have their own separate Fermi level without having equilibrium between the bands. These respective Fermi levels in local equilibrium are called quasi-Fermi levels E_{Fn} and E_{Fp} .

A substantial improvement of polymer:fullerene solar cells has been possible by the modulation of the HOMO_D LUMO_A energy levels resulting from the molecular engineering of new semiconducting organic materials. At fixed background illumination, and given the previous paragraph, the maximum open-circuit voltage V_{oc} is such that:

$$qV_{oc}^{\max}(I) = (E_{Fn} - E_{Fp})^{\max} \quad (2.20)$$

The splitting of the quasi-Fermi levels will depend on the magnitude of the polaron populations. Morphology and local crystallinity can affect the HOMO/LUMO levels at the heterojunction donor/acceptor. (Hawks et al., 2013) This will be further developed in Chapter 5. At fixed energetics of the conduction and valence band edges, many different processes can limit the maximum of the difference in these quasi-Fermi levels:

- during charge generation, geminate recombination will partially impede the population of the Fermi levels by limiting the total generation of free polarons due to recombination of a fraction of electrons and holes originating from the same exciton.

- once polarons are generated, some can recombine non-geminately due to their finite lifetime.

Furthermore, at the active layer/electrodes interface, in the case of ohmic contacts, the Fermi levels of the interlayers and electrodes are pinned to the Fermi levels of the blend. In this case, the open-circuit voltage will be a result of the combination of bulk energetics and dynamic properties. Here, the measured (real) open-circuit voltage is the difference of Fermi levels measured at the contacts:

$$qV_{oc} = E_{Fn}(\text{cathode}) - E_{Fp}(\text{anode}) \quad (2.21)$$

However, it is suggested that generally a small voltage drop is possible at the active layer/electrode interface. (Bisquert et al., 2008; Bisquert and Garcia-Belmonte, 2011) This energy barrier between the blend LUMO (HOMO) and the Fermi level of the cathode (anode) can occur due to the formation of interfacial dipoles.

2.7 Problem statement and project objectives

Research in the synthesis of low band gap polymers, which could eventually enable the production of cheap active material, is very active and many families of polymers are currently being explored leading to a substantial range of types of available blends. To date, internal quantum efficiencies near 100% have been achieved in some polymer:fullerene systems. (Park et al., 2009) Although HOMO/LUMO level engineering is crucial, charge transport is as critical since it has been shown over the last years that non-geminate recombination limits the performance of many efficient organic solar cells. In this context, one of the challenges remaining is whether there are experimental techniques which allow quantification of these non-geminate losses on the wide range of systems available and then finding the fundamental parameters which would eventually enable those specific losses to be reduced.

In this thesis, I attempt to address these questions in three stages. First, after a brief description of a few key notions which will be used throughout the whole thesis, in Chapter 3, I describe charge extraction and transient photovoltage measurements, two optoelectronic techniques proposed recently to study the recombination dynamics in polymer:fullerene solar cells. In Chapter 4, I show that the method is robust and it can be successfully extended to many radically different systems (although in the past it was applied in the past to poly(3-hexylthio/selenophenes) only). Furthermore, applying this approach, I demonstrate in Chapter 5 that the method is able to provide powerful insight into the

subtle changes in energetics at the heterojunction and recombination dynamics resulting from the slight blend ratio perturbation in an amorphous blend. In particular, this work suggests that it is possible in some systems to improve both carrier lifetime and mobility through an increase of PCBM content, which is going against what is understood from Langevin type recombination.

It is often assumed that the active layers are fully depleted. In addition, a key limitation of charge extraction is that it gives access to the spatially averaged excess carriers, rather than their spatial distribution. In particular, in Chapter 6, I show that the spatial distribution of carriers cannot be neglected for $< 100\text{nm}$ devices. Then in Chapter 7, I raise the possibility that polymer:fullerene solar cells may not, contrary to common belief, be intrinsic semiconductors. By combined modelling and experimental investigations, the apparent doping level is shown to have fundamental consequences on device performance and recombination dynamics. Resulting from these two chapters, I suggest that spatial distribution variation and doping can explain the apparent contradiction in the unusually high reaction orders observed recently in the literature, without necessarily having to invoke any change in basic mechanism of non-geminate recombination.

Finally, an analysis of Langevin and non-Langevin recombinations in organic solar cells is developed in Chapter 8 and after a review of the different explanations of the reduced Langevin recombination factor, the limitations of the common assumption that collisions are the limiting step in the recombination process is discussed before closing with conclusions and suggestions for future work.

Methods

3.1 Introduction

In the previous chapter, we saw that if surface states at the interface active layer/electrode can be neglected, the open-circuit voltage is controlled by the splitting of the quasi-Fermi levels measured at the contacts. In this chapter, the main methods employed to investigate charge transport in this thesis are presented. First, non-geminate recombination is further developed and mathematically defined. Then, charge extraction and transient photovoltage methods are presented and the limits of their applicability discussed. Finally, details of the other experimental methods employed are listed before presenting the drift-diffusion modelling performed in this thesis.

3.2 Describing non-geminate recombination

The creation of the bulk heterojunction architecture enabled a substantial increase in the performance of organic solar cells.(Yu et al., 1995) This intimate mixing of donor and acceptor at nanoscale allows the excitons formed upon light absorption to quickly reach an interface where they can dissociate and form free polarons. However, this architecture also substantially increases the interface area between electron rich and holes rich regions of the blend during the transport of polarons to the extracting electrodes.

The recombination of opposite carriers initially separated (non-geminate recombination) is known to be a major loss process of polarons in these systems.(Koster et al., 2005b, 2006) In particular, this loss process was shown to be strongly voltage (field) dependent and strongest close to open-circuit condition when the internal electric field is very weak. Although the term non-geminate recombination is a clear concept, it encompasses a variety of recombination events, including:

- Two opposite free carriers can recombine (often called band-to-band recombination); in this case this is a bimolecular second order loss process.

- The recombination can also be mediated by trap (free-to-trap); in that case, it is often assumed that one free carrier can recombine with a trapped opposite carrier. This is still a bimolecular recombination event, however this is no longer second order as one carrier is fixed. Trap-to-trap recombinations are usually not considered due to the extended space between two localised states.
- Finally, if a polaron in the vicinity of an infinite sink of opposite carriers (such as close to the counter electrode) can diffuse against the electric field, it can recombine mono-molecularly (surface recombination).

To date, the existence of recombination events involving more than two particles (e.g. Auger recombination) has not been proven in polymer:fullerene solar cells. We will see in Chapter 4 that dark and light ideality factors, in some conditions, can suggest which recombination mechanism, within the ones listed just above, is dominant.

The standard approach in bimolecular recombination is via Langevin type recombination where the loss of charge carrier is described by:

$$R = -\frac{dn}{dt} = -k(np - n_i^2) \quad (3.1)$$

where n and p are the total electrons and holes concentrations, n_i the intrinsic (thermally excited, present also in the dark) carrier concentration and the recombination rate k according to a Langevin description depends on the likelihood of two opposite carriers to find each other (see Chapter 2). As it is often assumed that the photogenerated population is larger than the intrinsic one, the recombination is usually simplified $R \approx -knp$ and finally assuming electric neutrality $n \approx p$:

$$R \approx -kn^2 \quad (3.2)$$

A measurement of carrier density and carrier lifetime allows those non-geminate losses to be quantified.

3.3 Measuring non-geminate recombination

Many different experimental techniques have been used over the last decade to analyse the recombination dynamics in polymer:fullerene solar cells.(Montanari et al., 2002; Westerling et al., 2003; Pivrikas et al., 2005a,b; Mozer et al., 2005a; Sliuaužys et al., 2006; Dennler et al., 2006; Pivrikas et al., 2007; Koster et al., 2006; Shuttle et al., 2008b) These typically employ different charge densities or field

strengths during operation. In particular, this thesis employs a combination of charge extraction and transient photovoltage/photocurrent to allow experimental quantification of carrier density and lifetime respectively.

3.3.1 Charge density

3.3.1.1 Charge extraction

Along with other approaches, (Mozer et al., 2005a; Pivrikas et al., 2005a; Juška et al., 2006) the charge extraction technique enables the charge density in solar cells to be determined under different operating illumination and voltage biases. It was applied initially to dye sensitised solar cells with Peter et al. (2002); Duffy et al. (2000) and then to polymer:fullerene solar cells.(Shuttle et al., 2008a,c,b; Lange et al., 2013). This technique will be frequently used in this thesis. In consequence, a description of this technique is given below.

3.3.1.2 Description

The charge extraction technique is conducted by placing the device at a particular and fixed operating condition (light intensity background L , applied bias V). Once the device has reached the steady state, the cell is then switched to discharge while switching off the light background (if any). The background illumination is provided by 12 white 1W (Lumileds Luxeon iii/start O) with the use of a fast switching MOSFET. The 1 sun equivalent illumination level was calibrated by matching the recorded short-circuit current J_{sc} and open-circuit voltage V_{oc} obtained under the AM1.5 solar simulator. The light on-time was approximately a few hundreds of milliseconds to allow a steady state to be reached (and a longer off-time is used). The sweep out of charge is usually done under short-circuit field condition. When it was necessary to push the system at an initial operating point different than open circuit or short circuit, a voltage bias was applied using a Keithley 2400 sourcemeter unit. As the cell discharges, a current transient was extracted, creating a voltage across a known external resistance load with the use of a high input impedance oscilloscope Tektronix TDS 3032B. The integration of this extracted transient current provides an estimate of the total charge in the device. The time length of each illumination is a compromise between reaching a steady state and not warming up the device being studied. The signal triggering is based on the command of another MOSFET which switches the cell from an operating point to short circuit. In general, there is a time delay between the physical command of the MOSFET and the actual switch between drain and source due to the charge of the parasitic capacitances. However, this time delay was assumed to be negligible,

in particular in front of the turn off time of the LEDs. The whole setup is pictured in Figure 3.1.

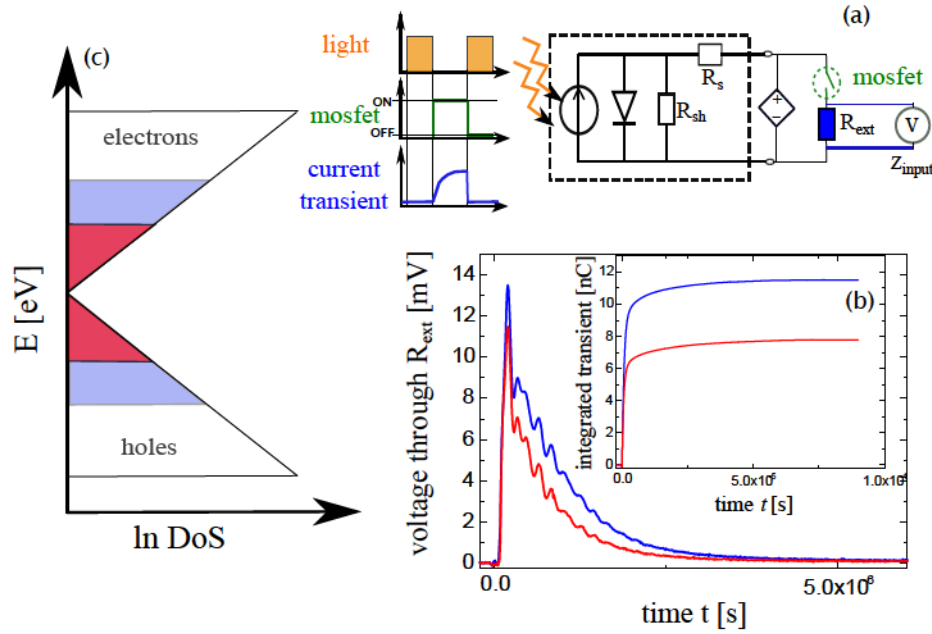


Figure 3.1: Schematic of the charge extraction technique. a) electric equivalent diagram with the solar cell, the controlled voltage source to impose an external bias, the light background illumination, the MOSFET switch to short the device to short circuit for charge extraction and the resulting current transient measured through an external load R_{ext} using an high input impedance oscilloscope. b) current transients through R_{ext} obtained with two levels of background illumination (inset the integrated current transient leading to the total number of charge at different operating point). c) population of the density of states (DoS) for these two different light levels.

3.3.1.3 Excess carrier and reference point: dark at short circuit

By sweeping the carriers out under short-circuit conditions in the dark, the charge extraction technique gives access not to the total number of charge carriers at any initial operating point of the cell but to the number of charges in excess compared with the ones present in the dark under zero applied bias. Indeed, due to the thermal radiation of the environment (here room temperature), there are distributions of dark charge within the active layer. If the latter is an intrinsic semiconductor, these two distributions of dark opposite charges mirror each other at 0V. Furthermore, if the active layer happens to be substantially doped, more dark carriers will be present. In this case, the distribution of carriers would not be symmetrical due

to the presence of dominant doping species.

3.3.1.4 Capacitive correction

The two electrodes are two conductive sheets sandwiching an active material of a certain permittivity $\epsilon_0\epsilon_r$ where $\epsilon_r < 10$. In consequence, the system anode/active layer/cathode has a certain capacitance and a certain amount of surface charge will be stored on the electrodes independent of any photophysical process occurring in the active layer. This capacitance is proportional to the electric field between the two electrodes.

However, between open circuit and short circuit, we saw in the previous chapter that the electric field is substantially different. If we assume for the sake of argument that initially the active layer is fully depleted in both field conditions, the electric field E can be approximated by the linear relationship:

$$E \approx \frac{\epsilon_0\epsilon_r(V_{BI} - V)}{d} \quad (3.3)$$

where d is the device thickness, V_{BI} the built-in potential. Moreover, the typical distance between the two electrodes (≈ 100 nm) is much smaller than the width of the pixel in the devices usually fabricated (typically in this thesis, $\sqrt{4.5}$ mm). In this case, the system behaves approximately like a plate capacitor in the dark. Under illumination, the major difference is that due to photogeneration, the active layer will accumulate charges, which is a deviation from the standard plate capacitor simple model. As a consequence, the capacitance of the solar cell can be called a chemical capacitance rather than geometric capacitance as Bisquert et al. (2008) pointed out. Nevertheless, simulations usually show that for most standard illuminations (see Chapter 6), the band bending is not too affected. Indeed we note that the open-circuit voltage V_{oc} is light dependent while the built-in voltage V_{BI} is fixed. Furthermore, we usually observe that $V_{BI} > V_{oc}(1 \text{ sun})$. In consequence, for most light levels used in the work presented in this thesis, we have $V_{BI} > V_{oc}$. As a result, during charge extraction, the switch from open circuit to short circuit creates a change in the accumulated surface charge which will add to the photo-generated charges within the active layer which are being extracted. A correction is therefore necessary to remove from the data the charges which sat on the electrodes. In the case where the active layer is fully depleted and the electric field can be approximated by the Equation 3.3, we use the following correction:

$$\Delta n_{\text{activelayer}} = \Delta n_{\text{raw}} - \frac{CV}{eAd} \quad (3.4)$$

where A is the effective surface of the two electrode facing each other (their pixel area). The capacitance C , under the assumptions stated just above can be approximated by the geometric capacitance $C = \frac{\epsilon_0 \epsilon_r A}{d}$. This formulation neglects the potential presence of dipole capacitance due to the presence of surface states at the interface between active layer/electrodes. (Bisquert et al., 2008) As this dipole capacitance is constant, there is no need to take it into account for the correction of charge extraction data.

The limits to the validity of the geometric capacitance correction will be considered more in details in Chapters 6 and 7. Overall, the geometric approximation for capacitance correction of the charge extraction data is only valid at high net electric field (reverse bias or low bias in the fourth quadrant), low light level and low doping level.

3.3.1.5 Limits

The charge extraction technique has a certain number of limitations which should not be overlooked. First, the charge densities obtained with this technique do not account for all the charges within the device. In fact, due to the nature of the sweep out, it gives access to the excess carrier densities $\Delta n = n_{\text{light}} - n_{\text{dark}}$, i.e. the difference in charge density compared with the reference point which is at short circuit in the dark. Consequently, it does not measure the dark charges. We will see in Chapters 7 and 6 some consequences of this.

Moreover, although every recombination process is local, spatial averaged excess carrier densities are accessed; which means that any variation in spatial distribution within the device is neglected. (Kirchartz and Nelson, 2012) In Chapter 6 of this thesis, the impact of spatial distribution of carriers on apparent recombination dynamics will be addressed.

Finally, although the sweep out is conducted under short-circuit conditions, where the internal electric field offers a strong drift to charge carriers, it might not be possible to extract all the excess carriers, especially when the mobility-lifetime product is not sufficient under this condition. Furthermore, although many trapped charges can be detrapped easily and eventually be collected with the technique employed, it is not certain that the deeper trapped charges will ever be collected under short-circuit conditions. The importance of deep trapped charges in device performance is currently a topical issue widely discussed in the literature. (Kirchartz and Nelson, 2013; Shuttle et al., 2012)

3.3.2 Effective drift mobility measurements

According to Shuttle et al. (2010a), charge extraction at short circuit can be performed to access to an effective drift mobility. The measurement of short-circuit current J_{sc} over the excess carrier density n_{sc} under different illumination levels allows the calculation of a drift mobility. Since no differentiation between electrons and holes is possible with this technique, the result can be considered as an effective drift mobility. Assuming that the current is mostly governed by the drift component at short circuit:

$$J_{sc} \approx J_{drift} = -e\mu^* n_{sc} E \times f(\delta) \quad (3.5)$$

where E is the electric field at 0 V bias (according to the previous chapter, E can be assumed to be proportional to the built-in potential V_{BI} so that $E \approx V_{BI}/d$) and $f(\delta) = [(2+\delta)(1+2\delta)/(1+\delta)^2]$ a correction factor function of the carrier dependence resulting from the presence of tail states within the bandgap as can be found in the supporting information of Shuttle et al. (2010a). Finally, the following equation is used to calculate the effective drift mobility:

$$\mu^* = \frac{J_{sc} d}{e n_{sc} V_{BI} f(\delta)} \quad (3.6)$$

Since the initial state of each charge extraction is at short-circuit and that the sweep out is conducted under short-circuit condition, no correction for capacitance is necessary.

Although limited by the fact that the opposite carriers cannot be distinguished, this technique will be used regularly in this thesis to allow consistent comparison between different polymer:fullerene systems.

3.3.3 Charge carrier lifetime by transient measurements

Transient photovoltage (TPV) is a small perturbation optoelectronic technique used to access the polaron lifetime. In the field of excitonic solar cells, it was first developed to study dye sensitised solar cells.(O'Regan et al., 2005, 2006) More recently, this technique has been shown to be adequate for the study of recombination dynamics in some poly(3-hexylthio/selo-phenes), PCPDTBT:fullerene devices and hybrid systems.(Shuttle et al., 2008c,b; Maurano et al., 2010; Böhm et al., 2014; Guo et al., 2013; Foertig et al., 2014) During this measurement, the device is first put at open circuit. Experimentally, this condition is realised if the input impedance of the oscilloscope used to monitor the difference of potential across

the device is substantially larger than the shunt resistance of the device. In the experimental setup developed, the 1 M Ω input impedance of an oscilloscope Tektronix TDS 3032B is used.

3.3.3.1 Description

As pictured in Figure 3.2 a), the device is held at a fixed V_{oc} using a light background provided by white LEDs whose power can be adjusted to tune the magnitude of splitting of the quasi-Fermi levels, similarly to the charge extraction experiment. An optical small perturbation is then applied to the device on top of the illumination background using a GL-330 PTI nitrogen laser pumped GL-301 PTI dye laser whose characteristics are as follows: frequency 4 Hz, pulse duration ≈ 1 ns, wavelength, depending on the dye used, selected to ensure light absorption in the low energy tail of the blend absorption spectrum studied (typically, around 650 nm). The resulting transient signal has an initial magnitude of ΔV_i . Particular attention must be paid to ensure a spatially homogeneous excitation of the active layer. In the current setup, the laser beam injected via an optical fiber excites the device in a spatially homogeneous manner thanks to the large aperture at the exit of the fiber.

The small perturbation regime requires $\Delta V_i \ll V_{oc_i}$ at every light level Φ_i . As the device is held under open-circuit condition at all time during the measurement, the generated charge carriers are forced to stay in the bulk or at the vicinity of the electrodes. Although there can be internal fluxes, no net current is possible. Therefore, the TPV decay can probe the kinetics of the polaron loss processes in the device. By ensuring the small perturbation condition, the profile of the decay accessed experimentally takes the form of a pseudo-first order process, simplifying the analysis.

If Δn is defined as the change in density of total photogenerated charges (holes and electrons) due to the small perturbation laser pulse and assuming the hole density equals the electron density at any time, macroscopically:

$$\frac{d\Delta V}{dt} \propto \frac{d\Delta n}{dt} = -\frac{\Delta n}{\tau_{\Delta n}} \quad (3.7)$$

where $\tau_{\Delta n}$ is the lifetime of the extra carriers photogenerated by the laser pulse. $\tau_{\Delta n}$ is found empirically to depend on the open-circuit voltage V_{oc} as follows:

$$\tau_{\Delta n} = \tau_{\Delta n0} \exp\left(-\frac{qV_{oc}}{\partial k_B T}\right) = \tau_{\Delta n0} \exp(-\beta V_{oc}) \quad (3.8)$$

where ϑ and β are respectively the dimensionless and with dimension parameters used to fit the TPV data.

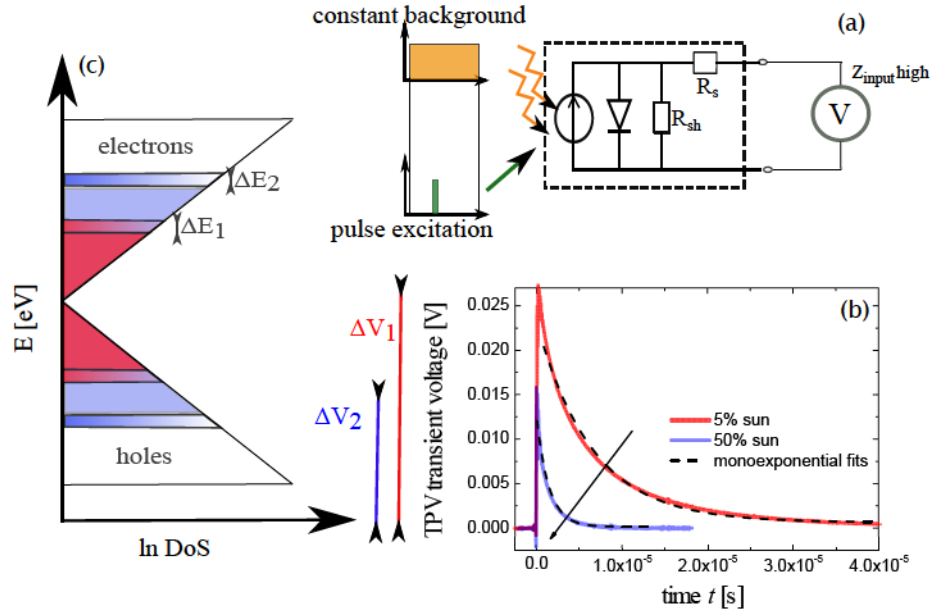


Figure 3.2: Schematic of the transient photovoltage technique. a) electric equivalent diagram with the solar cell held at open circuit, the light background illumination, the laser excitation pulse and the resulting small perturbation transient photovoltage were measured by a high input impedance oscilloscope. b) Transient photovoltage traces (solid lines) obtained with two levels of background illumination as well as their related mono-exponential fits (dashed lines). c) population of the Density of States for these two different light levels.

3.3.3.2 Effect of dark shunt on TPV lifetime

In practice, the TPV lifetimes obtained at different illumination levels are rarely the pure mono-exponential functions of the open-circuit voltage given by equation 3.8. At very low light levels, the open-circuit voltage is very dependent on the dark shunt (leakages), as pictured in Figure 3.4. This dark shunt was observed on a very thin device (20 nm) and prior to any experiment, the former was strong. After performing corrected photocurrent on it to reverse bias (≈ 15 V) at 1 sun equivalent, the device appeared to have lost irreversibly some of its dark shunt (probably some leakage pathways were burned during the measurement). The same device will be used later in Chapter 4 to look at the effect of dark shunt on the measurement of light ideality. In consequence, these early experimental points are not used for fitting. Furthermore, due to the higher number of states available

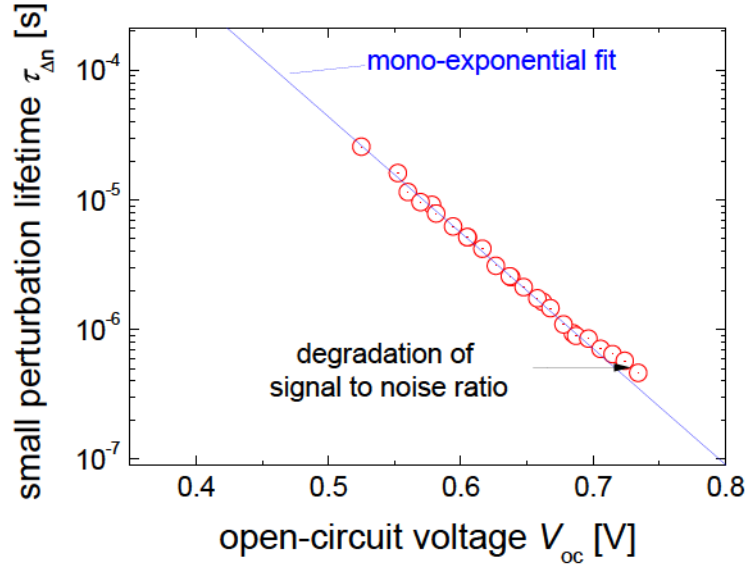


Figure 3.3: Small perturbation lifetime of the carriers injected by the laser pulse (open symbols) at different open-circuit voltages (and therefore illumination levels). The solid line is the mono-exponential fit over the range of standard light levels.

in the DoS at very high light levels, the magnitude of the transient photovoltage (at constant number of charges injected) will decrease and the signal-to-noise ratio will increase the uncertainty of the last data points. Most importantly, the fitting needs to correspond to light levels that the experimentalist is interested in, where the condition of small perturbation $\Delta n_{TPV}/n_{tot} \ll 1$ is verified as presented in Figure 3.3.

3.3.4 Incurred charge losses

So far, the macroscopic lifetime and the charge density can be experimentally accessed. We saw that a correction for capacitance of the device was necessary to obtain values relative to the bulk charges. However, at every bias, the competition between carrier transport and non-geminate recombination dictates the collection efficiency during charge extraction. Although the net electric field $\propto (V_{BI} - V)/d$ is usually strong enough at short circuit, a small proportion of the charges will recombine during experimental sweep out. In Figure 3.1, 50% of the extracted charges (corresponding to accumulated charges at open circuit under 1 sun illumination) needed $\approx 0.85 \mu s$ to be collected. In comparison, the small perturbation lifetime for this device was under this light level $\approx 1 \mu s$. Although faster, the

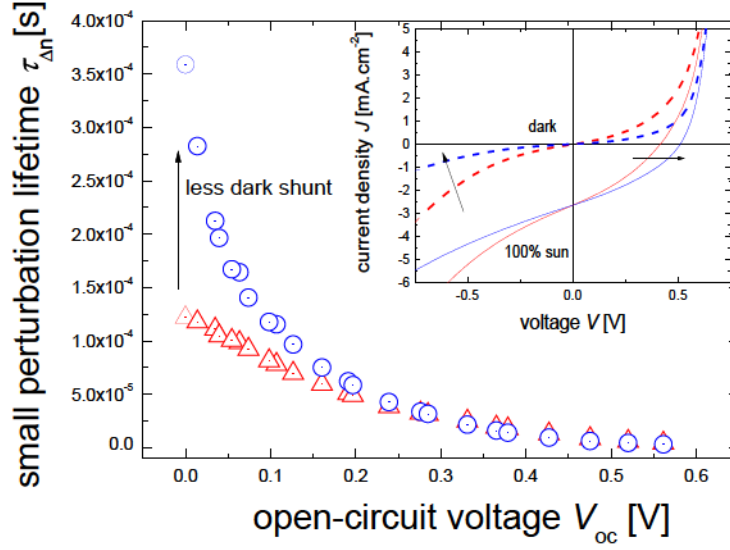


Figure 3.4: Small perturbation lifetimes (open-symbols) measured on the same device in two different states of dark shunt. Up triangles correspond to the device in a strong dark leakage state while circles refer to the lifetime of the same device once the dark leakages have been reduced (see text for details). In inset, dark (dashed lines) and AM 1.5 equivalent current-voltage responses in both states.

time needed to extract the remaining 50% of the charge carriers would be such that these latter carriers would not be necessarily immune to recombination. As mentioned previously, the longer the collection time through the active layer, the higher the accumulation of charges within the devices is. In consequence, a correction for this fraction of charge carriers which should have been extracted but recombined during sweep out is necessary.

To do so, a compensation routine written and used previously in the group was routinely applied. It is based on the assumption that at every trace obtained during charge extraction (total extracted charge against time as pictured in Figure 3.1 c)), the decay should follow the rate detailed above in Equations 3.1-3.11. The trace is cut into different time segments in which the losses are calculated, summed over all time segments and the process was iterated until a convergence was found:

$$n_{\text{loss}}^{\text{iteration}_i} = \sum_{t=t_0}^{t=t_{\text{final}}} \frac{dn_{\text{device}}}{dt} \Delta t = \sum_{t=t_0}^{t=t_{\text{final}}} \frac{n_{\text{device}}^{\lambda+1}}{(1+\lambda)\tau_{\Delta n_0} n_0^\lambda} \Delta t \quad (3.9)$$

where λ is a parameter accessed by conducting charge extraction and transient photovoltage ($\lambda = \beta/\gamma$). Δt is the time interval between two points during charge

extraction. A typical outcome of a charge extraction compensation for incurred charge losses is presented in inset of Figure 3.5. The correction becomes substantial at high light levels. The outcome of the total compensation treatments (capacitive correction and compensation for incurred charge losses) is presented in Figure 3.5. As previously shown by Shuttle et al. (2008a), the charge density in the active layer at open circuit is exponentially dependent on the cell voltage and is an indication of the shape of the density of states. Usually, the high light levels are used for the fitting of the mono-exponential growth:

$$\Delta n = \Delta n_0 \exp\left(\frac{qV_{oc}}{mk_B T}\right) = n_0 \exp(\gamma V_{oc}) \quad (3.10)$$

Overall, Figure 3.6 presents the final data after full corrections of charge extrac-

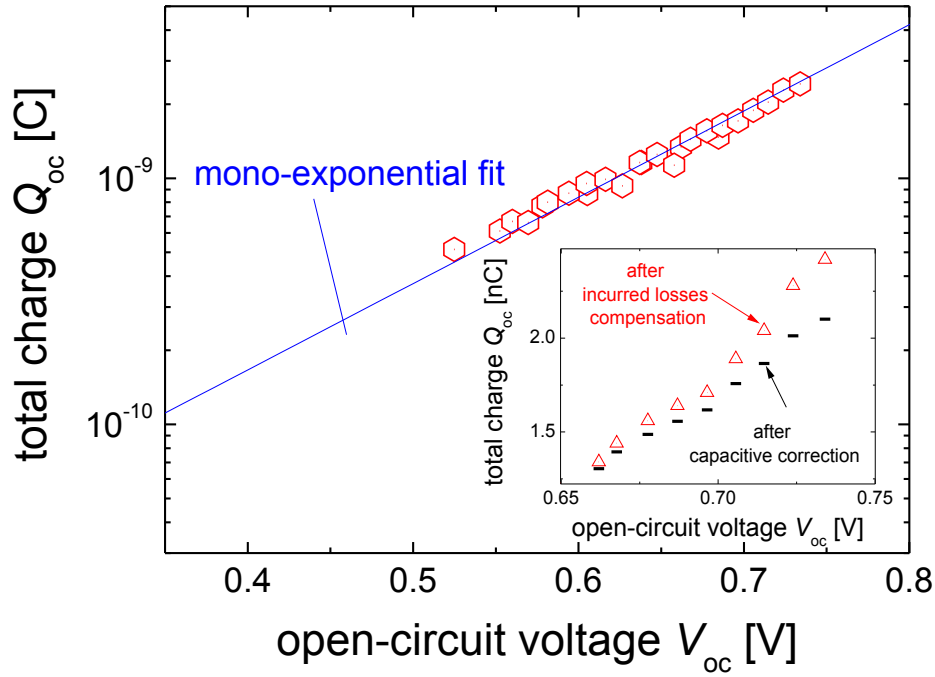


Figure 3.5: Final charge extraction data (open symbols) after full corrections (capacitance + incurred carrier losses). The solid line corresponds to the mono-exponential fit. The fits needs in particular to represent the high light levels if the overall dataset presents different modes. In inset: charge extraction data after correction for capacitance only (horizontal dashes) at different open-circuit voltages (therefore at different illumination levels). Final extracted charge after compensation for incurred charge carrier losses (up triangles). This compensation is mainly significant for high light levels.

tion at open circuit on different polymer:fullerene solar cells described further in the next chapter. Shallow or steep densities of states can be distinguished. Simulations show that the presence of a tail within the band gap can explain the shape of the obtained n versus V_{oc} data. Indeed, according to previous simulation work on P3HT:PCBM, the slopes presented here of $\ln(\Delta n(V_{oc})) = \ln(\Delta n_0 \exp(\gamma V_{oc}))$ are not strongly dependent on the open-circuit voltage. Also the steepest ($\gamma \approx 12 \text{ V}^{-1}$) is still much lower than the predicted value $q/(2k_B T) \approx 19.3 \text{ V}^{-1}$ if no tail of localised states was present within the band gap. (Kirchartz et al., 2011) This hints that many of the carriers are trapped in many different polymer:fullerene solar cells.

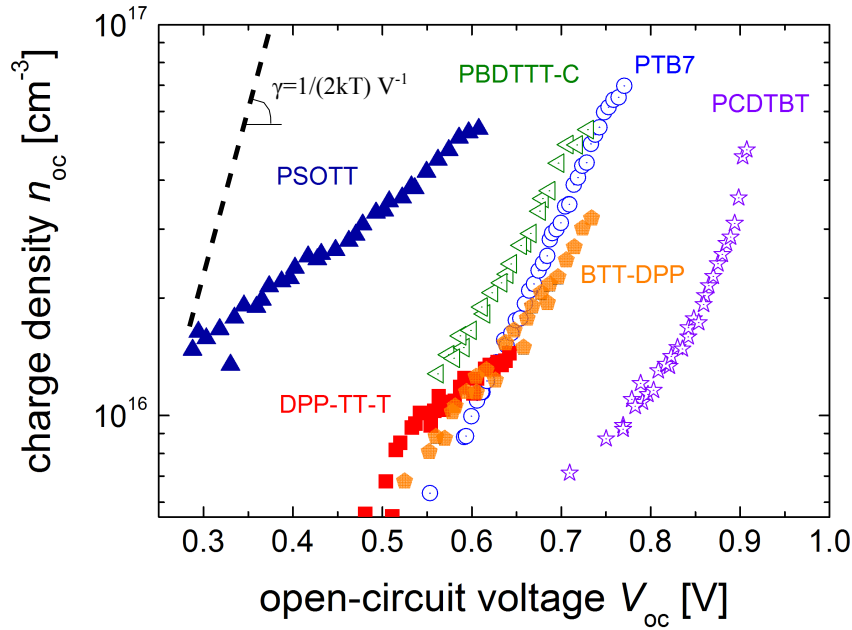


Figure 3.6: Experimental charge extraction at open-circuit data for different polymer:fullerene blends which are further described in Chapter 4. The dashed line corresponds to a slope proportional to $\exp(qV/2kT)$ at room temperature.

3.3.5 Small perturbation lifetime and macroscopic lifetime

Up until this stage, only the lifetime of the extra charges $\tau_{\Delta n}$ was measured experimentally. Ultimately, the macroscopic lifetime (of the total population of carriers n) τ_n is sought. These two lifetimes are linked by the calculation presented in what follows.

Using different techniques, the recombination lifetime was shown to be

strongly dependent on carrier density.(Montanari et al., 2002; Nogueira et al., 2003; Shuttle et al., 2008b). Nelson (2003) showed that the presence of an exponential density of trap states within the band gap could explain this dependence in polaron concentration. Normally this assumes that charge carrier distributions are equal and uniform ($n \approx p$). In its general form, the decay of the population of carriers can be written as: $\frac{dn}{dt} = -k_n n$ with the pseudo-first order rate $k_n = k_0 n^\lambda$, $\lambda \in (R)_+^*$. Here the carriers are either trapped or free and are relative to dark at short circuit. Therefore, the previous expression becomes:

$$\frac{d(n + \Delta n)}{dt} = -k_0(n + \Delta n)^{\lambda+1} \Leftrightarrow \frac{dn}{dt} + \frac{d\Delta n}{dt} = -k_0(n + \Delta n)^{\lambda+1} \Leftrightarrow \frac{d\Delta n}{dt} = -\frac{dn}{dt} - k_0(n + \Delta n)^{\lambda+1} \quad (3.11)$$

using the first relationship of $\frac{dn}{dt}$ in the previous equation:

$$\frac{d\Delta n}{dt} = k_0 n^{\lambda+1} - k_0(n + \Delta n)^{\lambda+1} = k_0 n^{\lambda+1} \left[1 - \frac{(n + \Delta n)^{\lambda+1}}{n^{\lambda+1}} \right] = k_0 n^{\lambda+1} \left[1 - \left(1 + \frac{\Delta n}{n} \right)^{\lambda+1} \right] \quad (3.12)$$

Moreover, as $\lambda > 0$ and the measurement is a small perturbation $\Delta n \ll n$, the last term can be approximated by the Taylor expansion:

$$\left(1 + \frac{\Delta n}{n} \right)^{\lambda+1} = 1 + (\lambda + 1) \frac{\Delta n}{n} + o\left(\frac{\Delta n}{n}\right) \quad (3.13)$$

$$\Rightarrow \frac{d\Delta n}{dt} \approx k_0 n^{\lambda+1} \left[1 - \left(1 + (\lambda + 1) \frac{\Delta n}{n} \right) \right] \Leftrightarrow \frac{d\Delta n}{dt} \approx -k_0 n^\lambda (\lambda + 1) \Delta n \quad (3.14)$$

and as the extra photogenerated charges have their own decay following $\frac{d\Delta n}{dt} = -k_{\Delta n} \Delta n = -\frac{n}{\tau_{\Delta n}}$ (see above), we can conclude that:

$$k_{\Delta n} \approx k_0 (\lambda + 1) n^\lambda = (\lambda + 1) k_n \quad (3.15)$$

As a result, the polaron lifetime is decreasing with carrier density. This can also be validated experimentally by other techniques like Impedance Spectroscopy.(Garcia-Belmonte et al., 2010). The fact that k is a function of charge density was shown to be consistent with the presence of localised tail states within the band gap.(Nelson, 2003)

3.4 Predictions of device performance

At open circuit, under illumination, although there can be internal fluxes of carriers, there is no net current (corresponding to an infinite external load plugged to the solar cell). Consequently, the generation flux is fully compensated by the total

loss flux, $J_{\text{gen}}(V_{\text{oc}}) = -J_{\text{loss}}(V_{\text{oc}})$.

3.4.1 Recombination dynamics and prediction of open-circuit voltage with illumination level

To double check the assumption that non-geminate recombination is the main loss process explaining the loss of photocurrent in the fourth quadrant and the open-circuit voltage, the non-geminate loss flux calculated from the measurements of charge density n and total carrier lifetime τ_n can be compared to the generation flux J_{NGloss} :

$$J_{\text{NGloss}} = ed \frac{n(\text{opencircuit})}{\tau_n(\text{opencircuit})} = ed \frac{n_0 \exp(\gamma V_{\text{oc}})}{(1 + \lambda) \tau_{\Delta n 0} \exp(-\beta V_{\text{oc}})} \quad (3.16)$$

Using this expression in the following equation, $J_{\text{gen}} = J_{\text{loss}}$, and assuming that $J_{\text{gen}} \approx J_{\text{sc}}$ (see comments on this assumption in the next paragraph) then:

$$\Rightarrow \exp((\gamma + \beta)V_{\text{oc}}) \approx J_{\text{sc}} \frac{(1 + \lambda) \tau_{\Delta n 0}}{ed n_0} \quad (3.17)$$

$$\Leftrightarrow V_{\text{oc}} \approx \frac{1}{(\gamma + \beta)} \ln \left(\frac{J_{\text{sc}} (1 + \lambda) \tau_{\Delta n 0}}{ed n_0} \right) \quad (3.18)$$

The comparison between the measured open-circuit voltage and the predicted open-circuit voltage assuming Equation 3.18 at different illumination levels enables validation a posteriori of the assumption that non-geminate losses are the predominant loss process of polarons between short-circuit and open-circuit conditions in case of successful prediction within a few millivolts (typically within ± 5 mV). Figure 3.7 shows the measured and predicted open-circuit voltage for a typical OPV device studied in this thesis in the case where those non-geminate losses assessed by charge extraction and transient photovoltage were governing the open-circuit voltage of the solar cell for a wide range of light intensities. Failing to do so indirectly highlights that the total loss flux was underestimated $J_{\text{NGloss}} < J_{\text{loss}}$ and that potentially other loss processes are occurring. At low light levels, the open-circuit voltage is strongly dependent on the dark shunt. Indeed, the photo-generated charges are still relatively small, or similar to, the ones being collected at the wrong electrode. In consequence, the measured open-circuit voltage may be substantially lower than the predicted one over a narrow illumination range (typically [0.1% sun; 10 % sun]).

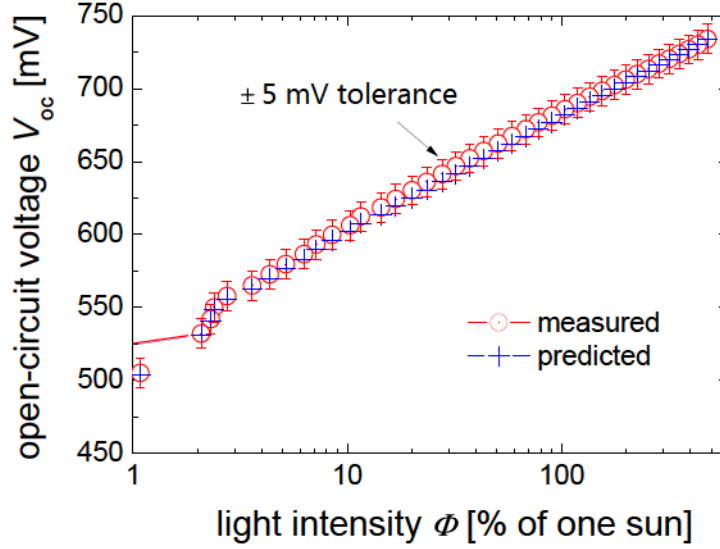


Figure 3.7: Measured open-circuit voltage V_{oc} (open circles) at different illumination levels Φ and the predicted photovoltage if the non-geminate recombination flux is assumed to compensate the generation flux at open circuit in BTT-DPP:PC₇₁BM presented in more details in the next chapter.

3.4.2 Predictions of current-voltage response in the fourth quadrant

As well as the non-geminate recombination flux which can be assessed at open-circuit condition, the current density is governed by the continuity equation at every operating point across the voltage range, in 1D:

$$\frac{1}{e} \frac{dJ}{dx} + G - R = 0 \quad (3.19)$$

Therefore, integrating the previous equation 3.19 across the active layer thickness and using charge extraction across the $J-V$ to assess the charge density at different operating points, we can obtain Equation 3.20:

$$J_{\Phi}(V) = -eG_{\Phi}(V)d + edR(n_{\Phi}(V)) \quad (3.20)$$

where

$$eG_{\Phi}(V)d = \begin{cases} J_{ph}^{saturated} & \text{if the generation is not field dependent} \\ J_{gen}(V) & \text{if the generation is field dependent} \end{cases}$$

(In this analysis, the recombination rate is assumed to depend only on the total charge density and not on its distribution within the device determined by external voltage. Thus, at a constant charge density, the recombination rate is voltage independent. It has been shown that this assumption becomes invalid in devices with very thin active layers, as there is a greater change in spatial distributions of charges in these devices. This consequently creates a more voltage dependent recombination rate, as will be discussed in Chapter 6)

In case of optimised charge transport and when no major dark leakage is present, the current density is relatively constant in reverse bias and therefore the generation term can be approximated by $J_{\text{gen}}(V) = J_{\text{gen}0} \approx J_{\text{sc}}$. If the generation process is field dependent, separate experimental follow-up of polaron yield under applied bias is necessary to be able to describe $J_{\text{gen}}(V)$ for the voltage range one is interested in. (Credgington et al., 2012; Dibb et al., 2013a)

We note here that the absence of field dependent generation does not necessarily mean that geminate recombination as a whole is negligible. In that case, there would be a voltage independent gap between the current predicted by Transfer Matrix modeling using measured refractive index ($\tilde{n}$) and extinction coefficient ($\tilde{k}$) and the saturated photocurrent obtained in far reverse bias. Nevertheless, the portion of geminate recombination which does not lead to field dependent generation cannot explain the loss of photocurrent between two bias conditions, like for instance short circuit and open circuit. Attempts to predict current density-voltage response at different light levels in case of field-dependent generation were presented in Credgington et al. (2012); Dibb et al. (2013a).

3.5 Reduction of signal-to-noise ratio of charge extraction by impedance matching

The charge extraction technique is a well established method to experimentally access the charge density at different operating points of an excitonic solar cell. As mentioned earlier, it was first used to study Dye Sensitised Solar Cell (DSSC) with Duffy et al. (2000); Peter et al. (2002) and then transferred for the study of polymer based solar cells. (Shuttle et al., 2008a). However, the charge collection process is fundamentally different between these two families of solar cells. In DSSC, the electric relative permittivity is high compared with BHJ polymer:fullerene solar cell: (typically $\epsilon_r^{\text{TiO}_2} \approx 80$ while $\epsilon_r^{\text{BHJ}} \approx 2 - 4$). Furthermore, the distance between the electrodes is typically micrometric $\approx 1 - 10 \mu\text{m}$ while in BHJ solar cells, the distance is smaller ($\approx 100 \text{ nm}$) which means that there is no net built-in field helping

charge collection in DSSC, unlike in polymer:fullerene solar cells. As a result, the process of collection of electrons in DSSC occurs via diffusion even at short circuit (Barnes et al., 2013) while, as most of the absorbing layer is fully depleted, the drift component (field assisted) in carrier transport is substantial in polymer:fullerene solar cells at short circuit. (Shuttle et al., 2010a)

Usually the external reading resistance used to discharge the cell during charge extraction (see R_{ext} in Figure 3.1 a) is selected so that the RC constant of the total system (solar cell + external reading resistance) is not too high so that the dynamics observed are indeed due to bulk transport properties and not simple electronic constraints. Nevertheless, the purpose of the charge extraction technique is to transfer the total density of excess charge carriers into the external load. From a signal point of view, the problem is similar to the transfer of power to an external load. We suggest that the signal-to-noise ratio of charge extraction data in polymer:fullerene solar cells can be increased and accuracy can be gained by adapting the external reading impedance to the impedance of the solar cell.

According to the theory of signals, a wave reaching an interface with a change in impedance will transmit a part of its energy through the interface and the rest of it will be carried by a reflected wave which will propagate through the media upstream. In the case of charge extraction, the transmission to the external load must be maximised. If the external load was infinite, the system would be at open circuit and there would be no transfer of energy from the solar cell, nor would there be transfer if the solar cell was short-circuited (cathode and anode connected together by a wire). Under illumination the solar cell is actually generating charges and should be considered as an electric generator rather than a classic voltage source. Depending on the operating point, the behavior of voltage and current sources varies. For a demonstration purpose, the cell is assumed to be a voltage source. $\bar{Z}_s = R_s + jX_s$ and $\bar{Z}_{\text{ext}} = R_{\text{ext}} + jX_{\text{ext}}$

$$P_{\text{ext}} = \frac{1}{2} R_{\text{ext}} I^2 \quad (3.21)$$

where

$$\bar{I} = \frac{\bar{U}}{(R_s + R_{\text{ext}}) + j(X_s + X_{\text{ext}})} \quad (3.22)$$

$$P = \frac{1}{2} R_{\text{ext}} \frac{U^2}{(R_s + R_{\text{ext}})^2 + (X_s + X_{\text{ext}})^2} \quad (3.23)$$

P is maximised when: $Z_{\text{ext}} = Z_s^*$

Usually BNC cables with a 50 Ω impedance (acting like a transmission line) are used. In that case, the phenomenon of mismatch of impedance mentioned

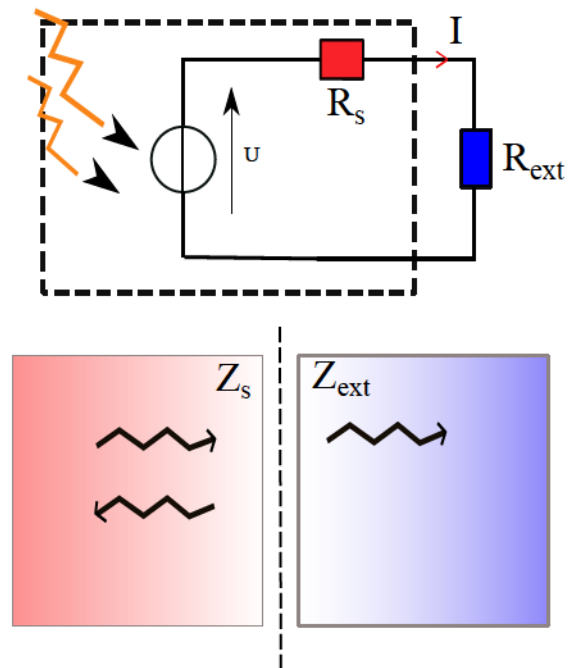


Figure 3.8: Schematics of charge extraction showing the device with an internal series resistance R_s and the external reading resistance R_{ext} . A mismatch of impedance along the charge extraction path is likely to create part transmission and reflection at every interface where the impedance is mismatched.

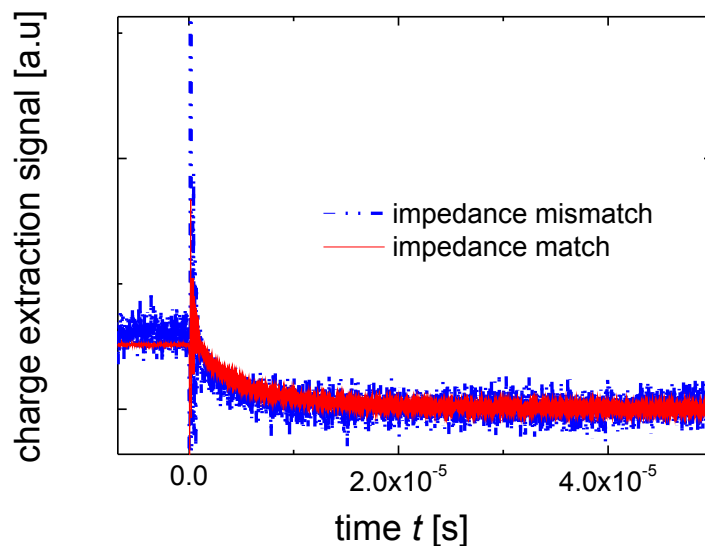


Figure 3.9: Charge extraction traces under 1 sun equivalent illumination of the same device (with internal series resistance $R_s=140\ \Omega$) with same protocol except the reading resistance has been changed so that in the first case (dashed blue line) $R_{\text{ext}}=50\ \Omega \pm 5\%$ and the second case (solid red line) $R_{\text{ext}}=140\ \Omega \pm 5\%$.

above also concerns the interface solar cell (sample under study)/BNC cable. This observation has an impact on the way charge extraction and transient photocurrent are conducted, in particular when the mismatch between total internal series resistance of the sample and the reading resistance is non negligible (either due to bulk series resistance or contact resistance).

3.6 Device fabrication

All the devices used in this thesis are in conventional architecture comprising ITO/PEDOT:PSS/polymer:fullerene blend/metal electrode as shown in 2.4. More details about the different polymer donors will be given in the next chapter. The series of PBDTTT-C:PCBM presented in Chapter 5 was prepared by Steve Hawks at UCLA (USA), following the preparation which can be found in the experimental section of Hawks et al. (2013).

The 6.8% PCE PTB7:PCBM device presented in Chapter 4 was prepared at SCUT university (China) according to the recipe in He et al. (2012b).

If not mentioned otherwise, all the other devices were fabricated by Dr. Pabitra Shaky Tuladhar at Imperial College London. Details of device fabrication are given in each result chapter. In addition, the details of the device fabrication of:

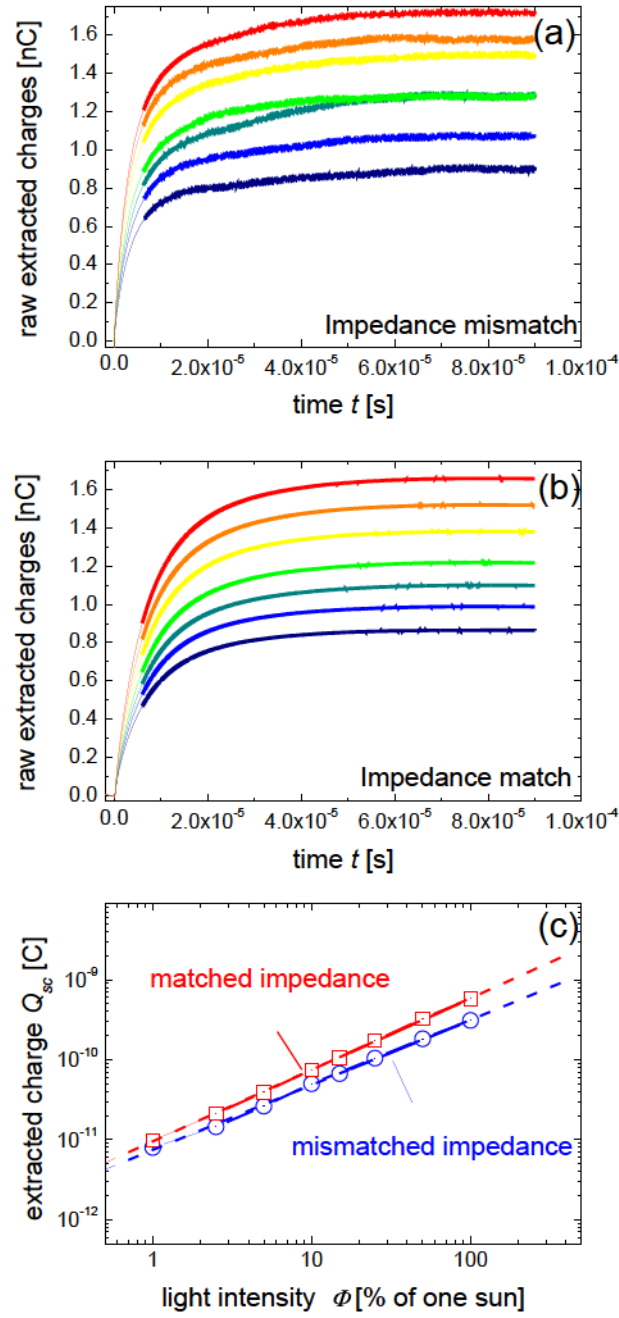


Figure 3.10: Charge extraction transients through an external known resistance under 1, 2.5, 5, 10, 25, 50 and 100% sun while a) there is an impedance mismatch between the internal device and the reading external load ($R_s=140 \, \Omega$, $R_{ext}=50 \, \Omega \pm 5$) b) when the two are matched ($R_s=140 \, \Omega$, $R_{ext}=140 \, \Omega \pm 5$). c) Consequences of impedance mismatch on the total extracted charges at short circuit.

- the PCDTBT based devices presented in Chapter 4 can be found in Kirchartz et al. (2013).
- the BTT-DPP based device presented in Chapter 4 can be found in Dimitrov et al. (2013).
- the PSOTT based device presented in Chapter 4 can be found in Shoaee et al. (2013).
- the DPP-TT-T based devices presented in Chapters 4 and 7 can be found in Bronstein et al. (2011).
- the PTB7 and the thin P3HT based devices presented in Chapter 6 can be found in Deledalle et al. (2014).

3.7 AM1.5 current density-voltage measurements

The $J-V$ characteristics presented in this thesis were obtained using a AM1.5, 100 mW.cm⁻² solar simulator using a 150W ozone free Xenon arc lamp Sciencetech 200 series with a water cooled IR filter. The illumination is calibrated using a silicon photodiode. The measurements are obtained with a Keithley 2400 source. The voltage sweep is generally made from -1.5V to +1V with steps of 10 mV.

3.8 Corrected photocurrent measurements

To avoid overheating the devices while measuring the JV response at far reverse bias between the dark and light conditions, pulsed measurements are used in Chapter 7 using the same LEDs ring as in the charge extraction experiment. This LEDs ring is made of 12 white 1W (Lumileds Luxeon iii/start O) with the use of a fast switching MOSFET. The 1 sun equivalent illumination level was calibrated by matching the recorded short-circuit current and open-voltage obtained under the AM 1.5 solar simulator described just above. The light on-time was approximately 2 ms to allow reaching steady state to be reached and a much longer off-time was used. The voltage bias was applied using a Keithley 2400 sourcemeter unit and the current is measured by obtaining the voltage across a known resistance using a Tektronix TDS3032B with a 1 MΩ input impedance. Light and dark responses were measured alternatively at different bias to calculate the corrected photocurrent ($J_{ph}(V) = J_{light}(V) - J_{dark}(V)$)

3.9 Thickness measurements

Throughout this thesis many thickness measurements were necessary. These were conducted using a Dektak profilometer precalibrated using a 100 nm gold deposited on quartz calibration module.

3.10 UV-Vis spectrometer

UV-Vis spectra presented in this thesis were obtained at room temperature on devices in absorbance mode using a PerkinElmer Lambda 25 spectrometer. Calibration was done using an ITO patterned on glass substrate used in the device fabrication. The scans are usually conducted from 350 to 1000 nm with a scan speeds of 460 nm/min and a slit width of 1 nm

3.11 Impedance spectroscopy

To measure the doping level, Mott-Schottky analysis on thick substrates are performed according to Kirchartz et al. (2012b). Unless differently mentioned, the measurement of the capacitance was conducted between $[-3V; +1V]$ with steps of 10 mV using a Schlumberger SI 1260 at 1, 10 and 100 kHz. During these measurements, the devices are kept in a nitrogen sealed chamber. The measurements were conducted by Prof. Dr. Thomas Kirchartz at Imperial College London.

3.12 ASA drift-diffusion modelling

One-dimensional macroscopic modelling based on drift-diffusion formalism is regularly performed in this thesis in parallel of the experimental methods presented just above. ASA (Advanced Semiconductor Analysis) is the device simulator used. It was first developed to model amorphous silicon solar cells by Zeman and Krc (2008) and has been shown to be appropriate as well for the simulation of the behaviour of organic semiconductors.(Schäfer et al., 2011; Kirchartz and Nelson, 2013, 2012)

ASA can simulate the spatially resolved generation rate based on the Matrix Modelling formalism using ellipsometry data as explained in the previous section 2.3.2.

The simulator solves the system of three equations formed by the continuity equations presented earlier in 2.3.3 Equations 2.4, 2.5 and the Poisson equation 2.3 in steady-state, following the Scharfetter-Gummel method.(Scharfetter

and Gummel, 1969) In this model, the probability of occupation of the traps is assumed to be in steady-state. Consequently, this would not be an appropriate framework to simulate transient experiments where the probability of occupation would be time dependent.

The boundary conditions are imposed by the currents at the contacts as shown in APPENDIX A, Equation A.1. The difference in electrical potentials at the two contacts is given by $V_{BI} - V_{applied}$.

Except when specified otherwise, the hole collecting electrode is assumed to be at $x=0$.

According to the depiction of the disordered semiconductors presented in this thesis in Figure 2.2, ASA is using two exponential band tails representing the shallow tail states in the band gap and are defined by the Equations 2.1.¹

Direct and trap-assisted recombinations are considered in the simulations presented in this thesis. The recombination through trap states in the sub-bandgap tails follows the Shockley-Read-Hall statistics. (Hall, 1952; Kirchartz and Nelson, 2013) More details about the different parameters used in the simulations can be found in APPENDIX A.

Figure 3.11 depicts the method used to implement the 1D drift-diffusion modelling using ASA. Measures of control devices are used to learn a proper set of parameters representing the system under investigation. The parameters are varied using MATLAB in a fitting loop which feeds ASA up to the point the constraints are met. Once a relevant set of parameters is found, in Chapter 4, ASA is used to simulate the light and dark ideality factors in different polymer:fullerene systems to investigate their sensitivity to dark shunt, series resistance and surface recombinations. These particular simulations about the ideality factors were performed by Prof. Dr. Thomas Kirchartz. In Chapter 6 ASA is used to simulate the variation of spatial distribution of carriers generated by a change in active layer thickness and subsequently the effect the active layer thickness has on the apparent recombination rate. In Chapter 7, a thin fully depleted device is used to acquire a relevant set of parameters. The effects of unintentional p-type doping on spatial distribution of carriers, apparent recombination rate and linearity of the short-circuit current with illumination are then investigated and compared with the obtained experimental data.

¹ Although it is possible to include one amphoteric Gaussian deep defect with ASA, no recombination via deep defect will be considered in this thesis.

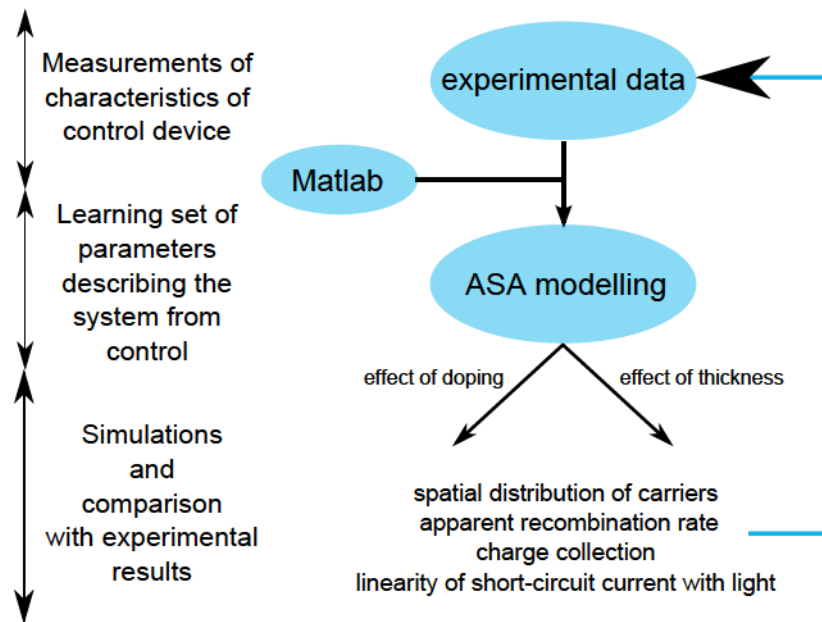


Figure 3.11: Methods followed when using ASA modelling. Control devices are used to learn a set of parameters representative of the system studied. Then, drift-diffusion modelling is performed to study the effect of active layer thickness on spatial distribution of carriers and the apparent recombination rate or the effect of unintentional doping on the apparent recombination rate, linearity of the short-circuit current with light.

3.13 Conclusion

In conclusion, charge extraction and transient photovoltage allow access to excess carrier densities under different operating conditions. As long as the sweep out of excess carrier during extraction is efficient, the combined techniques enable the determination of the non-geminate recombination dynamics, which have been shown to control the V_{oc} and $J - V$ response in the fourth quadrant. The method was previously applied successfully to predict performance of P3HT/P3HS fullerene solar cells. We will see in the next chapter that the method is robust to changes of the polymer:fullerene system studied.

Confirmation and extension of the methodology

4.1 Introduction

The synthesis of new donor polymers is very intense and represents a large proportion of the rapid growth in publications in organic photovoltaics over the last ten years. (Luber and Buriak, 2013) Open-circuit voltage and $J - V$ response in the fourth quadrant have been predicted based on the assumption that non-geminate losses were controlling the performance of P3HT:PC₆₁BM solar cells. (Shuttle et al., 2008c) These non-geminate losses were quantified using the experimental methodology explained in the previous chapter. However, a robust method should be able to be applied to very different types of systems. In this chapter, studies of charge transport and recombination using charge extraction and transient photovoltage on different polymer:fullerene solar cells of very different levels of crystallinity are presented. The use of ideality factors in polymer:fullerene solar cells is explained and its limit of applicability defined.

The motivation for including this chapter is primarily to demonstrate that these methodologies are indeed effective at analysing the current-voltage performance of many OPV devices. This is an important precursor to the following chapters (and particularly Chapters 6 and 7), which are substantially focused on specific limitations to these methodologies.

4.2 Model validation away from P3HT/PCBM

4.2.1 Achievements on different blends of diverse levels of crystallinity

Here a series of polymer:fullerene optimised devices are analysed using charge extraction and transient photovoltage according to the methodology detailed in Chapter 3, following Shuttle et al. (2008a). These were part of different projects and we note that these blends have different levels of crystallinity. The overall

performance of these devices are presented in Table 4.1. The full name according to the conventions of the IUPAC as well as the molecular structure are shown for all the different donor polymers as well as device fabrication are detailed in each section. More in depth analyses of the behaviour of OPV devices employing several of these donor polymers is presented in Chapter 5-8.

In all these systems, a constant generation rate of carriers was assumed between short-circuit and open-circuit conditions. This means that any field dependent generation was neglected in the fourth quadrant. The successful predictions of open-circuit voltage for a wide range of light intensities and the current density-voltage response in the fourth quadrant in the dark and under different light levels confirms a posteriori the validity of this assumption. This does not mean however that no geminate recombination was present but only that such recombination losses were not field dependent and therefore cannot explain the observed loss of photocurrent in the fourth quadrant.

Table 4.1: Overall performance of optimised devices presented in this study

blend donor/acceptor	V_{oc} [mV]	J_{sc} [mA.cm ⁻²]	FF [%]	PCE [%]	Thickness [nm]
PTB7:PC ₇₁ BM	719± 5	14.5 ± 0.3	65.5± 1	6.8± 0.1	85± 5
PBDTTT-C:PC ₇₁ BM	698± 3	14.6 ± 0.3	60.8± 1.2	6.18± 0.1	105± 5
PCDTBT:PC ₇₁ BM	861± 3	9.08 ± 0.5	57.3± 0.5	4.49± 0.1	80± 5
PSOTT:PC ₆₁ BM	532± 3	4.91± 0.1	58± 0.5	1.52± 0.1	68± 4
DPP-TT-T:PC ₇₁ BM	625± 5	17.11± 0.2	60.2± 0.5	6.45± 0.1	100± 5
BTT-DPP:PC ₇₁ BM	687± 3	9.48 ± 0.3	70± 0.2	4.55± 0.1	105± 5

4.2.1.1 PBDTTT-C:PC₇₁BM

The first example system presented here is poly[4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4-(2-ethylhexyloxy-1-one)thieno[3,4-b]thiophene-2,6-diyl] (PBDTTT-C): [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) blend. The core unit of PBDTTT-C is a modification of the PTB7 unit. The synthesis of this donor was published in Hou et al. (2009). Morphological studies suggest it forms a mostly amorphous blend showing little polymer/fullerene aggregation. In particular, UV-Vis spectrum on films and chloroform solution presented by Hou et al. (2009) are very similar. Its molecular structure can be found in Figure 4.1. The device were fabricated in UCLA, USA, in conventional architecture: ITO/PEDOT:PSS/PBDTTT-C:PC₇₁BM(1:2 wt%,105 nm)/Ca/Al. The donor/acceptor solution was prepared in a mixed solvent

dichlorobenzene (DCB)/1,8-diiodoctane (DIO) (97%:3% by volume). Each pixel area was 10 mm². Electrochemical cyclic voltammetry (C-V) measurements found a HOMO lying at -5.12 eV and a LUMO at -3.55 eV in neat film. (Hou et al., 2009) Further details about device preparation can be found in Hawks et al. (2013). The overall device performance are presented in Table 4.1.

We note that investigation of blend perturbation around the optimum blend ratio (1:1.5) was performed and the resulting study of the optoelectronic properties of the perturbed blend are presented in Chapter 5 of this thesis.

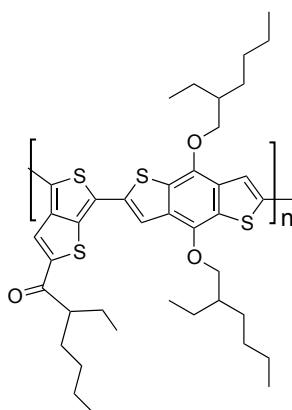


Figure 4.1: Molecular structure of PBDTTT-C. Blended with PC₇₁BM, the active layer shows an intimate mixing of polymer and PCBM.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.2 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [1;650]% sun. The predictions are well within the ± 5 mV margin for the whole range of illumination and confirm a posteriori the assumption that the generation can be assumed to be field independent between short-circuit and open-circuit conditions. However, it can be noticed that the open-circuit voltage tails off for high intensities for this system. This hints towards a transition around which the V_{oc} was governed by the blend optoelectronic properties and then capped by the built-in potential. The relationship between open-circuit and built-in voltages is further discussed in Chapter 6. On this basis, charge extraction was also performed across the current density-voltage response [-0.2;0.8]V in the dark and finally under 25, 50 and 100% sun. Figure 4.2 b) presents the measured (solid lines) and predictions (symbols) under these different light levels.

We note that similar successful predictions of open-circuit voltage and current-

density voltage response of PBDTTT-C:PC₇₁BM devices were performed while the blend ratio donor/acceptor was perturbed around the optimum 1:1; 1:1.5; 1:2 wt%. The results are presented in Chapter 5.

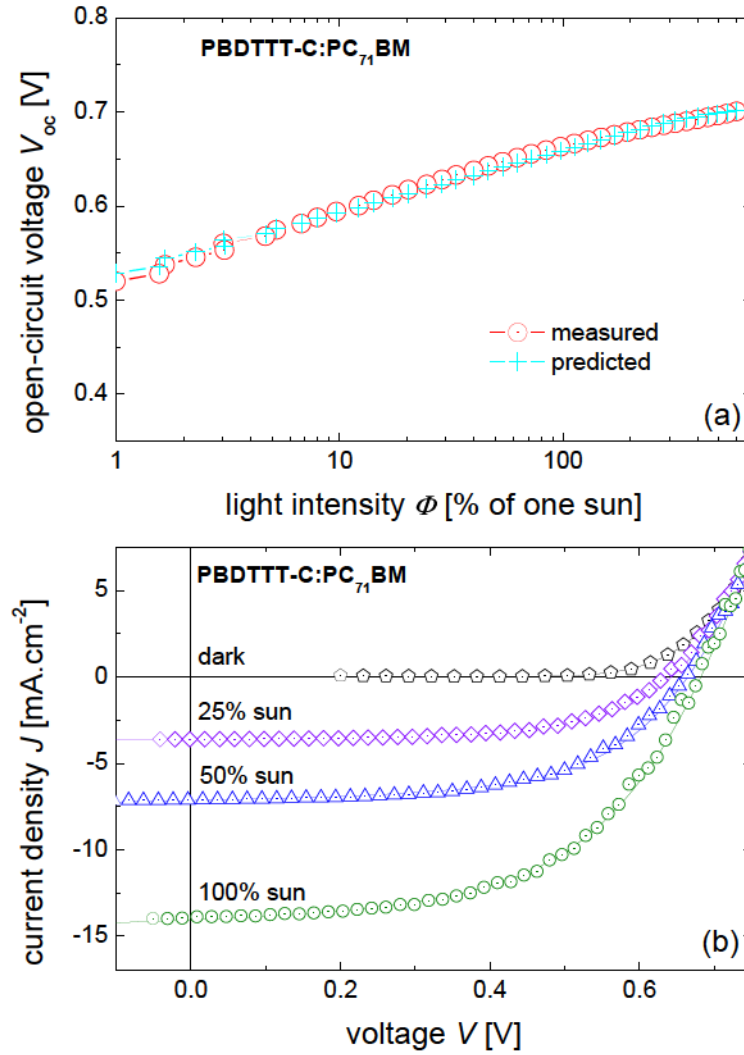


Figure 4.2: Study of PBDTTT-C:PC₇₁BM (amorphous blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

4.2.1.2 PTB7:PC₇₁BM

The second example system presented here is poly(thieno[3,4-b]thiophene/benzodithiophene(PTB7): [6,6]-phenyl C₇₁-butyric acid methyl

ester (PC₇₁BM) blend. PTB7 is a well known benzodithiophene based donor polymer by Liang et al. (2010) whose molecular structure can be found in Figure 4.3. This specific donor polymer was used in particular as it is currently the efficiency record holder for polymer:fullerene solar cells at 9.2% PCE.(He et al., 2012b) The device was fabricated in SCUT, China, in conventional architecture: ITO/PEDOT:PSS/PTB7:PC₇₁BM(1:1.5 %w , 85 nm)/Ca(5 nm)/Al. The donor/acceptor solution was prepared in a mixed solvent dichlorobenzene (DCB)/1,8-diiodoctane (DIO) (97 %:3% by volume). Each pixel area was 16 mm². Electrochemical Cyclic voltammetry (CV) measurements found an HOMO lying at -5.15 eV and a LUMO at -3.31 eV.Liang et al. (2010) Further details about device preparation can be found in Liang et al. (2010). The donor/acceptor blend shows no large phase separation by transmission electron microscopy (TEM) when prepared with this mixed solvent, with substantial miscibility of the polymer in PCBM. (Liang et al., 2010; Liu et al., 2013) The overall device performance are presented in Table 4.1.

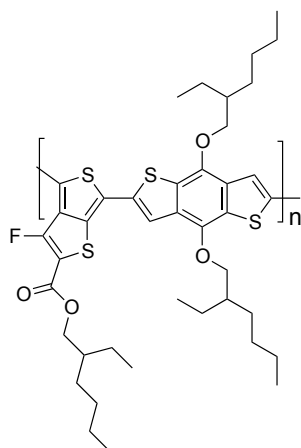


Figure 4.3: Molecular structure of PTB7. Blended with PC₇₁BM, a very fine interpenetrated network of polymer in PCBM is formed.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.4 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [1;600]% sun. The predictions are well within the ± 5 mV margin for the whole range of illuminations and confirms a posteriori the assumption that the generation can be assumed to be field independent between short-circuit and open-circuit conditions for this specific blend ratio. On this basis, charge extraction was performed across the current density-voltage response [-0.2;0.8]V in

the dark and finally under 25, 50 and 100 % sun. Figure 4.4 b) presents the measured (solid lines) and predictions (symbols) under these different light levels. A light dependent small underestimation of the fill factor visible in particular at 1 sun around the maximum power point can be noticed. There are several reasons which could explain this small mismatch:

- beyond the maximum power point, the current density-voltage response becomes strongly series resistant dependent. It is assumed for the correction of applied voltage to the device that the series resistance at forward bias is the identical to the one in the dark.
- non total collection efficiency would lead to a slight underestimation of the charge density and consequently of the total loss flux
- capacitance correction is usually performed using the geometric capacitance, which has been shown earlier to be a correct approximation at reverse bias and low illumination level. However, the correction could be overcompensating at high light level.
- the generation flux is assumed to be constant. However, it is sometimes difficult to experimentally observe very small field-dependent generation, which are yet not necessarily improbable.

4.2.1.3 PCDTBT:PC₇₁BM

The third example system presented here is poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)](PCDTBT):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) blend. The synthesis of this donor was published in Blouin et al. (2007b). In particular, morphological studies suggest it forms a quite amorphous blend though showing little polymer/fullerene aggregation, with in particular a vertical gradient of fullerene.(Staniec et al., 2011) Data from size-exclusion chromatography (SEC) conducted by Blouin et al. (2007b) show some degree of polymer aggregation in tetrahydrofuran and chloroform. Its molecular structure can be found in Figure 4.5. The device were fabricated at Imperial, in conventional architecture: ITO/PEDOT:PSS/PCDTBT:PC₇₁BM(1:2 %w ;80 nm)/Ca(25 nm)/Al(150 nm). The donor/acceptor solution was prepared in a chloroform. Each pixel area was 4.5 mm². Electrochemical cyclic voltammetry (C-V) measurements found an HOMO lying at -5.45 eV and a LUMO at -3.6 eV in neat film.(Blouin et al., 2007a) Further

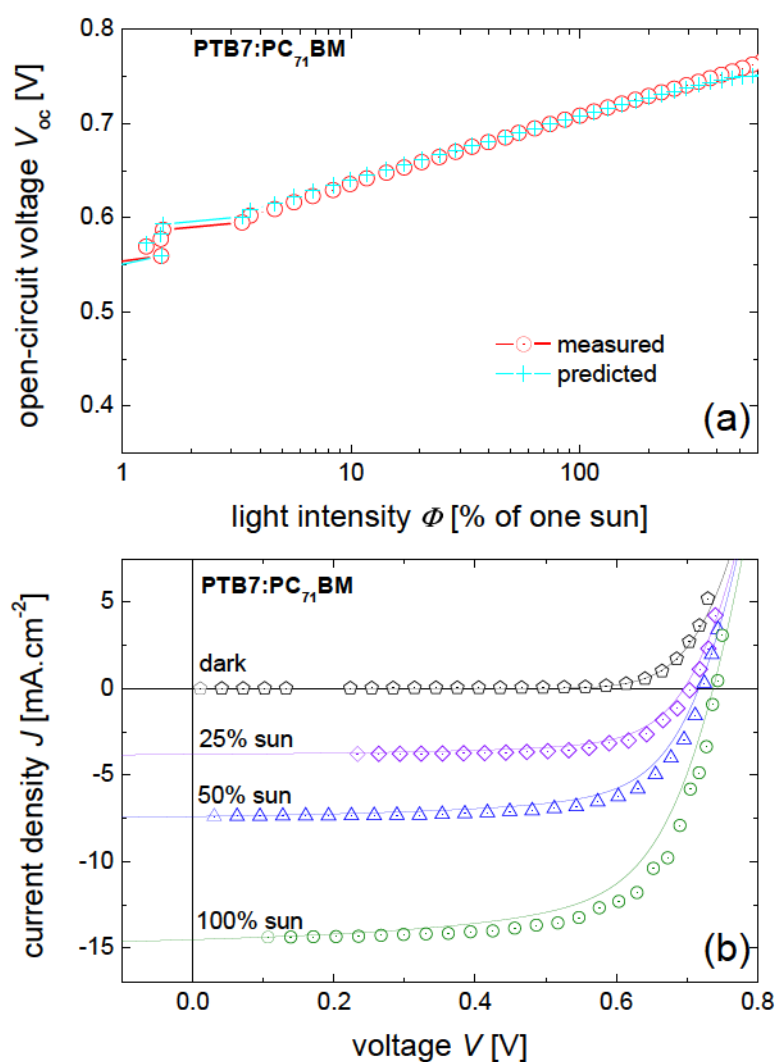


Figure 4.4: Study of PTB7:PC₇₁BM (amorphous blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

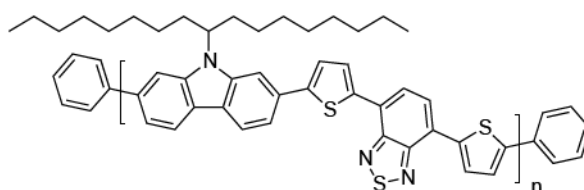


Figure 4.5: Molecular structure of PCDTBT.

details about device preparation can be found in Kirchartz et al. (2013). The overall device performance is presented in Table 4.1.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.6 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [1;750]% sun. On this basis, charge extraction was also performed across the current density-voltage response [-0.2;0.9]V in the dark and finally under 25, 50, 100 and 200% sun. Figure 4.6 b) presents the measured (solid lines) and predictions (symbols) under these different light levels.

4.2.1.4 PSOTT:PC₆₁BM

The fourth example system presented here is poly[(4,4'-bis(2-octyl)dithieno[3,2-b':3'-d']silole)-2,6-diyl-alt-(2,5-bis(3-octylthiophen-2-yl)thiazolo[5,4-d]thiazole)(PSOTT):[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) blend. The synthesis of this donor was published in Subramaniyan et al. (2011). In particular, morphological studies suggest it forms a very crystalline blend with fullerene. Subramaniyan et al. (2011) Its molecular structure can be found in Figure 4.7. The device were fabricated at Imperial, in conventional architecture: ITO/PEDOT:PSS/PSOTT:PC₆₁BM(1:2 wt% ;68 nm)/Ca(25 nm)/Al(150 nm). The donor/acceptor solution was prepared in a hot mixed solvent of 1,2-dichlorobenzene (ODCB) and 1,8-octanedithiol (ODCB:ODT in 100:2.5 % v) at 100°C. Each pixel area was 4.5 mm². Electrochemical cyclic voltammetry (C-V) measurements found an HOMO lying at -5.1 eV and a LUMO at -2.9 eV in neat film. Further details about device preparation can be found in Subramaniyan et al. (2011). The overall device performance are presented in Table 4.1.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.8 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [0.3;850]% sun. The prediction is well within the ± 5 mV margin for the whole range of illumination and confirms a posteriori the assumption that the generation can be assumed to be field independent between short-circuit and open-circuit conditions. The slight mismatch at very low light level is a shunt effect. On this basis, charge extraction were also performed across the current density-voltage response [-0.2;0.6]V in the dark and finally under 100 % sun. Figure 4.8 b) presents the measured (solid lines) and predictions (symbols) under

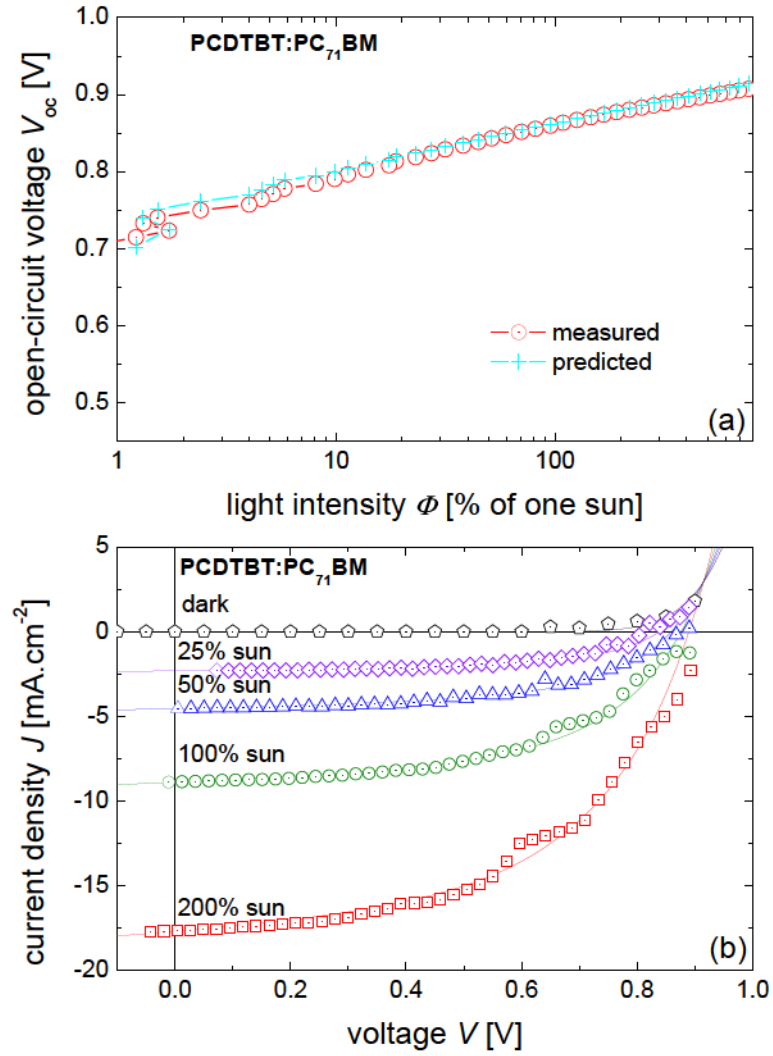


Figure 4.6: Study of PCDTBT:PC₇₁BM (rather amorphous blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

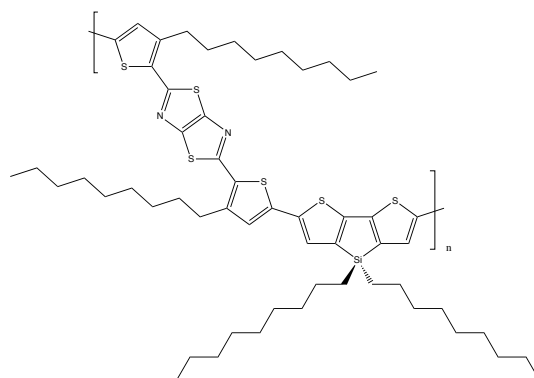


Figure 4.7: Molecular structure of PSOTT.

these different light levels.

4.2.1.5 DPP-TT-T:PC₇₁BM

The fifth example system presented here is poly[[2,5-bis(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-alt-[2,2'-(2,5-thiophene)bis-thieno[3,2-b]thiophen]-5,5'-diyl])(DPP-TT-T):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) blend. The synthesis of this donor particularly redshifted was published in Bronstein et al. (2011). In particular, morphological studies suggest it forms a quite crystalline blend with fullerene thanks to the planarity of the DPP units and their acceptance for hydrogen bondings which favour $\Pi - \Pi$ stacking. Its molecular structure can be found in Figure 4.9. The device were fabricated at Imperial, in conventional architecture: ITO/PEDOT:PSS/DPP-TT-T:PC₇₁BM(1:2 wt%; 100 nm)/Ca(25 nm)/Al(150 nm). The donor/acceptor solution was prepared in binary solvent(chloroform:dichlorobenzene in 4:1). Prior to electrode vacuum deposition the device was thermally annealed at 120° C for 10 minutes. Each pixel area was 4.5 mm². Electrochemical cyclic voltammetry (C-V) measurements found an HOMO lying at -5.06 eV and a LUMO at -3.68 eV in neat film.(Bronstein et al., 2011) Further details about device preparation can be found in Bronstein et al. (2011). The overall device performance is presented in Table 4.1.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.10 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [1;400]% sun. The slight mismatch at very low light level is a shunt effect. Charge extraction was performed across the current density-voltage

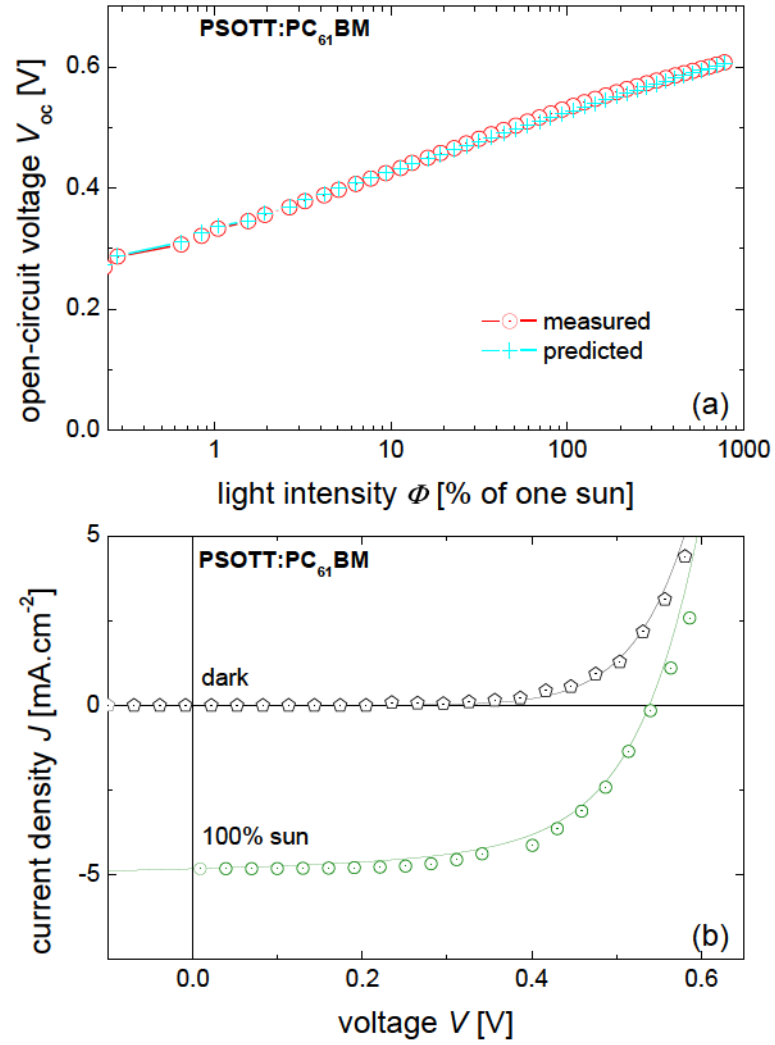


Figure 4.8: Study of PSOTT:PC₆₁BM (crystalline blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

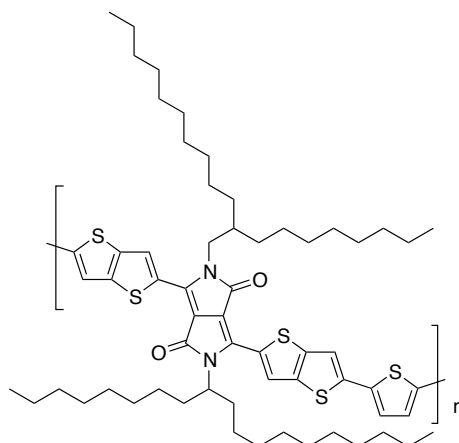


Figure 4.9: Molecular structure of DPP-TT-T.

response $[-0.2;0.7]$ V in the dark and finally under 25, 50 and 100% sun. Figure 4.10 b) presents the measured (solid lines) and predictions (symbols) under these different light levels.

4.2.1.6 BTT-DPP:PC₇₁BM

Finally, the sixth example system presented here is poly[(5-decylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene-2,8-diyl)-alt-co-(3,6-bis(2-thienyl)-2,5-dihydro-2,5-di(2-octyldodecyl)pyrrolo[3,4c]pyrrolo-1,4-dione-5,5'-diyl)](BTT-DPP)::[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) blend. The synthesis of this donor was published in Dimitrov et al. (2011). The specificity of this blend resides in the fact that most of the photocurrent comes from the PCBM absorption and hole injection into the donor at the heterojunction. Furthermore, another specificity from the device perspective is that with a high molecular weight fractionated batch (90 kg.mol^{-1}), high fill factor (70-71%) under 1 sun equivalent illumination have been obtained.(Dimitrov et al., 2012) In particular, morphological studies suggest it forms a crystalline blend with fullerene. Dimitrov et al. (2011) showed that TEM images of this polymer:PCBM blend shows the presence of of variety of PCBM rich domains. It was suggested that this blend was formed of more intimate mixed regions of polymer:fullerene and other relatively pure polymer and PCBM domains. Its molecular structure can be found in Figure 4.11. The device were fabricated at Imperial, in conventional architecture: ITO/PEDOT:PSS/BTT-DPP(90 kg.mol^{-1}):PC₇₁BM(1:2 wt%; 105 nm)/Ca(25 nm)/Al(150 nm). The donor/acceptor solution was prepared in binary solvent(a chloroform:o-dichlorobenzene (4:1)). Each pixel area was 4.5 mm^2 . Photoelectron

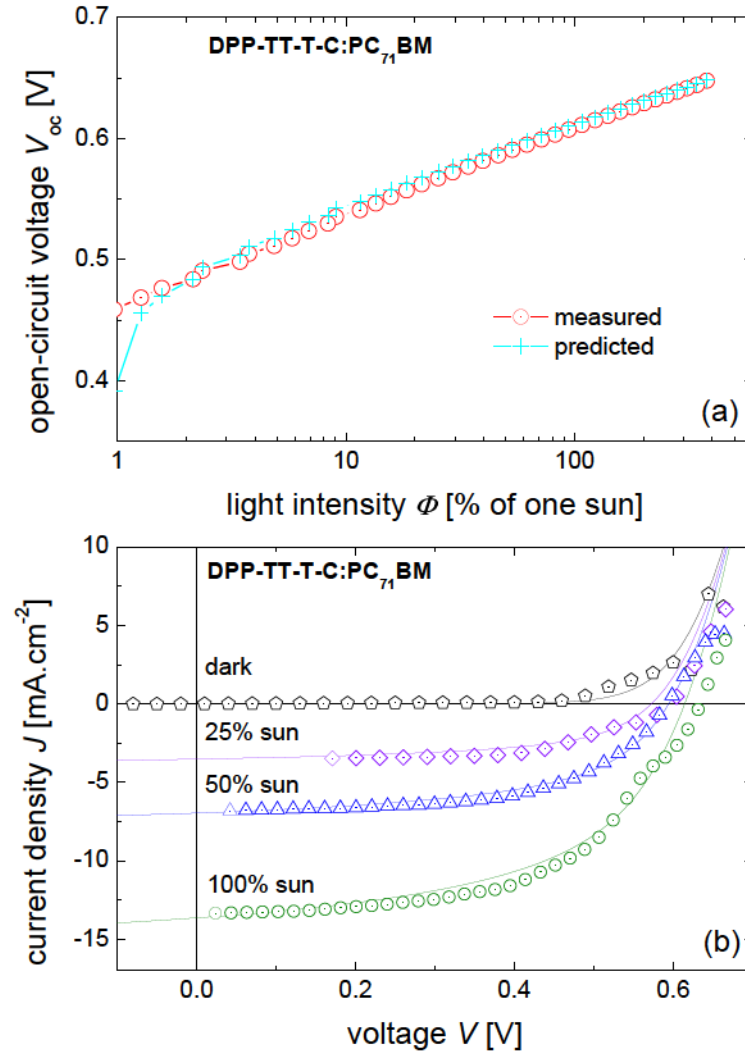


Figure 4.10: Study of DPP-TT-T:PC₇₁BM (crystalline blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

spectroscopy in air gives an HOMO lying at -5.20 eV and a LUMO at 3.65 eV in neat film.(Bronstein et al., 2011) Further details about device preparation can be found in Dimitrov et al. (2013). The Overall device performance can be found in Table 4.1.

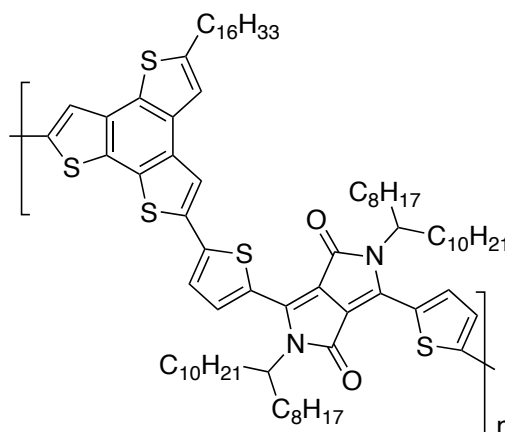


Figure 4.11: Molecular structure of BTT-DPP:PC₇₁BM.

Charge extraction and transient photovoltage were performed to investigate the recombination dynamics of this system according to the methodology exposed in the previous chapter. Figure 4.12 a) presents the prediction of open-circuit voltage (crosses) and the measured open-circuit voltage (open circles) for the range of illumination levels [1;500]% sun. The predictions is well within the $\pm 5\text{mV}$ margin for the whole range of illumination and confirms a posteriori the assumption that the generation can be assumed to be field independent between short-circuit and open-circuit conditions. The slight mismatch at very low light level is a shunt effect. Charge extraction was also conducted across the current density-voltage response [-0.2;0.7]V in the dark and finally under 25, 50, 75, 100, 150 and 200 % sun. Figure 4.12 b) presents the measured (solid lines) and predictions (symbols) under these different light levels.

4.2.2 Comparison between two high fill factor polymer:fullerene solar cells

Figure 4.13 shows a comparison of carrier transport properties between two of the efficient polymer:fullerene systems presented just above. From Figure 4.13 a), it appears that these systems have effective drift mobilities μ^* ranging from $[4 \times 10^{-5}; 4 \times 10^{-4}] \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and from Figure 4.13 b), the total carrier lifetime τ_n is ranging from $[1 \times 10^{-4}; 1 \times 10^{-6}] \text{ s}$ over the typical illumination range [10%;

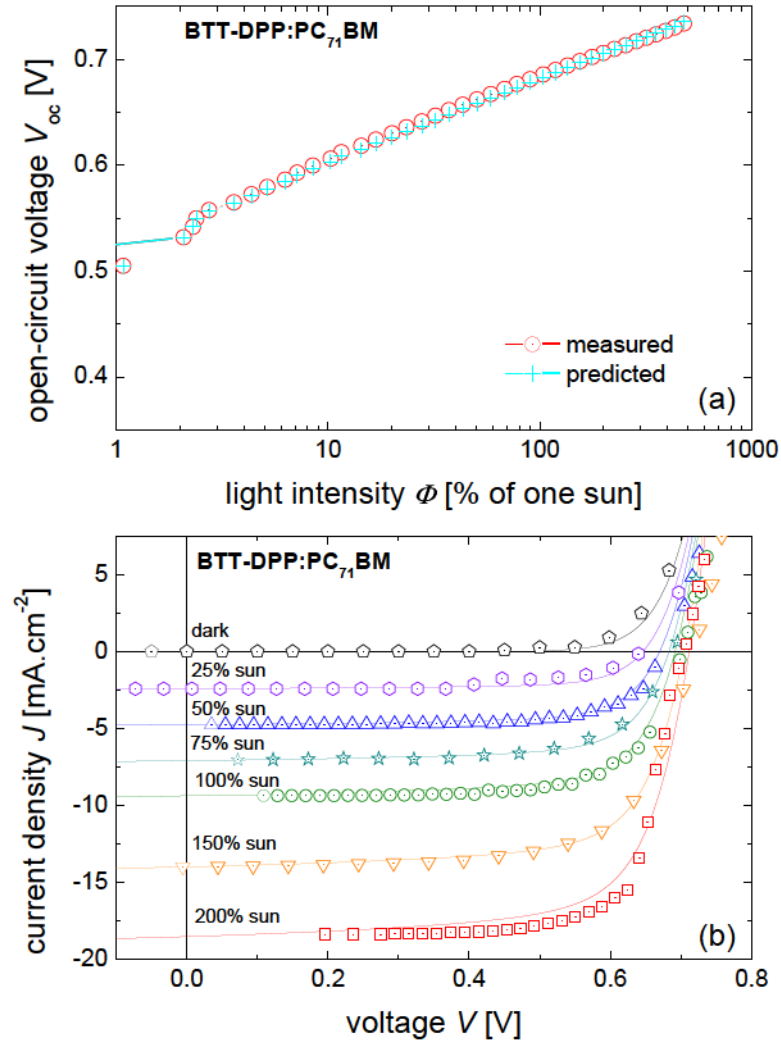


Figure 4.12: Study of BTT-DPP:PC₇₁BM (crystalline blend)(a)Measured (open symbol) and predicted (crosses) open-circuit voltage at different background illumination level Φ . b) Prediction of current-voltage response at different light levels in the fourth quadrant.

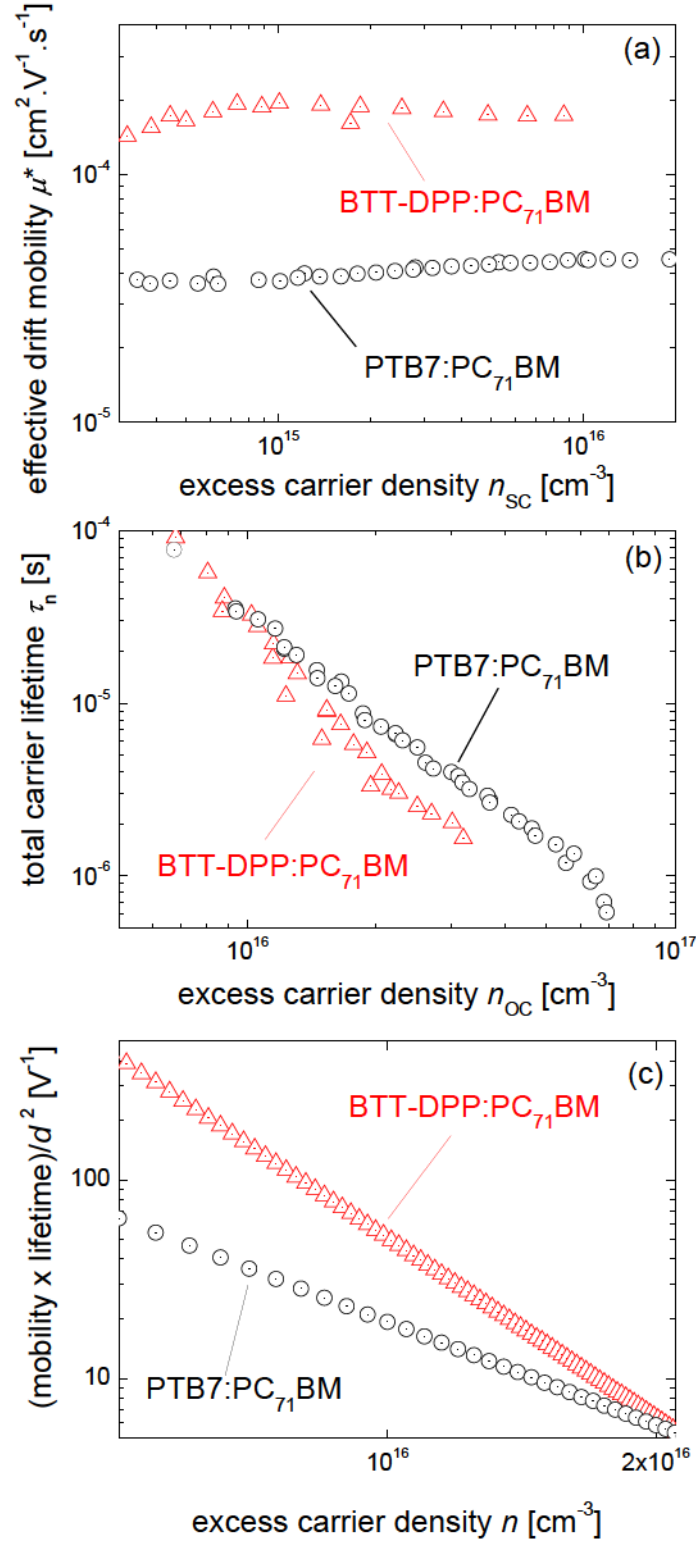


Figure 4.13: Comparison of two systems with high fill factors optimised around their first interference maximum: BTT-DPP:PC₇₁BM (crystalline blend) and PTB7:PC₇₁BM (amorphous blend). a) Effective mobility obtained by charge extraction at short-circuit, (b) total carrier lifetime and (c) ratio between mobility-lifetime product and the square of the active layer thickness with mobility and lifetime used from short-circuit and open-circuit measurements respectively.

500-600%] suns. The devices here have a similar thickness ≈ 100 nm. We saw just above that the main loss process in the fourth quadrant in both systems is non-geminate recombination. Combining the two previous graphs can give an insight into the reason why the fill factor of BTT-DPP based device is higher than the PTB7 based device (70% and 64% respectively). Although the PTB7 based device shows slightly longer carrier lifetimes at any given excess carrier density, its effective mobility is lower than that of BTT-DPP device. Overall, the ratio of the drift length $L_D = \mu\tau V_{BI}/d$ to the device thickness d is slightly superior for the BTT-DPP device, as shown in 4.13 c). Here both built-in voltages are around 0.7 V. Hence probably the higher fill factor.

We note this method to access experimentally to the mobility-lifetime product represents an upper bound for the drift length as the measured lifetime has been conducted here at open-circuit and overestimates the lifetime at short-circuit. This should therefore be more considered as a qualitative comparison more than quantitative. A more detailed comparison of transport versus recombination is given in Chapter 8.

4.2.3 Limit of the methodology in its current setup in case of poor fill factor

It is apparent in the previous sections that quantifying non-geminate recombination using charge extraction and transient photovoltage is successful in predicting the device performance of many efficient polymer:fullerene devices. However, all these devices present relatively high fill factor, in other words, relatively good collection efficiency. This thesis is limited to the analysis of such devices. There are however several cases where the same methodology would fail predicting with sufficient accuracy the device performance:

- Field dependent generation: we saw in the previous chapter that the generation flux at open-circuit could be approximated by the short-circuit current. In other words, the generation of polarons in the device is assumed to be independent of the voltage. However, this method applied to some devices with relatively low fill factors can show poor agreement with device performance, in particular the response of the open-circuit voltage to illumination level, indicative of extra loss pathways. It is the case for instance when the generation term is field dependent as found for example with poly(2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) APFO3:PC₇₁BM by Dibb et al. (2013a). In this specific case, the generation flux needs to be modelled with a voltage dependent com-

ponent. Usually, the voltage dependence of the polaron yield can be followed by Transient Absorption Spectroscopy (TAS) if the non-geminate recombination does not occur too early (10-100 ns), as shown earlier in Chapter 3. Alternatively, Albrecht et al. (2012b) showed field dependent photogeneration in poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] PCPDTBT:PC₇₁BM using time-delayed collection field (TDCF).

- Photoactivated leakages: the selectivity of the contacts can usually be assessed by studying the dark curve as being shown later in this chapter in Figure 4.16: in reverse bias, the current in the dark with selective contacts should be zero. However, this selectivity can only hold up to a finite reverse bias. Compensating for leakage at the wrong contact can be taken into account if it is already visible in the dark current-voltage response. However, it is much harder (if not too complex) if the carrier leakage is activated by light, what is called sometimes photoactivated shunt. (Mülbacher et al., 2006; Schilinsky et al., 2004)
- Deep trap states: in Chapter 2, we described an exponential density of tail states within the bandgap. These traps are usually shallow enough that the carriers can be collected under short-circuit condition. However, it is possible that some carriers are located too deep relative to the mobility edge to be detrapped under no applied bias. The presence of deep trap states was experimentally shown for example using X-rays by Street et al. (2012). In this case, the total excess carrier density would be underestimated by charge extraction, while these specific traps can be actively involved into recombination processes. The charge extraction occurs usually at short-circuit and we saw that the time needed to extract charges accumulated under open-circuit condition under 1 sun illumination was typically on the order of 1 μ s, as shown in Figure 3.1. However, using transient photoconductivity, Shuttle et al. (2012) showed that some long lived carriers in the 100 μ s timescale could be observed in N-alkylthieno[3,4-c]pyrrole-4,6-dione (TPD) based polymer:fullerene systems, which in this particular experiment represented 30% of the total extracted charges. Those deep trap states were assessed to be deeper than 0.45 eV below the band edge. To counter this issue of deeply trapped carriers, the extraction method could be performed under higher field strength than the one at short-circuit (typically $\propto V_{BI}/d$). Bias Amplified Charge Extraction (BACE) has been recently proposed to operate for that purpose by Lange et al. (2013) and is a logical development of

the charge extraction method, but beyond the scope of this thesis.

4.3 Investigating the different types of non-geminate recombinations: light and dark ideality factors

We saw just above that non-geminate recombination was a major loss process in many efficient polymer:fullerene bulk heterojunction solar cells. According to Chapter 3, many different types of recombination events can be considered as non-geminate. There is currently intense debate and sometimes conflicting results, on which type of recombination is dominating the carrier losses. (Street et al., 2010, 2012; Wetzelaer et al., 2011; Street, 2010; Deibel and Wagenpfahl, 2010; Wetzelaer et al., 2012) To target higher power conversion efficiencies and reduce those losses, a more precise knowledge of the dominant recombination mechanism is necessary. (Garcia-Belmonte and Bisquert, 2010; Nayak et al., 2011, 2012) The analysis of the order of the recombination via the study of how the recombination rate scales with carrier density can, in some cases, inform on which mechanism is dominating the non-geminate losses. (Shuttle et al., 2008c,b; Mozer et al., 2005a; Leong et al., 2011; Garcia-Belmonte et al., 2010) However, we will see in Chapter 6 that it is sensitive to the variations in spatial distribution of carriers. (Kirchartz and Nelson, 2012; Deledalle et al., 2014) Another way to differentiate recombination mechanisms is via the study of ideality factors. (Foertig et al., 2012a; Giebink et al., 2010; Kirchartz and Nelson, 2012; Cowan et al., 2011b; Foertig et al., 2012b; Tress et al., 2013)

4.3.1 Describing ideality factors

The main question regarding non-geminate recombination is the extent of which the presence of localised states within the band gap are involved into the dominant recombination pathway. The ideality factor describes the way the local recombination rate $R(x)$ is exponentially dependent on voltage, according to the Equation 4.1:

$$R(x) = R_0(x) \exp\left(\frac{\Delta E_f(x)}{n_{id} k_B T}\right) \quad (4.1)$$

where $\Delta E_f(x)$ is the local splitting of the quasi-Fermi levels, $k_B T$ the thermal energy and $R_0(x)$ the recombination rate at equilibrium. From this relationship, the ideality factor n_{id} can in theory be defined in all cases by:

$$\Rightarrow n_{id} = \frac{1}{k_B T} \frac{d\Delta E_f}{d\ln(R)} \quad (4.2)$$

According to this definition, the ideality factor is expected to change between the case where the local recombination is free-to-free and in the case where the recombination event is mediated by a trap (we only consider the free-to-trap recombination here):

- if the active layer is assumed to be intrinsic semiconductor and that there are as many free holes as free electrons ($n_{\text{free}} = p_{\text{free}} \propto \exp\left(\frac{\Delta E_f}{2k_B T}\right)$), with equal capture coefficients by traps on both types of carriers, then these traps are occupied with a probability $n_{\text{free}}/(n_{\text{free}} + p_{\text{free}}) = 0.5$. Consequently, the probability of occupancy is independent of the local splitting of quasi-Fermi level and the recombination of a free hole with a trapped electron would be described by $R(x) \propto p_{\text{free}} \propto \exp\left(\frac{\Delta E_f}{2k_B T}\right)$. In the case of trap mediated bimolecular recombination, the local ideality factor would be equal to 2.
- if the recombination is free-to-free, then on the other hand $R(x) \propto n_{\text{free}}p_{\text{free}} \propto \exp\left(\frac{\Delta E_f}{k_B T}\right)$. In this case the ideality factor is 1.

When the distribution of traps is more complex, the ideality factor is expected to be ranging from [1;2].(van Berkel et al., 1993) Consequently, in principle, the more the traps are mediating the majority of the recombination events, the higher the ideality factor should be.

However, local recombination rate and quasi-Fermi levels are not easily experimentally accessible. Instead, the ideality factor is commonly measured either by the dark current density-voltage ($J_{\text{dark}} - V$) response (dark ideality factor) or via the way the open-circuit voltage is scaling with light intensity $V_{\text{oc}} = f(\phi)$ (light ideality factor) according to the two relations:

$$n_{\text{id}}^{\text{dark}} = \frac{q}{k_B T} \frac{dV}{dJ_{\text{dark}}} \quad (4.3)$$

$$n_{\text{id}}^{\text{light}} = \frac{q}{k_B T} \frac{dV_{\text{oc}}}{d\ln(\phi)} \quad (4.4)$$

Although the two ways of measuring the ideality factor should coincide, substantial differences between light and dark ideality factors can be measured in organic solar cells.(Wetzelaer et al., 2011) Figure 4.14 shows the obtained values calculated according to the equations presented just above. While both ideality factors quantitatively agree at least in some voltage range for P3HT:PC₆₁BM device, these are completely different for DPP-TT-T:PC₇₁BM device. Moreover, when calculated differentially for many light levels, the obtained light ideality factor is strongly voltage dependent and can easily range from values ≈ 1.5 at low voltages to ≤ 1 for high voltages.

Furthermore, the dependence in voltage of the current density in the dark is influenced by both shunt resistance (at low bias) and by the total series resistance (internal and external to the active layer) at high forward bias. Shunt resistance is also influencing how the open-circuit voltage is function of light intensity at low illumination background. On the other hand, the latter is immune to the influence of series resistance as no net current exists at open-circuit.

Consequently, the observed differences between ideality factors measured either through the dark current voltage response or by the open-circuit voltage function of light intensity lead sometimes to completely different conclusions to what kind of dominant recombination mechanism is occurring in some bulk heterojunction solar cells. For instance, dark and light idealities shown for P3HT in Figure 4.14 are both substantially higher than 1 which would hint that the localised trap states are involved in the dominant recombination mechanism, which is consistent with other publications.(Wetzelaer et al., 2011; Street, 2010; Deibel and Wagenpfahl, 2010; Wetzelaer et al., 2012) However, other reports mention ideality factors for P3HT:PCBM near 1, concluding that free-to-free recombination is dominant and showing that the loss mechanism can be controlled by film deposition process.(Cowan et al., 2010)

In what follows, experimental results comparing light and dark ideality factors on different polymer:fullerene solar cells are presented. These experimental observations are completed by drift-diffusion analysis to understand the effects of some crucial parameters which can vary when comparing one device to another on the obtained experimental ideality factors.

4.3.2 Results and discussion

First, in this study, the light ideality factor is calculated from the measurement of open-circuit voltage at many different light levels (with enough close data points) so that the differential can be defined over a sufficient voltage range, unlike previous reports.(Wetzelaer et al., 2011, 2012; Cowan et al., 2010) Figure 4.15 shows a typical measurement of the open-circuit voltage over a wide range of light intensities (45 points over [0.1;400]% sun). A simple fit of the data would give a unique value of the light ideality very close to 1, while the differential measured on the same device and presented in Figure 4.14 allows better resolution and allows to differentiate transition of types of recombination mechanism $n_{id} > 1$ to $n_{id} \approx 1$. Furthermore, it enables comparing both idealities as the dark ideality factor is, as explained just above, either constrained by the shunt resistance at too low bias or the series resistance at too high bias. Consequently, the only range

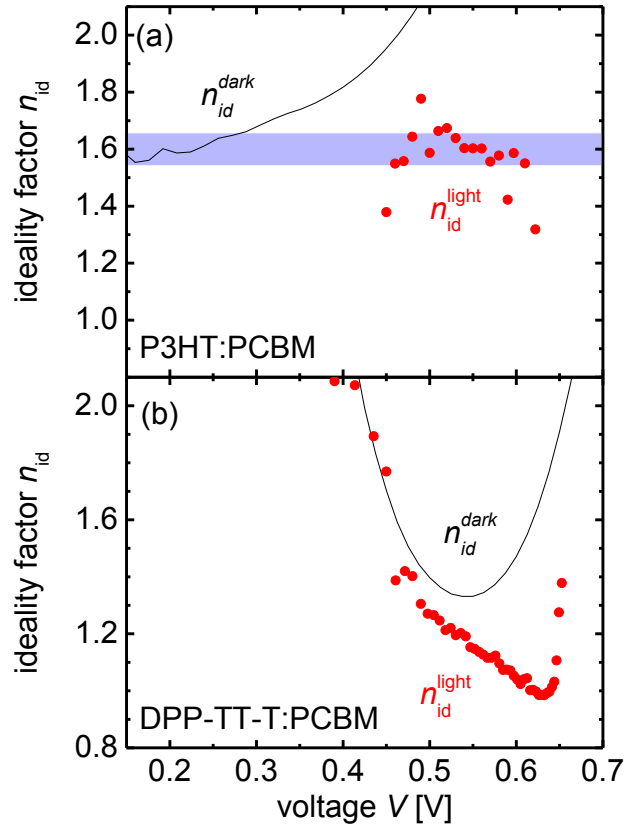


Figure 4.14: Dark and light ideality factors for a) P3HT:PCBM and b) DPP-TT-T:PCBM. Although the two ideality factors are relatively consistent for P3HT:PCBM device, they are substantially different for DPP-TT-T:PCBM. Furthermore, the light ideality factor for DPP-TT-T is very voltage dependent.

over which the dark ideality could potentially give real insight into the recombination mechanism is during the exponential rectification of the dark $J - V$ curve, before being capped by the series resistance. Nonetheless, it is difficult in some cases to know for sure if the region of lowest dark ideality factor (In Figure 4.14 b) around ≈ 0.55 V) is probing the dependence of the recombination rate on the splitting of the quasi-Fermi levels or if it is still capped by a combination of shunt and/or series resistance. Overall, the single fit of the dependence in light intensity

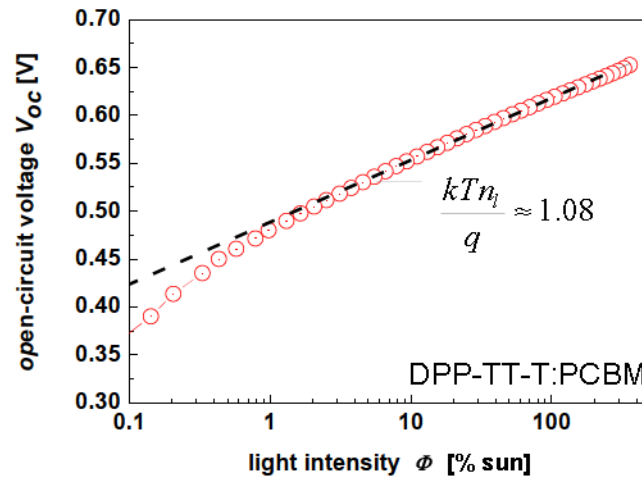


Figure 4.15: Open-circuit voltage (open-circles) at different light levels ϕ of DPP-TT-T:PCBM device as well as simple fit (dashed line) over the entire range of illumination. While in the previous figure the differential calculation of the ideality factor was giving values ranging from $n_{id} > 1$ at low voltages to values around 1 at high voltages and seems to indicate a change in the dominant recombination mechanism over the voltage range, the value of the ideality obtained by the fit is close to 1.

of the open-circuit voltage of DPP-TT-T:PC₇₁BM would conclude that a free-to-free recombination was the dominant loss process, while the calculation of the light ideality factor as plotted in Figure 4.14 allows to differentiate two regimes. First, at low bias, either shunt resistance is still influencing the apparent ideality or trap-mediated recombination is dominant while at higher light intensities (4-5 suns), the recombination rate scales much more with voltage than it would do with a trap-mediated recombination mechanism. In this latter case, previous modeling studies showed that either the main loss process becomes more bulk (band-to-band) non-geminate recombination in the bulk or surface recombination at the interface active layer/electrode becomes predominant. (Kirchartz and Nelson, 2012)

In one study, we have been able to inadvertently modify the dark leakage of a device with a very thin active layer (< 20 nm) using corrected photocurrent. First, the device showed strong dark leakage as presented in Figure 4.16 a) and after corrected photocurrent (when the device has been put into far reverse bias (≈ -15 V)) the device dark current response shifted to the second sets of JV curves with less leakage (at that stage the device was stable into its new state and the modification of the shunt was irreversible). Although the origin of the shift is unclear, one can speculate that the current driven into reverse bias might have burned some leakage pathways between the two electrodes. This has been observed previously in amorphous silicon solar cells (Johnson et al., 2003) and previously suggested in organic solar cells (Mihailetchi et al., 2006). Figure 4.16 b) shows the apparent dark (solid lines) and light (open symbols) ideality factors of the same device into these two different leakage states. Although non intended, this study showed clearly the effect of the dark shunt on the measured idealities. While the series resistance and the right side of the parabolas of the dark ideality factors were unchanged, the decrease of the dark leakage (increase in shunt resistance) substantially and irreversibly decreased the calculated idealities in the dark and in the light at low voltages.

To further explore the effect of series resistance onto the apparent dark ideality factor, a thickness series of PCDTBT:PC₇₁BM was performed. The device architecture was the following: ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/LiF (10 nm)/Al(150 nm). The solution was in 1:2 wt% in chloroform at 13 mg/mL concentration. Spin speed was varied to obtain 65 ± 5 nm, 85 ± 5 nm and 158 ± 10 nm thick active layers. We note here that the evaporation of the metal electrode was conducted on the three devices at the same time. This allows, to some extent, to reduce any change in energetics at the interface active layer/metal electrode between the devices that would otherwise be very likely if the metal electrode was evaporated on the active layers at different runs. Figure 4.17 a) shows experimental dark (solid lines) and light (open symbols) idealities for the three different thicknesses. The observation of the dark ideality curves could lead to conclude that the minimum of the three dark ideality factors follows a trend in thickness. However, at low bias (on the left side of the parabolas), the dark ideality of the thinnest device is apparently the highest, while it becomes the lowest at high bias (the right side of the parabolas) as the total series resistance of the device (internal to the bulk+contacts) is the lowest of the three devices. Consequently it is most likely that the thick devices have an apparent high dark ideality factors due to their higher series resistance rather than due to a localised states within the band gap which are more involved into recombination of polarons.

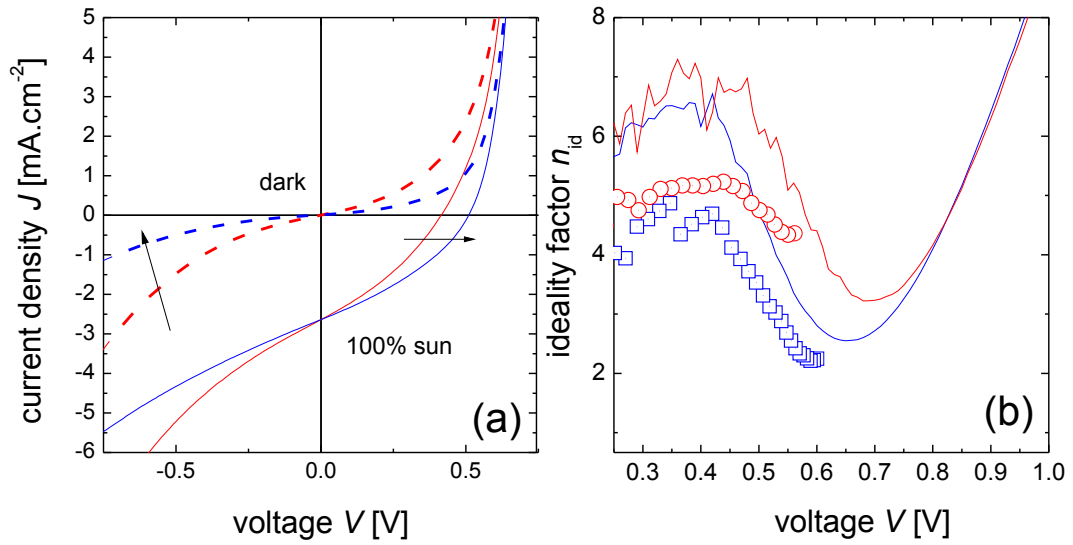


Figure 4.16: a) Dark (dashed lines) and AM1.5 equivalent (solid lines) current density-voltage response of the same device in two different leakage states. b) Ideality factors, light (open symbols) and dark (solid lines) calculated according to Equations 4.3 and 4.4 relative to the two shunt states of the same device. The left part of the parabolas of the dark curves are directly governed by the shunt resistance while in forward bias while the series resistance governed right side of the parabola are unchanged. The light ideality factors is strongly influenced by the change in shunt resistance. The lower the shunt resistance (the higher the dark leakages), the higher the apparent light ideality factor.

To further support this argument of the series resistance effect on the dark ideality factor, drift-diffusion simulations according to previous publications were performed. (Kirchartz et al., 2011; Kirchartz and Nelson, 2012) The software used was ASA implemented by Pieters et al. (2011), in which band-to-band and trap mediated non-geminate recombination as well as surface recombination were all considered. The lists of parameters used in these simulations are presented in Appendix A1-A2. Figure 4.17 b) presents the result of the simulated dark and light ideality factors when no manual change in external series resistance was necessary to reproduce the same trend at high voltages as in the experimental data. Indeed, the increase in the bulk series resistance due to transport for thicker devices directly causes the change in dark ideality at high bias while the surface recombination velocity, the capture of traps and the free-to-free recombination coefficients were all kept constant from one device to the other.

Finally, while the light ideality factors presented in this study are usually above 1 over a wide range of voltages, they tend to fall down to 1 at high bias. In the case of PCDTBT thickness series, on Figure 4.17, the light ideality factors can be observed falling substantially towards and below 1. We hypothesize here that increased surface recombination at high illumination could explain this low value on the ideality observed in the thickness series based on modelling and experimental studies recently published, in particular on the change in PCDTBT:PCBM performance by modification of the contacts interfaces. (Kirchartz et al., 2009; Wagenpfahl et al., 2010; Schäfer et al., 2011; Ratcliff et al., 2011, 2013; Xia et al., 2013) While the illumination level is increased, the open-circuit voltage increases and becomes closer to the built-in potential. At some point, the carrier concentration of the minority carrier (holes at the cathode for instance) keep accumulating, while the voltage does not increase further. When the open-circuit voltage reaches the built-in voltage, there is absolutely no net electric field remaining in the device, nor helpful concentration gradients to extract one charge carrier to its electrode rather than the counter electrode. The electrodes to this stage are not selective any longer. According to Equation 4.1, the light ideality factor is decreasing substantially.

Figure 4.18 a) shows the measured idealities on two devices of same thickness ($\approx 80\text{nm}$) of PCDTBT:PCBM (same solution, same deposition process of the active layer) with two different contacts: in the first case (circles), the electrode is a sequential evaporation of Ca(25 nm)/Al(150 nm) and in the second case (squares) only Aluminium is directly deposited onto the active layer. These experimental data show that the change in electrode has directly influenced the ideality factor. Calcium has a lower workfunction than Aluminium. (Brabec et al., 2001a) As a re-

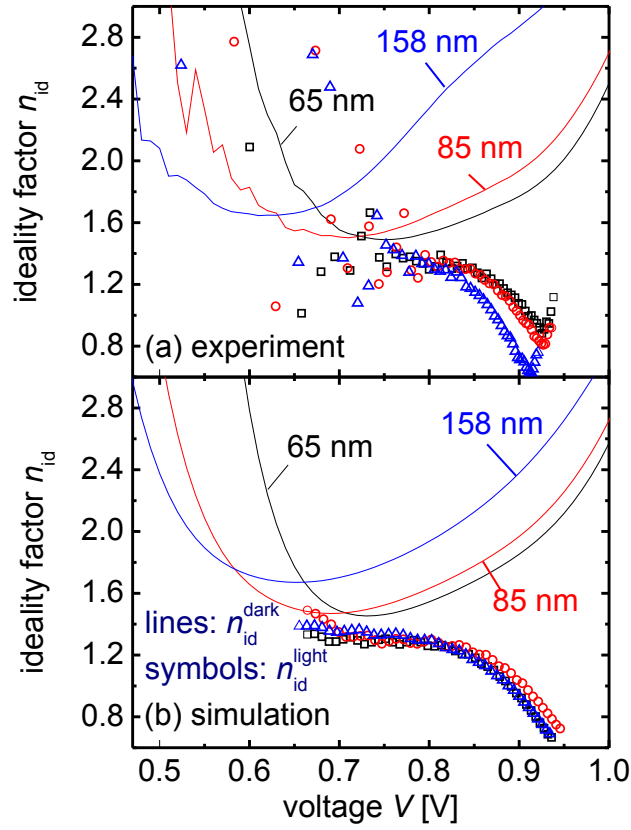


Figure 4.17: a) Experimental data of light (open symbols) and dark (solid lines) ideality factors of three different thickness of active layer of PDCTBT:PC₇₁BM. b) simulated equivalent ideality factors obtained by drift-diffusion by changing the thickness of the active layer from 65 nm to 158 nm. The simulations were conducted by Pr. Dr. Thomas Kirchartz.

sult, the built-in voltage of the device with Ca/Al is expected to be higher than just Aluminium if any change in impurities at the interface electrode active layer is neglected. In this study, according to Table 4.2, the higher V_{BI} resulted directly in higher open-circuit voltage. This indicates that the open-circuit voltage at high light level is constrained by the electrode in this particular system.

Figure 4.18 shows that simulations conducted by Prof. Dr. Thomas Kirchartz support further these experimental observations as the change of back contact energy barrier ($\phi_{bc} = 100$ meV (Ca/Al) and 240 meV (Al)) and surface recombination velocities $S = 10^5$ cm.s⁻¹(Ca/Al) and 10 (Al) cm.s⁻¹) did reproduce the high voltage decrease of light ideality factors for the two different types of contact, all the other parameters being kept constant. The list of parameters used can be found in Appendix A2 with in particular further explanations on the parameters related to energy barrier at the contacts ϕ_{bc} and surface recombination velocities S . Altogether, ideality factors below 1 can be observed and these can be explained at high light levels by increased surface recombination at the interface active layer/electrode. Therefore, despite the measured idealities observed dropping below 1 at high voltages, these measurements are still compatible with previous reports of trap assisted recombination in PCDTBT:PCBM system at lower light levels.(Beiley et al., 2011)

Table 4.2: Overall performance of optimised devices for ideality factor study

Blend donor/acceptor	V_{oc} [mV]	J_{sc} [mA.cm ⁻²]	FF [%]	PCE [%]	Thickness [nm]
PCDTBT:PC ₇₁ BM	897± 5	8.93± 0.1	58± 1	4.63± 0.1	65± 5
PCDTBT:PC ₇₁ BM	884± 5	8.34± 0.2	54± 1	3.95± 0.1	85± 10
PCDTBT:PC ₇₁ BM	880± 5	7.56± 0.1	45± 1	2.98± 0.1	158± 10
PCDTBT(Ca/Al):PC ₇₁ BM	859± 5	8.51± 0.1	53± 1	3.89± 0.1	80± 5
PCDTBT(Al only):PC ₇₁ BM	760± 5	9.9± 0.1	34± 1	2.59± 0.5	80± 5
DPP-TT-T:PC ₇₁ BM	725± 5	17± 0.2	60± 1	6.4± 0.2	100± 10

4.4 Conclusions

To conclude this chapter, non-geminate recombination quantified by charge extraction and transient photovoltage enabled the prediction of performance of many different polymer:fullerene systems. As non-geminate losses are shown to be crucial in the power generating quadrant of different polymer:fullerene blends, it seems logical to attempt to reduce their effect by understanding more precisely

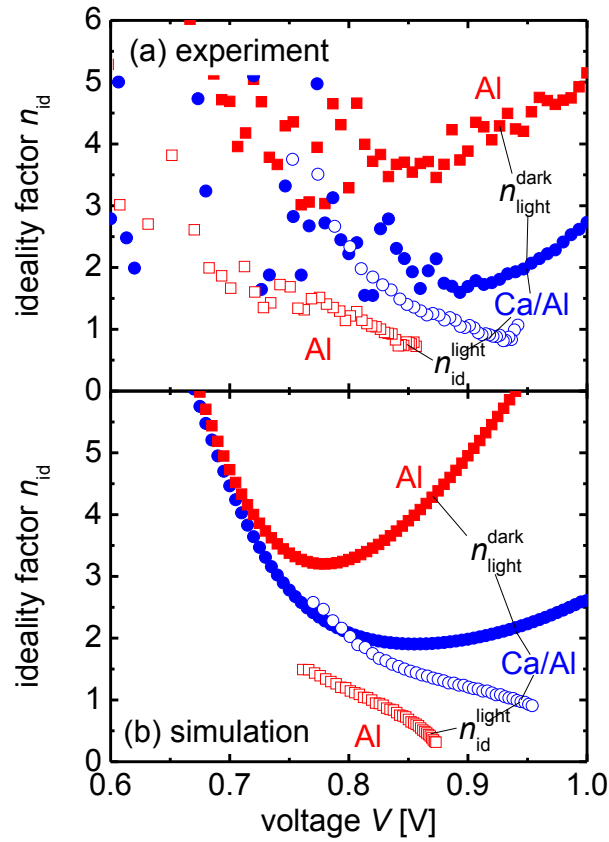


Figure 4.18: a) Experimental data of light (open-symbols) and dark (solid lines) ideality factors for two PCDTBT:PC₇₁BM devices of same active layer (same solution, same deposition process, thickness ≈ 80 nm) with two different contacts Aluminium (150 nm) evaporated or Ca(25 nm)/Al(150 nm) coevaporated onto the active layer. b) simulated equivalent ideality factors obtained from drift-diffusion by changing the surface recombination coefficient (contact barrier $\Phi = 100$ meV (Ca/Al) and 240 meV (Al) and surface recombination velocity $S = 10^5$ cm.s⁻¹ (Ca/Al) and 10 cm.s⁻¹ (Al). The simulations were conducted by Prof. Dr. Thomas Kirchartz.

what exact recombination mechanism is predominant. Ideality factors can do so under specific conditions. As influenced both by shunt at low bias and series resistance at forward bias, the dark ideality factor calculated traditionally from the dark current density-voltage response happens to be complicated to interpret if not misleading. On the other hand, on the condition that shunt resistance is sufficiently high, the light ideality factor measured differentially with enough data points from the response of open-circuit voltage to light intensity can distinguish field regions where trap mediated recombinations are predominant and where free-to-free recombination is. We observe that at high light intensities, surface recombination becomes predominant in all the systems studied. We proved by a combined drift-diffusion modeling and experiments that surface recombination can explain low values of light ideality falling to 1 or even below. In particular, Auger type recombination has not been observed in the polymer:fullerene systems studied and does not match with the hypothesis of trimolecular recombination. (Juška et al., 2008)

Variations of electronic properties upon blend ratio perturbation

5.1 Introduction

Device optimisation is a long, often tedious process aiming at obtaining the highest performance from a definite donor/acceptor couple. The choice of blend ratio, contacts, active layer and deposition technique will inevitably have to find a balance between charge generation and charge transport/extraction. Using an amorphous efficient polymer:fullerene blend, the electronic properties of the active layer are explored while the blend ratio donor/acceptor was slightly perturbed around its optimal. Validated techniques presented in the previous chapters combined with electroluminescence were used to quantify the resulting shifts in energetics and kinetics.

5.2 Methods

To understand the effect of the perturbation of the blend on device recombination dynamics and performance, a representative, high efficiency polymer:fullerene system has been chosen. The donor was poly[4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4-(2-ethylhexyloxy-1-one)thieno[3,4-b]thiophene-2,6-diyl] (PBDTTT-C) and the acceptor was [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). PBDTTT-C:PC₇₁BM is an efficient system relatively close to the most performant systems published to date and has been already presented in Chapter 4. (Liang et al., 2010; Chen et al., 2009a; Tan et al., 2012; He et al., 2012b; You et al., 2012; He et al., 2012a; Zhou et al., 2012; Seo et al., 2012; Liang et al., 2008, 2009a; He et al., 2011) The synthesis of this donor was published in Hou et al. (2009). In particular, morphological studies suggest it forms a mostly amorphous blend showing little polymer/fullerene aggregation. Figure 5.1 presents the structures of the donor and acceptor as well as the complete architecture of the devices chosen in this study. The perturbation of the

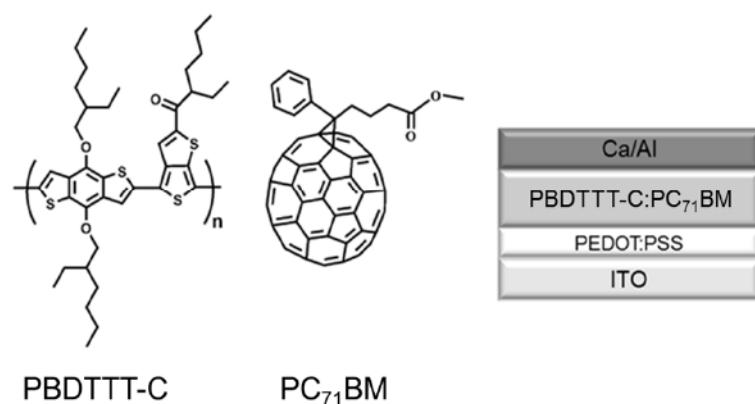


Figure 5.1: Molecular structure of the donor polymer PBDTTT-C, acceptor fullerene PC₇₁BM and overall conventional architecture of the devices used in this study. The blends formed are amorphous.

blend ratio was chosen relatively close to its optimal at 1:1.5 wt%. The choice of these ratios was governed by the willingness to work with good operating devices with, for instance, little dark leakages which were likely to be observed if the ratio donor/acceptor was too imbalanced. Three different blend ratios were decided: 1:1 wt%, 1:1.5 wt% and 1:2 wt%. To obtain a fair comparison between the different blend ratios, each blend was separately optimised for the thickness of the active layer. This device optimisation was conducted by Steve A. Hawks. As the amount of PCBM is slightly changing between the three blends, a slight change in viscosity should result from it. In consequence, identical deposition treatment using spin coating would result in slight variations of the obtained film thickness. Moreover, different blend ratios are expected to require different active layer thickness to perform at best. The registered performance under AM1.5 equivalent illumination during the process of thickness optimisation can be found in Figure 5.2. Table 5.1 summarises the performance of the optimised device for each of the three blend ratios.

According to previous reports including Hou et al. (2009) the 1:1.5 wt% is indeed the optimal blend ratio for PBDTTT-C:PC₇₁BM. Two main observations relating the device performance and the perturbation of the blend ratios can be extracted from this data. These observations have been reproduced from batches to batches and the errors bars used to in Figure 5.2 correspond to the standard deviations out of 6 pixels (same substrate). First, it can be noticed that the 60 wt%

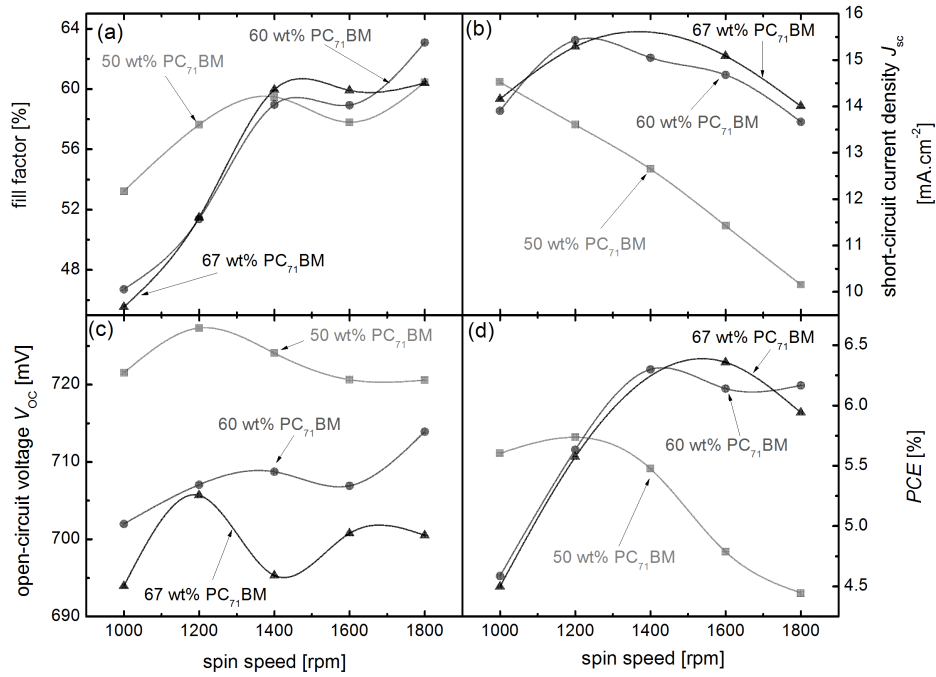


Figure 5.2: Thickness optimisation process realised by Steve A Hawks for the three blend ratios 50, 60 and 67 wt%. Overall performance function of spin speed during spin coating a) fill factor, b) short-circuit current c) open-circuit voltage and d) total power conversion efficiency. While 60 and 65 wt% can maintain high fill factor and increase the short-circuit current close to the first interference maximum, 50 wt% cannot. A robust trend in open-circuit voltage is noticed with the highest for the 50 wt%.

Table 5.1: Overall performance of optimised devices for each blend ratios 50, 60 and 67 wt%

Composition [wt%]	V_{oc} [mV]	J_{sc} [mA.cm ⁻²]	FF [%]	PCE [%]	Thickness [nm]
50 wt% PC ₇₁ BM	715 ± 3	11.4 ± 0.1	61.3 ± 0.5	4.98 ± 0.1	67 ± 4
60 wt% PC ₇₁ BM	708 ± 1	13.6 ± 0.2	64.5 ± 0.5	6.22 ± 0.1	82 ± 2
67 wt% PC ₇₁ BM	698 ± 3	14.6 ± 0.3	60.8 ± 1.2	6.18 ± 0.1	105 ± 5

and 67 wt% PCBM blends can maintain a high fill factor while increasing the J_{sc} with increasing thickness (and consequently in thin devices, this leads to an increased photon absorption). However, with the 50 wt% blend, a high fill factor cannot coincide with high short-circuit current. Although it has not been possible to access to measured refractive index $\tilde{n}$ and extinction coefficient $\tilde{k}$ of our particular system, it can be hypothesised that the total thickness (see table 5.1) of the optimal 60 wt% and 67 wt% devices are closer to their first interference maximum than is the 50 wt%. (Burkhard et al., 2010; Albrecht et al., 2012a; Hadipour et al., 2011; Dennler et al., 2009) This might hint to a loss of collection efficiency with a reduced content of PCBM which would inherently prevent from making the most of the better absorption of the polymer related to PCBM. Furthermore, a robust trend in open-circuit photovoltage V_{oc} with PCBM loading can be observed. Here, as presented in Figure 5.2 c) and table 5.1, the less PCBM, the higher the open-circuit voltage. This has been observed between batches and over different device fabrication runs in two different laboratories. It is not the first time that the open-circuit voltage is reported to increase with less PCBM loading over a certain range of compositions leading to operating devices. (Piersimoni et al., 2011; Vandewal et al., 2008; Tvingstedt et al., 2009; Mihailetschi et al., 2005; Parmer et al., 2008; Yuen et al., 2009; Scharber et al., 2003) Although the effect of contacts cannot be completely ruled out here to account for this effect of composition over the open-circuit voltage, the fact that it is generally observed over different batches, from one electrode evaporation run to another, in different laboratories (UCLA and Imperial College London), leads to conclude that these changes in open circuit are rather consequences of changes in the optoelectronic properties of the bulk. In this context, according to the methodology exposed in a previous chapter, the change of open-circuit voltage can be expected to result from shift in energetics at the heterojunction and/or change in charge carrier dynamics. (Cowan et al., 2010; Credgington and Durrant, 2012; Dibb et al., 2013a; Kirchartz et al., 2008a) Furthermore, previous reports showed a shift of CT-state energy levels with change in fullerene loading on other systems. (Piersimoni et al., 2011; Tvingstedt et al., 2009) To attempt to pinpoint the exact reasons for this change in V_{oc} with compositions, charge extraction, transient photovoltage and electroluminescence have been used.

Charge extraction and transient photovoltage were conducted as detailed previously in Chapter 3.

Electroluminescence measurements were conducted by D.G. Rebois and T. Kirchartz. EL spectra were measured using a Princeton Instruments Acton SP 2500 spectrograph combined with a liquid nitrogen-cooled InGaAs photodiode array

(Acton OMAV:1024). The spectral intensity was corrected with the spectrum from a calibrated halogen lamp according to Faist et al. (2011).

5.3 Results and discussion on the Optoelectronics

5.3.1 Energy levels: change of Density of States

Following the methodology presented in Chapter 3, charge extraction at open circuit enables accessing the apparent density of states.(Shuttle et al., 2008c,a,b, 2010b; Dibb et al., 2011; Maurano et al., 2011; Credgington et al., 2012; Dibb et al., 2013a; Credgington and Durrant, 2012; Credgington et al., 2011) As tackled just above, potential change in energy barriers for extraction at the contacts with the electrodes is not likely to be the cause of the recurrent change in open-circuit voltages with composition in this study. Moreover, the three devices being each optimised for their related blend ratio have sufficient fill factor (see table 5.1) to be confident the collection efficiency in these devices under study are high enough to have access to an accurate value of the total charge in the bulk under different operating conditions. Indeed, by sweeping charges out under short-circuit conditions, high collection efficiency is required to access to the real number of charges present under different illumination levels. With these safeguards in place, the data presented in figure 5.3 a) were obtained after correction for geometric capacitance (at these thicknesses, the active layers are fully depleted, which makes the correction using the geometric capacitance a reasonable choice) and compensated for incurred charge carrier losses. The data, as explained earlier in the methodology chapter, are analysed using the empirical relations at open circuit:

$$\tau_{\Delta n} = \tau_0 \exp\left(-\frac{qV_{oc}}{\vartheta k_B T}\right) \quad (5.1)$$

$$n = n_0 \exp\left(\frac{qV_{oc}}{mk_B T}\right) \quad (5.2)$$

$$\delta = \frac{m}{\vartheta} + 1 \quad (5.3)$$

$$\tau_n = \tau_{\Delta n} \delta \quad (5.4)$$

$$k_{rec} = \frac{n^{\delta-2}}{\delta \tau_0 n_0^{\delta-1}} \quad (5.5)$$

The fitted parameters are presented in the tables below. In particular, to attempt to reproduce the effect of the change in dielectric properties of the blend induced by an increase in PCBM loading, a slight increment in relative permittivity was been implemented in the calculations. We note that the uncertainty in relative permit-

tivity was included in the calculation of the uncertainty for the calculation of the recombination rate k_{rec} shown below. It can be noted that over the entire range of illumination levels, at constant open-circuit voltage V_{oc} , the charge density of the three blends required to split the quasi-Fermi levels to the same magnitude at the contacts are different and the trend follows: $n(50\text{wt}\% \text{ PC}_{71}\text{BM}) < n(60\text{wt}\% \text{ PC}_{71}\text{BM}) < n(67\text{wt}\% \text{ PC}_{71}\text{BM})$. As a result, the perturbation of the blend over this narrow range of compositions has significantly induced a change in the apparent density of states. In this context, two possible changes in the DoS might have happened which could result both in the same experimental observation: as depicted in Figure 5.3 b), either at constant energy level, less states are available in the band tails of the polymer HOMO and PCBM LUMO or the two band tails were pushed further away from each other when reducing the PCBM loading. A combination of both is also possible, the technique in itself cannot distinguish the two cases. Nevertheless, these changes happened without modifying the shape of the DoS as the shape of the curves $n(V_{\text{oc}})$ at high background illuminations is relatively constant. (Kirchartz et al., 2011) Table 5.2 shows that the parameter $q/mk_{\text{B}}T$ is constant at $12.25 \pm 10\%$.

Table 5.2: Recombination dynamics fitting parameters and their uncertainty margins from the data obtained during charge extraction at open circuit and transient photovoltage on the three optimised devices of different blend ratios.

Composition	Parameter	measured	high value	low value
50 wt% PC ₇₁ BM	$q/\partial k_{\text{B}}T$	23.9 V ⁻¹	24.4 V ⁻¹	23.6 V ⁻¹
60 wt% PC ₇₁ BM	$q/\partial k_{\text{B}}T$	21.6 V ⁻¹	22 V ⁻¹	21.2 V ⁻¹
67 wt% PC ₇₁ BM	$q/\partial k_{\text{B}}T$	22.8 V ⁻¹	22.9 V ⁻¹	22.3 V ⁻¹
50 wt% PC ₇₁ BM	$q/mk_{\text{B}}T$	13.5 V ⁻¹	13.8 V ⁻¹	12.7 V ⁻¹
60 wt% PC ₇₁ BM	$q/mk_{\text{B}}T$	10.9 V ⁻¹	11 V ⁻¹	10.7 V ⁻¹
67 wt% PC ₇₁ BM	$q/mk_{\text{B}}T$	10.9 V ⁻¹	11 V ⁻¹	10.7 V ⁻¹
50 wt% PC ₇₁ BM	$\tau_{\Delta n_0}$	2 s	2.8 s	1.7 s
60 wt% PC ₇₁ BM	$\tau_{\Delta n_0}$	2.5 s	3.2 s	2 s
67 wt% PC ₇₁ BM	$\tau_{\Delta n_0}$	4.8 s	5 s	3.5 s
50 wt% PC ₇₁ BM	n_0	$2.1 \times 10^{12} \text{ cm}^{-3}$	$4.1 \times 10^{12} \text{ cm}^{-3}$	$1.6 \times 10^{12} \text{ cm}^{-3}$
60 wt% PC ₇₁ BM	n_0	$2.1 \times 10^{13} \text{ cm}^{-3}$	$2.5 \times 10^{13} \text{ cm}^{-3}$	$1.9 \times 10^{13} \text{ cm}^{-3}$
67 wt% PC ₇₁ BM	n_0	$2.8 \times 10^{13} \text{ cm}^{-3}$	$3.3 \times 10^{13} \text{ cm}^{-3}$	$2.7 \times 10^{13} \text{ cm}^{-3}$

Previously, correlations between PCBM loading, open-circuit voltage and CT-state emissions have been observed in different polymer:PCBM systems. (Vandewal et al., 2010; Tvingstedt et al., 2009; Veldman et al., 2008). To confirm the trend observed in energetics measured by charge extraction, electroluminescence study was conducted on the different blends. 5.4 a) shows the spectrum of the three

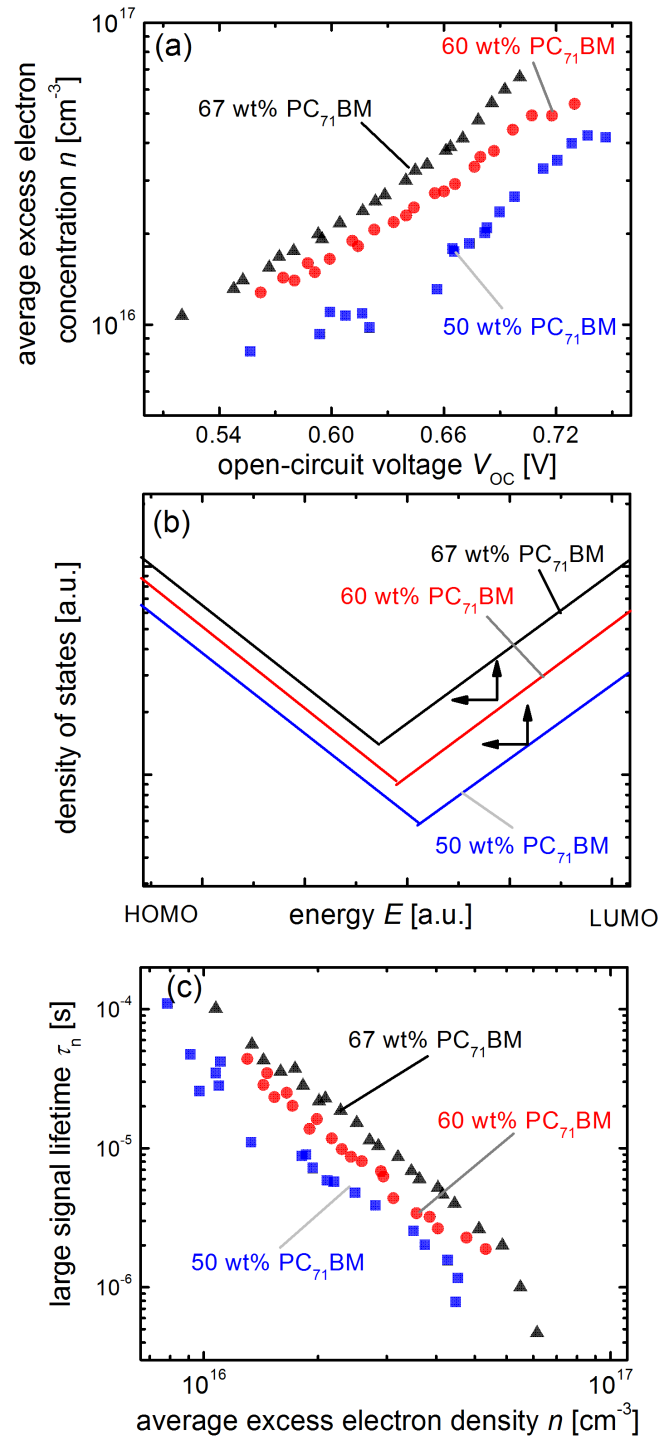


Figure 5.3: a) Excess charge carrier densities at open circuit obtained by charge extraction for the three blend ratios 50, 60 and 65 wt% b) schematics of the potential change in Density of States which could explain the data obtained by charge extraction. The lower the fullerene content, the higher the energy levels at the heterojunction donor/acceptor. c) total lifetime at different charge density for the same three blend ratios. Here, at constant charge density, the higher the fullerene content, the longer the carrier lifetime.

Table 5.3: Electric parameters and thickness of active layer of the three optimised devices used during data treatment.

Composition	ϵ_r	Built-in Voltage [V]	Thickness [nm]
50 wt% PC ₇₁ BM	3.7	0.790	67 ± 4
60 wt% PC ₇₁ BM	3.8	0.805	82 ± 2
67 wt% PC ₇₁ BM	3.9	0.780	105 ± 5

blends as well as that of pure polymer film. The normalised 50 wt% PCBM blend is very similar to that of the pure polymer, with an energy downshift of ≈ 0.1 eV as well as a stronger low-energy emission tail. While the loading of the acceptor is increased, the EL spectra keeps being gradually redshifted. The intermediary blend ratio 60 wt% PCBM seems to be in a transition phase between the spectrum of 50 wt% and 67 wt% PCBM. However, while in these two latter ratios, the position of the emission maximum peaks are quite stable, the one of the 60 wt% PCBM is strongly dependent on the injection current. For instance, 5.4 shows that for low injection currents (≤ 40 mA.cm⁻²) the emission is similar to that of the 67 wt% PCBM blend while at higher injection currents, the spectrum shifts towards the one of 50 wt% PCBM blend.

As a result, this luminescence transition observed over the composition range is consistent with the observation of shifts in the density of states measured by charge extraction. The emission spectra seem to be a sum of two emission bands: one of them being centered around ≈ 1 -1.15 eV and the second at ≈ 1.4 eV. Each spectrum can be reduced and deconvoluted into the two gaussians as has been done previously by Vandewal et al. (2010). The first peak around 1.4 eV was attributed to the pure polymer singlet emission and the low energy one to the CT-state emission. As a result, it appears that CT state energy and PBDTTT-C singlet energy are relatively close and as the PCBM loading modulated the DoS, the singlet activation can be observed in some cases like here in the 50% w blend ratio, which is also the worst performing photovoltaic blend, as empirically observed previously by Faist et al. (2011) during singlet activation process. Recently, Hoke et al. (2013); Di Nuzzo et al. (2013) highlighted that a certain number of processes could occur when the energy levels at the heterojunction are close to each other. In the case of PBDTTT-C:PC₇₁BM blends, it seems that the injected electrons from the acceptor phase can more easily transfer to the donor phase when the PCBM loading is low. Hence, maybe, the observed higher non-geminate recombination rate in the 50 wt% blend. Finally, the shifts in energetics have been observed using two different methods, namely charge extraction at open circuit and electrolumi-

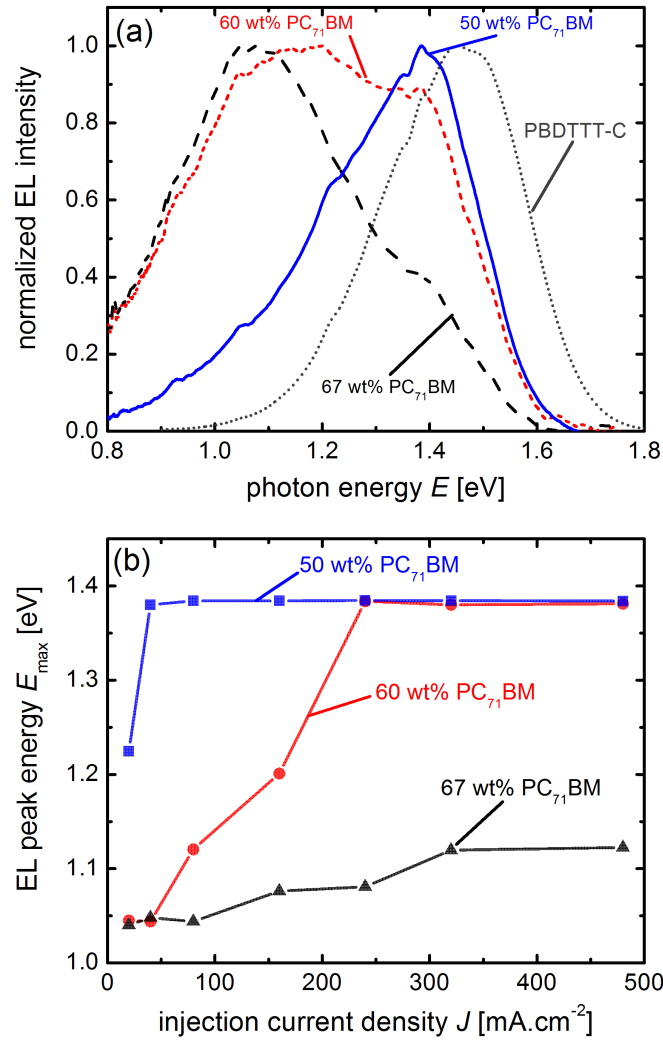


Figure 5.4: a) Electroluminescence spectra for the three blends as well as PBDTTT-C neat film (injection current $J=160 \text{ mA.cm}^{-2}$). b) Variation of the EL emission maximum of the three blends with injection currents. The EL emission peak confirms the observation of the shift in energetics at the heterojunction measured by charge extraction at open circuit. The more PCBM the more redshifted the EL spectrum is. While the spectrum of 50 wt% PCBM is similar to (slightly redshifted) to the neat polymer singlet emission, addition of PCBM results in an apparent transition from polymer singlet emission to CT state. 60 wt% PCBM blend possess both gaussian emission and is the only blend whose EL peak position is strongly correlated with injection current.

nescence, and it is the first time that a quantitative agreement between these two techniques is reported. Figure 5.5 shows the measured open-circuit voltage at equivalent charge density (here $n=2 \times 10^{16} \text{ cm}^{-3}$) and the position of the centre of mass of the CT emission band for the three blend ratios. The $V_{oc}(\text{at } n = \text{cst})$ and E_{CT} vary in a 1:1 manner and the trend is robust for most of the illumination levels (i.e different open-circuit voltages) and injection currents.

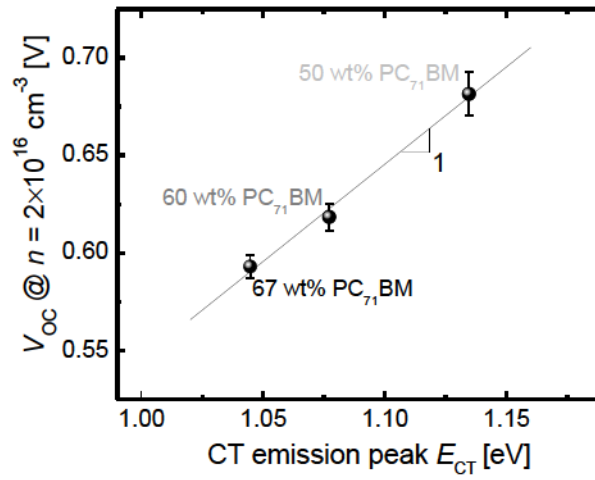


Figure 5.5: Measurements of the shifts in energetics at the heterojunction upon blend perturbation measured by charge extraction at open circuit and electroluminescence. Both techniques probe the same phenomenon and vary in a 1:1 manner with the blend ratios 50, 60 and 67 wt%.

However, according to the table 5.1, the observed difference in open-circuit voltage between 50 wt% PC_{71}BM and 67 wt% PC_{71}BM is $\approx 17 \text{ mV} \pm 6$ while at constant charge density, the shift in the DoS observed in the charge extraction data is $\approx 60 \text{ mV} \pm 10$. Therefore, the shift in energetics at the heterojunction donor/acceptor cannot explain alone the change in open-circuit voltage. Further insights into charge carrier dynamics are consequently required.

5.3.2 Kinetics

To investigate the recombination dynamics of the three blends, charge carrier lifetimes and effective mobilities were experimentally determined.

5.3.2.1 Carrier lifetime

Following the approach described in the method section, transient photovoltage measurement has been conducted on the three optimal devices. The resulting macroscopic lifetime τ_n is deduced from the measurement of the small perturbation lifetime $\tau_{\Delta n}$ by the relation:

$$\tau_n = \tau_{\Delta n} \times \delta \quad (5.6)$$

In this experiment, the measurements of $\tau_{\Delta n}$ were performed with a pulsed excitation centered at $\lambda = 620$ nm. Figure 5.3 c) shows the total carrier lifetime function of space averaged charge density. Once again, the carrier lifetimes of the three blends show differences across the entire range of charge concentrations studied herein. At a fixed charge density n_0 over the range $[1 \times 10^{16}; 1 \times 10^{17}] \text{ cm}^{-3}$, $\tau(50 \text{ wt\% PC}_{71}\text{BM}) < \tau(60 \text{ wt\% PC}_{71}\text{BM}) < \tau(67 \text{ wt\% PC}_{71}\text{BM})$. At high charge density ($\approx 7 \times 10^{16} \text{ cm}^{-3}$), the magnitude of the transient photovoltage created by the injection of the small optical perturbation is small and the signal to noise ratio degrades substantially. This explains the apparent higher variations in the last data points. Regarding the recombination lifetime, the observed trends are opposite from the shift in the density of states with fullerene loading. Although the energetics at the heterojunction are favorable for the 50 wt% PC₇₁BM to maximise the open-circuit voltage at the interface donor/acceptor compared with the other blends ratios, the recombination lifetime of the polarons seem the shortest. Therefore, the change in open-circuit voltage upon perturbation of the blend over the narrow window [50 wt% PC₇₁BM; 67 wt% PC₇₁BM] are partly compensated by the recombination processes during charge transport to the electrodes. The exact origin of these loss processes will be scrutinised below. We show that non-geminate recombination alone can explain the behavior of the devices within the fourth quadrant.

5.3.2.2 Carrier mobility

As the carrier lifetimes were studied just above, further measurements focused on carrier mobility. Although FET mobilities are a very meaningful way of assessing the carrier mobility in transistors, it is not guaranteed that the sheet like transport close to the gate will be similar to the vertical transport of charge carrier through the active layer in bulk heterojunction solar cells, in particular under low macroscopic field. This leaves SCLC (Kettle et al., 2011), photo-CELIV (Kumar et al., 2009) and charge extraction at short circuit (Shuttle et al., 2010a)) methods. The latter was implemented since it did not require significant change of

the setup used for the study of recombinations dynamics at open circuit. Furthermore, it has been previously shown to provide reasonable values of mobilities in P3HT:PC₆₁BM operating devices,(Shuttle et al., 2010a) although it should be more considered as an effective mobility as the two opposite carriers cannot be distinguished by this method. Figure 5.6 presents the effective drift mobility of the three optimised devices measured using charge extraction at short circuit and the methodology explained earlier in the relevant experimental chapter. The y-axis error bars represent the uncertainty of thickness of the active layer and uncertainty of the correction factor $f(\delta)$ on carrier effective mobility, where δ depends on the recombination dynamics. First, it can be noticed that the dependence of the effective mobilities is weakly dependent in carrier concentration. This observation seems to show that traps in the three optimised blends are only weakly affecting the carrier mobility under short-circuit conditions. Although the changes in effective mobility are not major, it can be noticed that an increase in PCBM content leads to an increase in the effective mobility. This observation is consistent with previous reports on the effect of PCBM loading on electron mobility in some polymer:fullerene solar cells.(Cho et al., 2008)

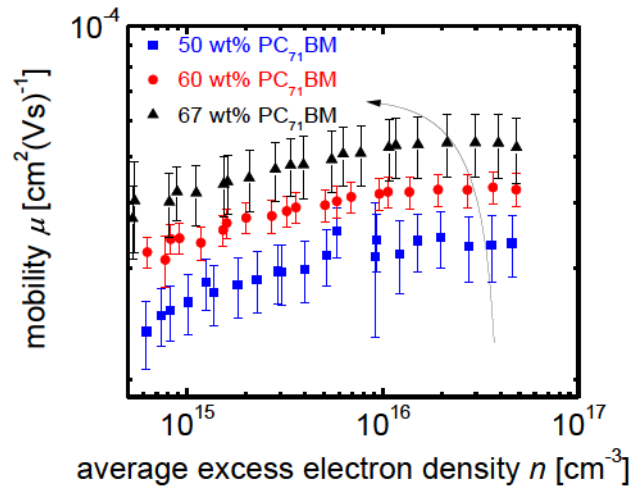


Figure 5.6: Effective mobility measured by charge extraction at short-circuit function of carrier density for the three blend ratios 50, 60 and 67 wt%. The more fullerene, the higher the effective mobility.

5.3.2.3 Mobility-lifetime product

It becomes apparent from the two previous measurements that the higher the fullerene content, the higher the product *mobility* $\times$ *lifetime* in the PBDTTT-

C:PCBM blends, by a combination of both improvement in mobility and carrier lifetime. Figure 5.7 shows the experimental product $\mu \times \tau$ over the range of carrier concentrations common between the measurements of drift mobility and carrier lifetime. It becomes clear from this study that the slight perturbation of the blend ratio resulted in significant change in transport properties and resulted in a change of near one decade in mobility lifetime product. As a result, the drift length $L_{\text{drift}} = \mu\tau \times E/d$ is lower for the 50 % w PC₇₁BM and as the ratio drift length over thickness is function of $1/d^2$, the transport properties of this blend ratio degrades quickly with the active layer thickness as pictured in the continuous decrease of short-circuit current with active layer thickness in Figure 5.2 b) and c). This explains in particular why the 50 wt% blend could not be optimised around its first interference maximum. Indeed, it has been only possible to obtain a reasonably high fill factor at 1 sun illumination for the 50 wt% blend ($61.3\% \pm 0.5$ compared with 64% for 1:1.5 and 60% for 1:2) at the cost of active layer thickness and as a result at the cost of more limited light absorption ($J_{\text{sc}} = 11.4 \text{ mA.cm}^{-2}$ for 50 % w blend while $J_{\text{sc}} = 14.6 \text{ mA.cm}^{-2}$ for the 1:2 blend, while the spectral absorption of the blend is lower than that of 1:1).

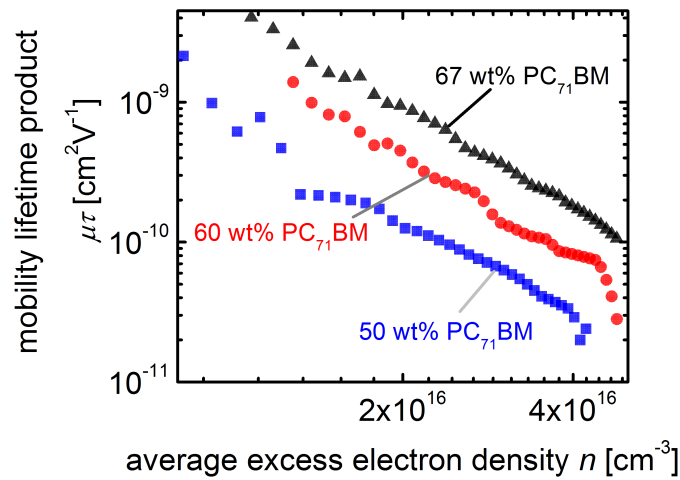


Figure 5.7: Product mobility lifetime for the three blend ratios 50, 60 and 65 wt%. The measured degraded transport properties of the 50 wt% blend explain the overall performance with thickness and why the active layer of the optimised device is lower than the two other blends.

5.4 Results and discussion on the open-circuit voltage and current-density responses

Following the approach developed earlier in the method section, we assume that in these systems, non-geminate recombination, i.e. recombination of initially separated opposite charges, is the major loss process in the fourth quadrant. From the measurements of recombination dynamics, prediction of the open-circuit voltage over a wide range of light intensities was attempted assuming no field dependence of generation according to the equation as detailed in Chapter 3:

$$V_{oc} = \frac{1}{\beta + \gamma} \ln \left(\frac{J_{sc}(1 + \lambda)\tau_{\Delta n_0}}{edn_0} \right) \quad (5.7)$$

Figure 5.8 presents the predictions (open symbols) and the measured open-circuit voltages (solid symbols) for the three optimised blends. The predictions are well within the ± 5 mV margin and confirms a posteriori the validity of the assumptions. To further support the hypothesis that non-geminate recombination only can explain the entire loss of photocurrent in the fourth quadrant for the polymer:fullerene blends under study, charge extraction across the $J - V$ curve with the sweep under short-circuit condition, at different light intensities, has been conducted. Completed with the recombination dynamics, predictions of the current-voltage curves in the fourth quadrant have been calculated with the same sets of assumptions than for the prediction of the open-circuit voltages according to the equation:

$$J = J_{sc} + J_{darkshunt} + J_{nongemloss} \quad (5.8)$$

Figure 5.9 presents the predicted current-voltage responses of the three blends (open symbols) at different light intensities (dark, 25, 50, 100 % sun) and the measured ones in solid lines. The excellent agreements of the predictions of open-circuit voltages and current-voltage responses in the fourth quadrant under different illumination levels confirm that the losses are mostly non-geminate and that the generation in these systems seems to be field independent for all the different blend ratios in this study.

5.5 Further discussion: non Langevin type recombination, effect of fullerene aggregation

We just saw that non-geminate recombination was the dominant recombination process in these polymer:fullerene systems that morphology studies show are sub-

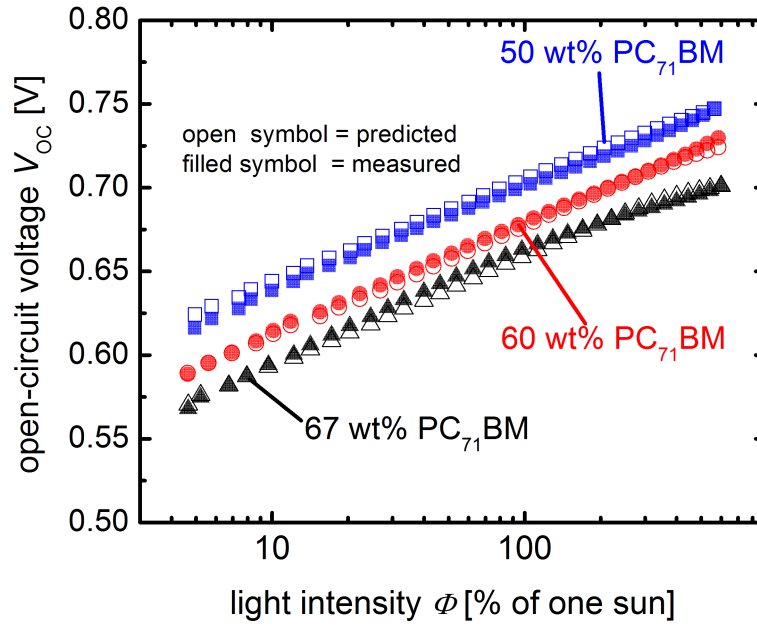


Figure 5.8: Predictions (open symbol) and measured (solid symbol) open-circuit voltage V_{oc} for the three optimised devices. No field-dependent generation and non-geminate recombination as main loss process seem a valid set of assumptions. This does not rule out the presence of geminate recombination in itself. Nevertheless, experimental evidence show that if geminate losses there are, these do not result in field-dependent generation, in other words, these do not explain the loss of photocurrent between short-circuit and open-circuit conditions.

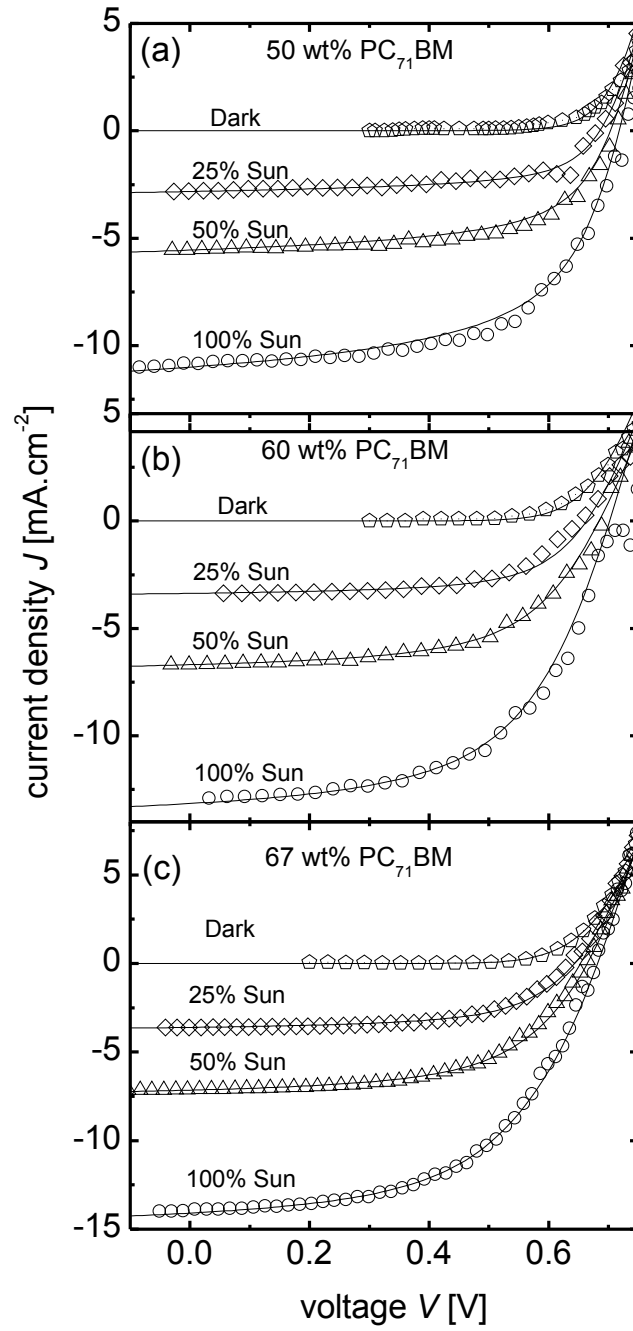


Figure 5.9: Predictions (open symbol) and measured (solid lines) current-voltage response of the three devices in the dark, 25 % 50 % and 100 % sun. Successful prediction of the JV curves in the fourth quadrant confirms non-geminate losses are the main loss process and explain the open-circuit voltage and fill factor of three devices.

stantially amorphous. Understanding the fundamental mechanisms involved in this loss process seems therefore of interest given their impact on device performance, as mentioned in Chapter 4. A common approach for the description of non-geminate losses is using the extreme case of Langevin type of recombination (polarons getting into the coulomb capture radius of each other result in recombination with a probability of 1) where the recombination rate of opposite charge carriers is proportional to their local mobility, according to the following equation, developed in a previous chapter:

$$k_{\text{langevin}} = \frac{q}{\epsilon} \mu \quad (5.9)$$

This principle is very widespread and commonly used to draw design rules for bulk heterojunction solar cells. (Deibel and Dyakonov, 2010) Figure 5.10 shows together the effective carrier mobility measured by charge extraction at short circuit and the recombination rate k_{rec} calculated according to equation 5.1 using open-circuit measurements. First, it can be seen that the mobility μ and recombination rate k_{rec} , do not share the same dependency in carrier concentrations contrary to Shuttle et al. (2010a). This has been already observed by Rauh et al. (2012) in (thieno[3,4-b]thiophene/benzodithiophene) PTB7:PC₇₁ BM. We will see in the next chapter that this is the result of a complex variation of spatial distribution of excess carriers throughout the active layers when those are thin (< 100 nm). However, the most important observation is indeed that the effect of blend perturbation on mobility and recombination rate is completely opposite to what is expected if the fundamental mechanism of annihilation of carriers was of Langevin type. Here, we saw that increasing the fullerene content improved simultaneously the carrier mobility and lifetime. Given the weak dependency in carrier concentration of the effective mobility, it seems that at least close to short-circuit conditions, the traps are not influencing substantially the carrier transport. This is further supported by the values of light ideality factors from open-circuit voltage function of light intensity which are, for most of illumination levels, near 1. This is likely to suggest that the main loss process is rather free to free recombination. As the blends have been shown to be amorphous, it is difficult to access to the change of morphology at the nano scale resulting from the slight change in blend ratio donor/acceptor. Nevertheless, it is well known that fullerenes tend to aggregate. (Veldman et al., 2008) In consequence, the blend should rather be considered as a multi phase system rather than binary system, according to Jamieson et al. (2012). Here based on the measurements of charge extraction and electroluminescence, we suggest that the effect of phase segregation was responsible for the change in recombination

dynamics in these systems, according to the schematics presented in 5.11.

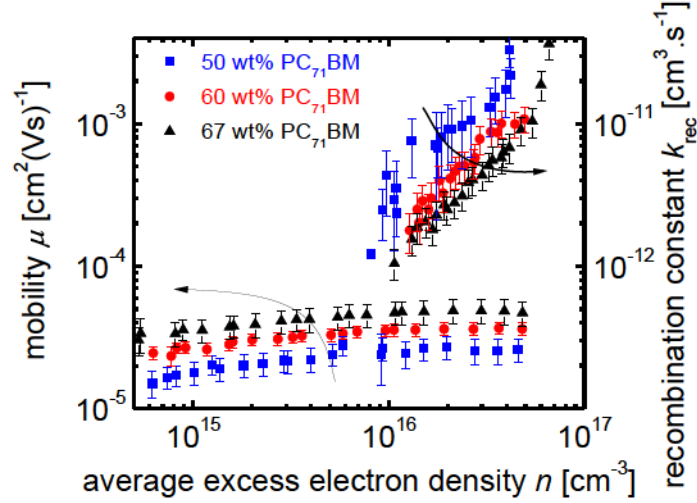


Figure 5.10: Effective drift mobility μ and recombination rate k_{rec} of the three different blend ratios 50, 60 and 65 wt% function of average excess carrier density. The higher the fullerene loading, the higher the effective mobility and the slower the recombination rate. This idea is going against the common understanding of Langevin type recombination.

5.6 Conclusions

Using charge extraction, transient photovoltage and electroluminescence, the effects of a slight perturbation of the blend around the optimal blend ratio of efficient PBDTTT-C:PC₇₁BM devices were investigated. A combination of clear shift in energetics at the heterojunction and charge carrier dynamics upon blend perturbation have been proven to explain the regular difference observed in open-circuit photovoltage. According to successful predictions of open-circuit voltage and current-voltage response at different light intensities, no field dependence generation seems to occur in these systems. Non-geminate recombination has been shown to be the major loss process over the composition range studied herein. In particular, it has been possible in these rather amorphous polymer:fullerene systems to increase simultaneously carrier mobility and lifetime, which is going against the common approach of Langevin type recombination. This puts in a new and different perspective how design rules to address problems of carrier transport in polymer:fullerene solar cells can be formulated. Unfortunately here, simultaneous enhancement of carrier mobility and lifetime seem to be only possible upon

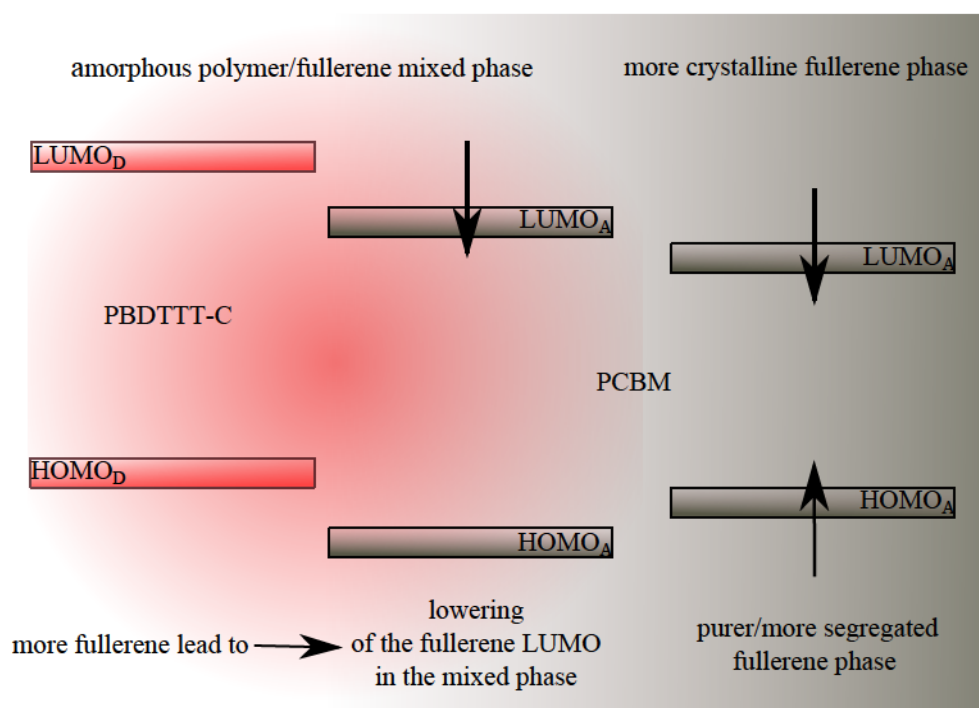


Figure 5.11: Three phases schematics of the blend PBDTTT-C and PC₇₁BM and the effect of the blend ratio perturbation on the energy levels of the fullerenes.

increase in fullerene content and consequently at the cost of blend absorption capacity.

Shifts in spatial distribution of carriers

6.1 Introduction

As we saw in the previous chapter investigating charge transport in PBDTTT-C:PCBM blends, despite the substantial improvements in overall efficiencies of polymer:fullerene solar cells, the electronic properties of the blends with low band gap polymers still hardly ever allow fabrication of efficient devices with absorber thickness much larger than 100 nm due to low mobilities and/or insufficient long charge carrier lifetimes.(Faist et al., 2013; Kirchartz et al., 2012a; Li et al., 2013; Peet et al., 2011) The resulting non-geminate recombination of carriers follows recombination dynamics in the general form: $\frac{dn}{dt} = -k_{\text{rec}}np$ where $k_{\text{rec}} = k_{\text{rec}}(n)$ with n and p the total carrier concentrations and k_{rec} the non-geminate recombination rate. Extensive studies have investigated the recombination rate constant and it has been reported in the early studies on P3HT:PC₆₁BM that the decay dynamics were showing an approximately third order dependence in charge density i.e. $(\frac{dn}{dt} \propto n^3)$. This has been experimentally found for instance using large perturbation techniques such as Transient Absorption Spectroscopy (TAS) and confirmed later with small perturbation measurements like transient photovoltage (TPV).(Clarke et al., 2009; Shuttle et al., 2008c)

The origin of the carrier dependence in recombination rate k_{rec} was shown by modeling to be possible when integrating an exponential tail of trapped states within the band gap.(Nelson, 2003) Within the framework of the multiple-trapping model, both recombination rate and carrier mobility should increase with carrier concentration.(Tanase et al., 2003, 2004; Street et al., 2011; Nelson, 2003; Gill, 1972; Borsenberger et al., 1992) In the past, k_{rec} was reported to show different degrees of carrier density dependence varying with the crystallinity of the P3HT:PCBM blend.(Kim et al., 2006; Ohkita et al., 2008)

Currently, with the development of the techniques and the intense supply in new polymer:fullerene blends, comparative studies between a range of different systems are possible. Empirically, the recombination follows the general power

law dependence in space average density $R = dn/dt \propto \bar{n}^\delta$ where δ is known as the order of the reaction. Recently, investigations using different characterisation techniques observed large variations in these reaction orders, (Shuttle et al., 2008c,b; Mozer et al., 2005a; Leong et al., 2011; Garcia-Belmonte et al., 2010; Fortig et al., 2009; Chen et al., 2011) and intense debate to whether the origin of the recombination process is changing according to these observed changes in reaction order is currently ongoing in the literature. (Rauh et al., 2012; Leong et al., 2011)

The concept of disorder is therefore used to interpret observed mobilities and reaction orders however, normally under the assumption that charge carriers distributions are uniform. Yet, every recombination event is local. Recent device simulation studies have shown that limited device thickness can result in inflated apparent reaction orders as a result of strong spatial variations in charge density at open circuit. (Kirchartz and Nelson, 2012) In this chapter, we build upon this study by showing experimentally that the observed differences in reaction orders between several experimental polymer:fullerene systems can be explained by taking into account their different thicknesses without having to invoke any different recombination mechanisms.

6.2 Theoretical and simulation background

6.2.1 Recombination dynamics assuming $n = p$

If we assume for the moment that recombination of one free carrier with free or trapped charges of opposite polarity dominates recombination in the blend and follows a Langevin type relation, (Kirchartz et al., 2011; Kuik et al., 2011) we would obtain locally for the recombination rate (of for example a free electron and a hole) under forward bias ($V \gg k_B T$):

$$R \propto n_{\text{free}} p_{\text{tot}} = \frac{n_{\text{free}}}{n_{\text{tot}}} n_{\text{tot}} p_{\text{tot}} \propto k_{\text{rec}}^* n_{\text{tot}} p_{\text{tot}} \quad (6.1)$$

Here, n_{free} is the free electron concentration, n_{tot} and p_{tot} are the total electron and hole concentrations and k_{rec}^* is the effective recombination constant accessed experimentally representing recombination within exponential trap states in the sub bandgap. (Monroe, 1985; Nelson, 2003) The effective mobility μ^* of an electron in the same model would be:

$$\mu^* = \frac{n_{\text{free}}}{n_{\text{tot}}} \mu_{n_0} \quad (6.2)$$

where μ_{n_0} is the mobility of free electrons above the mobility edge, which means that the effective mobility of electrons is reduced relative to the mobility of free electrons by the fraction of those electrons that are trapped (note that the term $n_{\text{free}}/n_{\text{tot}}$ appears in both equations just above). Therefore, the effective recombination constant k_{rec}^* is expected to be proportional to the effective mobility μ^* in this model and has also the same dependence on total electron concentration n_{tot} .

Shuttle et al. (2010a) showed that experimental evidence investigating carrier transport dynamics resulted in the non-geminate recombination rate being of Langevin type in poly(3-hexylthiophene): [6,6]-phenyl C₆₁-butyric acid methyl ester P3HT:PC₆₁BM devices indicated the same dependency in carrier concentrations for both recombination rate and drift mobility, as one would expect from a multiple trapping model. (MacKenzie et al., 2011; Rauh et al., 2012) However, more recently Rauh et al. (2012) proposed a similar study with (thieno[3,4-b]thiophene/benzodithiophene(PTB7): [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) in which these two key variables were found to show a different dependence on carrier density at room temperature, with reaction orders substantially higher than two (3.5), similar to what has been presented in the previous chapter.

These experimental observations investigating the reaction order are apparently inconsistent with the multiple trapping model discussed above and might suggest that the fundamental recombination mechanism is different for different devices made from the same polymer:fullerene blend or from one material to another. Since we do not observe $k_{\text{rec}}^*(n_{\text{tot}}) \propto \mu(n_{\text{tot}})$ in some experiments one of our assumptions must be violated.

6.2.2 Net electric field and variation in spatial distribution of carriers

Another interpretation is that Equation 6.1 describes a local model valid at a point x in the device, while the experiment only measures spatially integrated values of n_{tot}^- and p_{tot}^- . Indeed, experimental methods are usually limited to the macroscopic scale, for instance the overall change in optical density (ΔOD) or the spatially averaged charge density using charge extraction technique access to $n_{\text{CE}}^- = \frac{1}{d} \int_0^d n_x dx$. Moreover, when investigating experimentally the recombination dynamics in operating devices, the presence of electrodes with different work functions will necessarily lead to an external field proportional to their difference. In particular, at short circuit, in the dark, the macroscopic field across the active layer of thickness d is proportional to the built-in field $E_{\text{built-in}} = \frac{e(\phi_{\text{anode}} - \phi_{\text{cathode}})}{d}$ and while this external field is absent in film studies, Ohms law requires the carriers within the bulk in a device contacted with different electrodes to respond to $E_{\text{built-in}}$. As the blend

is here assumed to be an intrinsic semiconductor, the distribution of opposite carriers are mirror of each other in the dark. Consequently, while the spatial average of n_{tot}^- and p_{tot}^- are identical (if only excess carriers are counted) they are not identical at any point in the volume of the absorber, (Deibel et al., 2009) but instead are strongly function of the external field and position.

Yet, for recombination to occur, the opposite carriers involved in the recombination process need first to meet. Whatever the operating point of the device under illumination, the probability of non-geminate recombination at the point x in the blend will be first and foremost dependent on the overlap of the distribution of carriers in this precise location. The weaker the external electric field, the more these spatial distribution will overlap. There are different ways of acting on this net field:

- the thickness d of the active layer by spacing the two electrodes at fixed potentials.
- the external applied bias V leading to a net applied electric field:

$$E_{\text{field}} = \frac{(V_{\text{BI}} - V)}{d} \quad (6.3)$$

- the illumination level as the more the bulk is populated, the more the distribution of excess carriers is governed by the photogenerated population and the more the spatial distribution of opposite carrier overlap.

In the early experiments reported with P3HT:PCBM, the devices investigated via TAS and transient photovoltage/charge extraction employed relatively thick active layers ≈ 200 nm. (Shuttle et al., 2010a; Li et al., 2007) On the other hand, many more devices in the literature recently, like the ones based on PTB7, have optimised thicknesses in the range 80-110 nm, usually assigned to inferior properties of carrier transport compared with P3HT. (He et al., 2012b) Moreover, the measurements related to effective mobility are done under short-circuit condition while the measurements of decay dynamics are conducted at open circuit, in other words, at different states of the electric field across the active layer and consequently in different state of overlap of the distribution of carriers.

6.3 Methods

This chapter is a combined modelling and experimental study of the reaction order at different thicknesses.

6.3.1 Simulations of spatial distributions of carriers

The simulations of the spatial distribution of carriers were performed using the drift-diffusion based modelling as explained in Chapter 3 using ASA. Based on the experimental data relative to the control devices (60 nm thick PTB7 and 85 nm thick P3HT devices) presented in what follows, a representative set of parameters were found to simulate via ASA the thickness behaviour of PTB7 and P3HT based solar cells. The influence of active layer thickness on the apparent reaction rate k_{rec}^* is then crosschecked between simulations and experiments.

6.3.2 Device fabrication

The devices used in the experiment are PTB7:PC₇₁BM and P3HT:PC₆₁BM, as detailed in Chapter 4. In particular, the protocol for device preparation is as follows. PTB7 based solar cells were designed in conventional architecture ITO/PEDOT:PSS/PTB7:PC₇₁BM/Ca/Al. ITO on glass substrates were all pre cleaned with isopropanol and acetone and plasma treated during 7 min at 2.5 mbar. The solution was prepared in 1:1.25 wt% blend ratio in chlorobenzene (CB) with 3 vol% of 1,8-Diiodooctane (DIO) leading to a final concentration of 25 mg/mL. The solution was kept under stirrer at 80°C overnight. The films were made by spin casting the solution on preheated substrate at 80°C. Likewise, P3HT based solar cells were prepared in conventional architecture ITO/PEDOT:PSS/P3HT:PC₆₁BM/Ca/Al. The solution was prepared in 1:1 blend ratio in CB at the concentration of 30 mg/mL. The solution was kept stirring overnight at 60°C. The P3HT based films were made by blade coating. In both systems, the cathodes were deposited by evaporation to obtain Ca and Al whose thicknesses were assessed to be 25 nm and 150 nm respectively. Each pixel area was 4.5 mm². For the series based on PTB7 blends, the devices originate from the same solution and the same run of cathode evaporation, to be in a position where any effect on the interfaces active layer/electrodes can be neglected. The overall performances of the devices used in this study are presented in the Table 6.1.

6.3.3 Experimental determination of reaction order

The recombination dynamics were studied using charge extraction and transient photovoltage as explained in Chapter 3.

Table 6.1: Overall performance of the two thickness series of PTB7:PC₇₁BM and P3HT:PC₆₁BM

Material donor/acceptor	Thickness [nm]	V_{oc} [mV]	J_{sc} [mA.cm ⁻²]	FF [%]	PCE [%]
PTB7:PC ₇₁ BM	60±5	635±5	11.8±0.1	58±1	4.3±0.1
PTB7:PC ₇₁ BM	90±10	625±5	13.2±0.1	51±1	4.2±0.1
PTB7:PC ₇₁ BM	130±10	631±5	13.4±0.1	50±1	4.1±0.1
P3HT:PC ₆₁ BM	85±8	574±5	13.1±0.1	56±1	1.9±0.1

6.4 Results and discussion on the simulations of spatial distributions

In order to verify that the spatial gradient of charge carriers is responsible for the observed high reaction orders and the discrepancy between $k_{rec}^*(n_{tot})$ and $\mu^*(n_{tot})$ observed, 1D device simulations were conducted. These simulations are based on a drift diffusion model where recombination via tail states has been considered alongside direct band to band recombination to maintain the generality of the results to different recombination types. The device simulation based on Advanced Semiconductor Analysis (ASA) has been previously used in Kirchartz and Nelson (2012); Kirchartz et al. (2011); Schäfer et al. (2011). More details about the modeling including the tables of parameters can be found in Appendix B1-B2. Figure 6.1 presents the simulated spatial distribution of excess carriers (compared with short circuit in the dark condition) at open circuit, similarly to what Kirchartz and Nelson (2012) published previously with the addition of short circuit condition for two different thickness of the active layer 50 nm and 150 nm. First we can compare the excess electron and hole concentrations at open circuit for the two thicknesses. The built-in voltage V_{BI} is the change of the electrostatic potential over the absorber layer, which is defined by the difference of work functions of the two electrodes while the open-circuit voltage V_{oc} represents the splitting of the quasi-Fermi levels measured at the contacts and is therefore light dependent, i.e. the difference of electrochemical potential over the absorber layer. Thus, for a wide range of light intensities V_{BI} is larger than V_{oc} and the bands are never completely flat. In this case, the excess carriers are created by a combination of both optical absorption and injection at the contacts and the lower the illumination level, the more the injected carriers will dominate the population of excess carriers within the active layer. Figure 6.1a shows that for a rather low thickness of

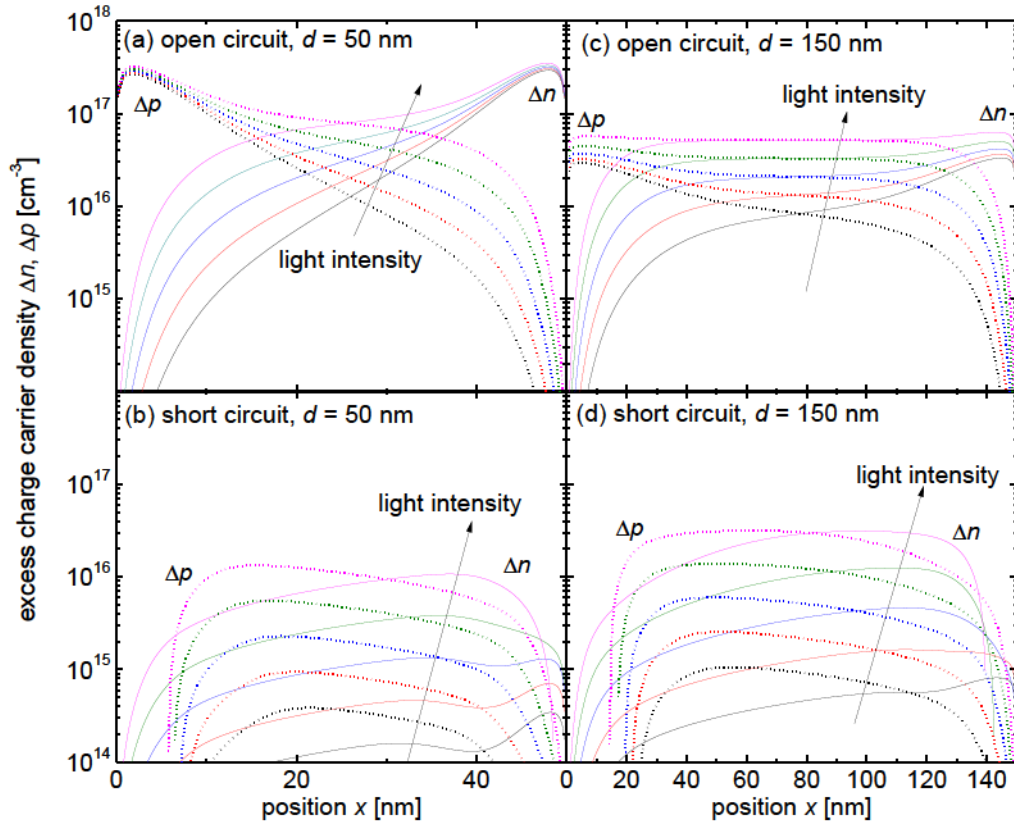


Figure 6.1: Simulations using Advanced Semiconductor Analysis (ASA) of spatial distributions of excess electrons (solid lines) and holes (dashed lines) at open circuit (top graphs a) and c)) and short circuit (bottom graphs b) and d)) for 50 nm thick (left) and 150 nm thick (right) devices. The position of the anode corresponds to $x=0$.

50 nm, the excess carrier profiles at open-circuit are rather steep and the increase in concentration vs. voltage is strongly position dependent. The excess hole concentration for instance increases strongly with voltage at the cathode, i.e. where the hole concentration is very low, and will be weakly voltage dependent close to the anode. The integral hole concentration will not change much with voltage at least for low light intensities and open-circuit voltages because the large increase close to the cathode will hardly contribute to the integral. At higher light intensities, the open-circuit voltage will approach the built-in voltage and the excess carrier concentrations will be more homogeneous and the average excess carrier concentrations will increase with voltage more strongly.

In essence, the large spatial gradient leads to a situation where the measured average excess carrier density $\Delta\bar{n} \approx \frac{1}{d} \int_0^d n_{\text{tot}}(x) dx$ over the thickness of the active layer d , increases with illumination (differently said open-circuit voltages) only very slowly. Since the recombination rate is usually expressed as:

$$R = k_{\text{rec}}^* \times (np - n_0p_0) \quad (6.4)$$

in forward bias and given it is commonly assumed that $n = p$ within the active layer as well as the photogenerated population of carriers (mostly trapped) is largely superior to the one at equilibrium (which is usually similar to implying the material is not doped), the effective recombination constant k_{rec}^* needs to increase quite steeply with $\Delta\bar{n}$ to obtain the observed exponential voltage dependence of the recombination rate. Therefore, the steep gradients in Δn directly cause large apparent reaction orders as has been predicted in previous simulations. (Kirchartz and Nelson, 2012) Figure 6.1c shows the excess electron and hole concentrations for a device with an active layer of 150 nm thickness. Here, the spatial gradients of electron and hole concentrations are substantially less steep relative to the 50 nm thick device. Thus, the situation at 150 nm thickness will much more resemble the zero-dimensional model discussed in the context of Equations 6.1 and 6.4 and the reaction orders will be more consistent with the charge density dependence of mobility. Figures 6.1 b) and d) show the dependence of excess electron and hole density at short circuit for the same two thicknesses (50 nm and 150 nm). In this case, the spatial distribution of charges is controlled by absorption rather than injection from the contacts. Since the optical generation rates are not strong functions of position in these thin films (compared to the charge carrier gradients simulated for open-circuit), the thickness will not have a strong influence on the result and a zero-dimensional model will result in a good agreement with the one-dimensional simulation. The calculated profiles of optical absorption across

the active layer thickness at 50 nm and 150 nm thick devices are presented in Figure 6.2. Finally, we note that the measurements of mobility are done at short-circuit condition while the carrier lifetimes are usually measured at open-circuit. This crucial observation might result in a fundamentally different way the observed mobility will scale with carrier concentration compared with the apparent recombination rate. Moreover, one change in the dependence on carrier concentration between mobility and recombination rate would not necessarily hint to a change in recombination mechanism.

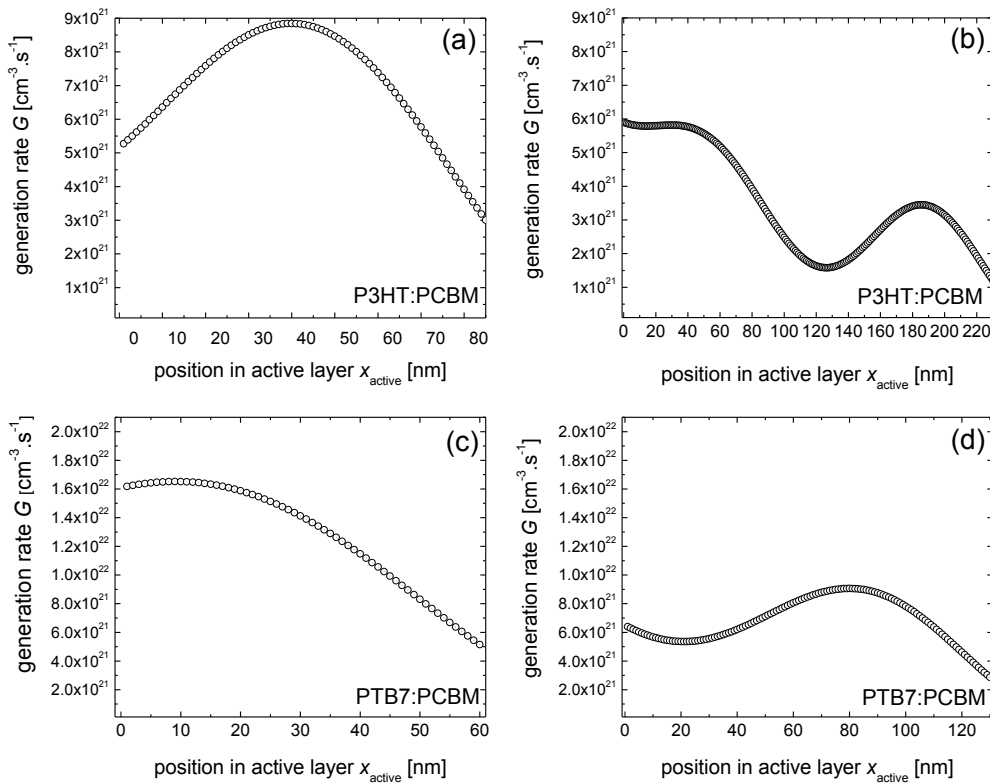


Figure 6.2: Calculated profiles of optical absorption function of position within the active layer based on published refractive index $\tilde{n}$ and extinction coefficients $\tilde{k}$ for P3HT:PC₆₁BM at 85 nm a), 230 nm thick b) and PTB7:PC₇₁BM at 60 nm c) and 130 nm thick d). Although the generation profiles are not constant throughout the entire active layer due to interference effects at multiple wavelengths, these are not as strong function of position as the charge carrier gradients found in simulations at open-circuit condition.

6.5 Results and discussions on the experimental determination of the recombination dynamics

To further investigate the effect of thickness on the dependence in charge density of k_{rec}^* and μ^* as well as to confirm the trends observed in the simulations, several thickness studies of devices based on PTB7:PC₇₁BM and P3HT:PC₆₁BM have been conducted using charge extraction and transient photovoltage measurements.

The range of thickness for the PTB7 series was limited by the number of devices whose measurements of charge densities using charge extraction method using 0V sweep out could lead to accurate values; in other words, whose collection efficiencies are still adequate. Following the approach used in the past, (Shuttle et al., 2008b, 2010a) predictions of the open-circuit voltage V_{oc} for a long range of light intensities assuming no field dependence generation has been calculated for the devices used herein. The accurate predictions of V_{oc} are well within ± 5 mV for a wide range of light intensities and confirm that for all the devices used in this study, non-geminate recombination thus governs the loss of photocurrent in the fourth quadrant (see Figure 6.3). Figure 6.4 a) shows the dependence in excess carrier density of the non-geminate recombination rate k_{rec}^* calculated from the measurements of Δn using charge extraction (after correction of geometric capacitance and incurred charge carrier losses occurring during sweep out) (Shuttle et al., 2008a) and carrier lifetime measured by transient photovoltage, according to the empirical relations used previously 5.1-5. The dashed lines represent the recombination rate calculated from the monoexponential fits of excess carrier density $\Delta n(V_{\text{oc}})$ and carrier lifetimes $\tau_{\text{TPV}}(V_{\text{oc}})$ while the dots represent the recombination rate obtained from direct calculation via $1/(\Delta n \times \tau_n)$ and the effective drift mobility (open symbols) of PTB7:PC₇₁BM systems at three different thicknesses, namely 60, 90 and 130 nm. Similar to the results presented by Rauh et al. (2012) for PTB7:PC₇₁BM and Hawks et al. (2013) for PBDTTT-C:PC₇₁BM, the carrier dependence of drift mobility μ^* and recombination rate k_{rec}^* show a clear discrepancy for thicknesses around 100 nm. However, the thicker the active layer, the less steep k_{rec}^* becomes. This observation is consistent with what was developed in the previous subsection.

An intentionally suboptimal thin P3HT:PC₆₁BM device, measured to be 85 ± 5 nm thick, was fabricated. Figure 6.4 c) shows both the data published previously using a 230 nm thick device for reference (in triangles) and the results obtained for the 85 nm thick device (in circles). It becomes clear that although the thick P3HT device presents a similar dependency in excess carrier concentration for both k_{rec}^* and μ^* , the former is still strongly thickness dependent just like in the case ob-

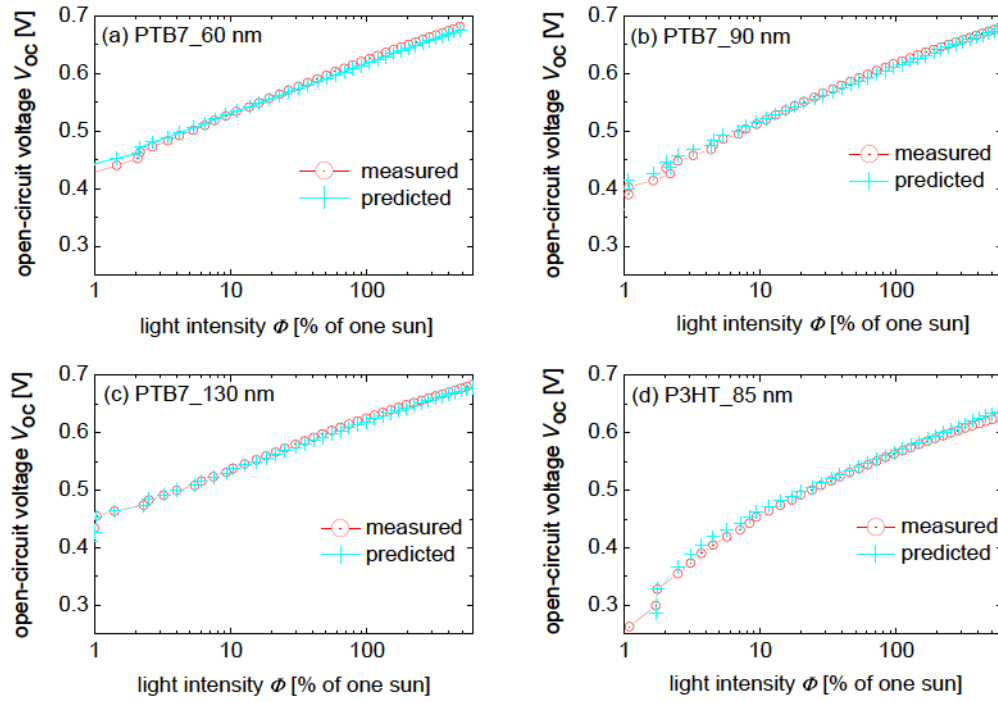


Figure 6.3: Predictions (open circles) and measured (crosses) open-circuit voltage at different background illumination levels for PTB7:PC₇₁BM thickness series at (a) 60 nm, (b) 90 nm and (c) 130 nm as well as (d) thin P3HT:PC₆₁BM device 85 nm thick. Accurate predictions of the open-circuit voltage assuming no field dependent generation in the fourth quadrant confirms non-geminate recombination only can explain the loss of photocurrent in the fourth quadrant. If there are geminate recombination events, these are not voltage dependent and are not therefore responsible for a loss of photocurrent between short-circuit and open-circuit conditions.

served in the PTB7:PC₇₁BM series. This threshold, beyond which the mobility and the apparent recombination rate do not share the same dependency in carrier density highlights indirectly when the distribution of carriers varies within the bulk. For the simulations, we used parameters representing the thin P3HT:PCBM device which is the only P3HT based device fabricated for this study. To make sure we were consistent, the thickness was then increased for the active layer and everything else was kept constant. The outcome of the simulations is reproducing what was expected from the recombination rate.

The simulated mobility of the thick device is lower than the published one by Shuttle et al. (2010a), but this should not be that surprising given:

- unlike the PTB7 experiment, these P3HT devices are from two different batches.
- vertical segregation in P3HT:PCBM has been covered in the literature (see for instance Kim et al. (2005); Xu et al. (2009)) and makes the choice of parameters very thickness specific, especially between 85 nm and 230 nm films.

Consequently, observing lower mobility for the thicker device, which is assumed to be fully depleted and unchanged at all in morphology, is then not necessarily contradicting anything as the two thicknesses of P3HT:PCBM are different in many ways.

Moreover, it can be noticed that these observations were obtained for two different systems with different blend morphology, (Li et al., 2007, 2005; Hammond et al., 2011; Erb et al., 2005) as well as for another system with intermediate crystallinity PCDTBT:PC₇₁BM whose results can be found in Figure 6.5.

6.6 Further discussion: high reaction orders

It becomes clear from experimental and modeling observations on the thickness series of PTB7:PC₇₁BM that the apparent reaction order increases to values substantially greater than 2 for thin devices, as for instance summarised and depicted in Figure 6.6. However, it is extremely unlikely that the predominant loss process involves more than two carriers. Furthermore, while the reaction order decreases with increasing thickness, the light ideality factors, as presented below in Figure 6.7, are within the same range, constantly larger than 1 and do not noticeably change when increasing the thickness of the active layer. According to what has been explained earlier in Chapter 4, this supports the idea that within the range of thickness [60; 130] nm of absorber thickness, the main mechanism

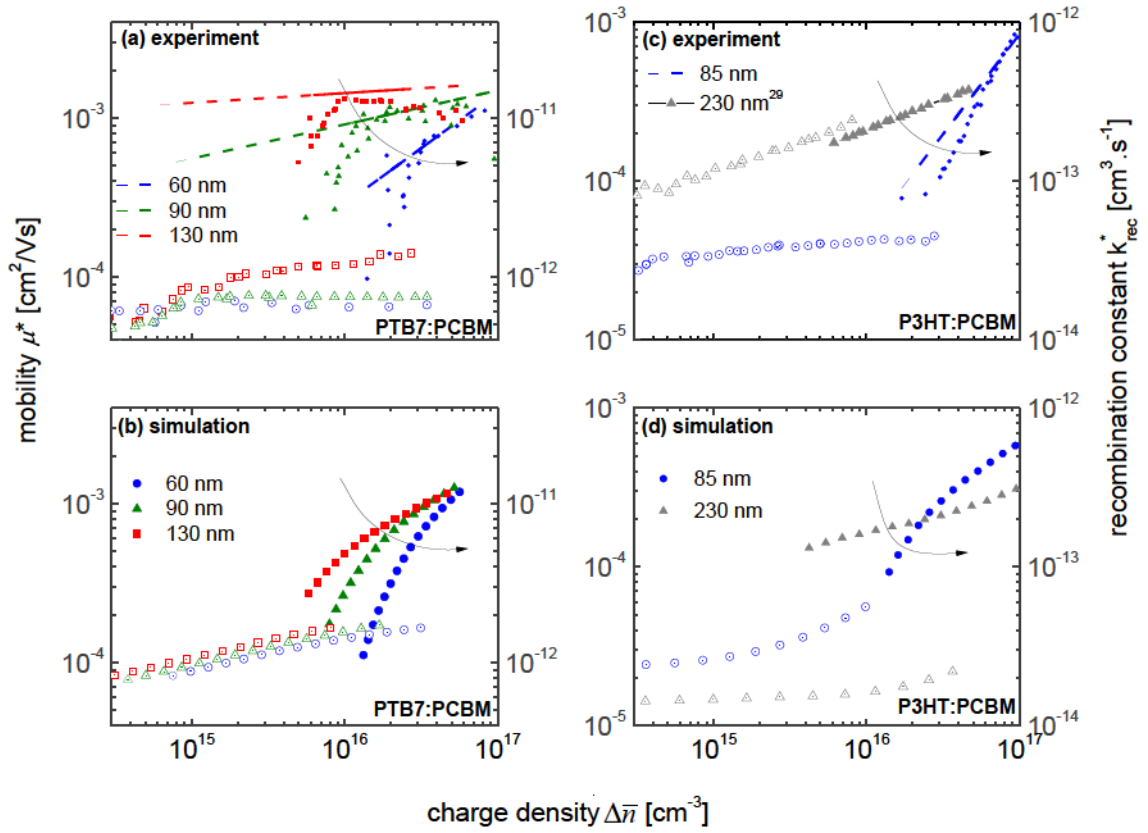


Figure 6.4: Effective mobility μ^* (left axis, open symbols) and non-geminate recombination rate k_{rec}^* (right axis, solid symbols) function of space averaged excess carrier concentration $\Delta \bar{n}$ for PTB7:PC₇₁BM thickness series (60, 90 and 130 nm, left graphs) and P3HT:PC₆₁BM device (85 nm, right graphs). Data obtained through experimental measurements are shown in (a) and (c) and the simulated ones are in (b) and (d). Data previously published on thick (230nm) P3HT device has been added in c) for comparison. In both systems, a substantial change in how k_{rec}^* (measured at open-circuit) scales with spatially averaged excess carrier concentration is observed with increasing thickness, while the mobility is affected to a much lesser extent. The reaction orders are much superior to 2 in thin devices as consequence of the more heterogeneous spatial distribution of carriers within the active layer compared with thicker layers as presented in Figure 6.4.

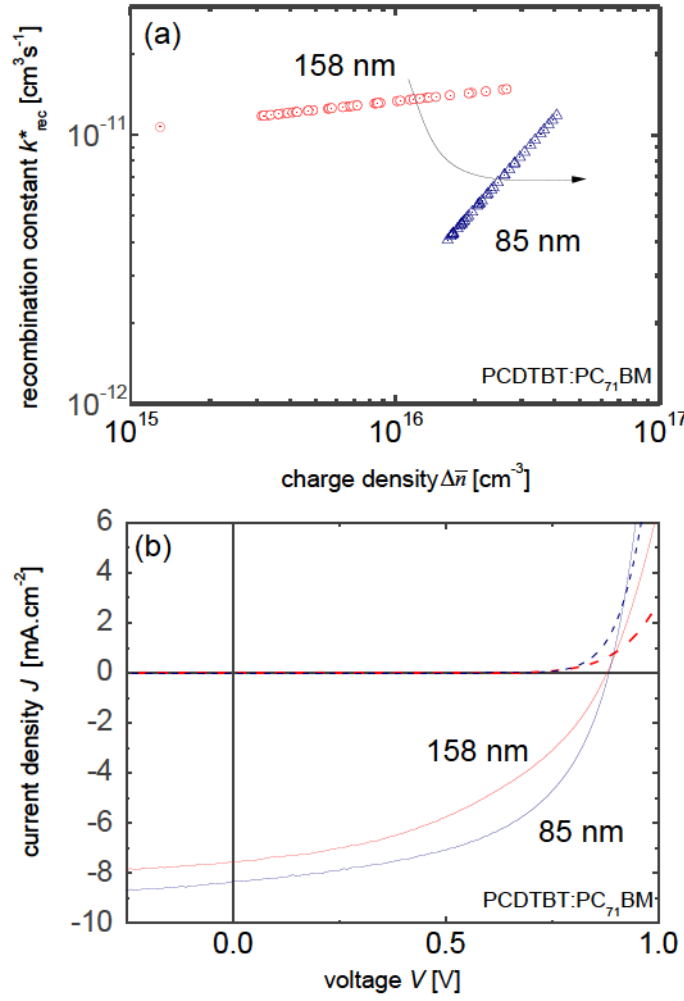


Figure 6.5: Non-geminate recombination rate k_{rec}^* calculated from charge extraction and transient photovoltage measurements as a function of space averaged excess carrier concentration $\Delta\bar{n}$ for PCDTBT:PC₇₁BM thickness series at 85 nm and 158 nm thick. With a blend of intermediate crystallinity between PTB7:PC₇₁BM and P3HT:PC₆₁BM, the same trend is observed experimentally on the effect of device thickness on the dependence in excess carrier density.

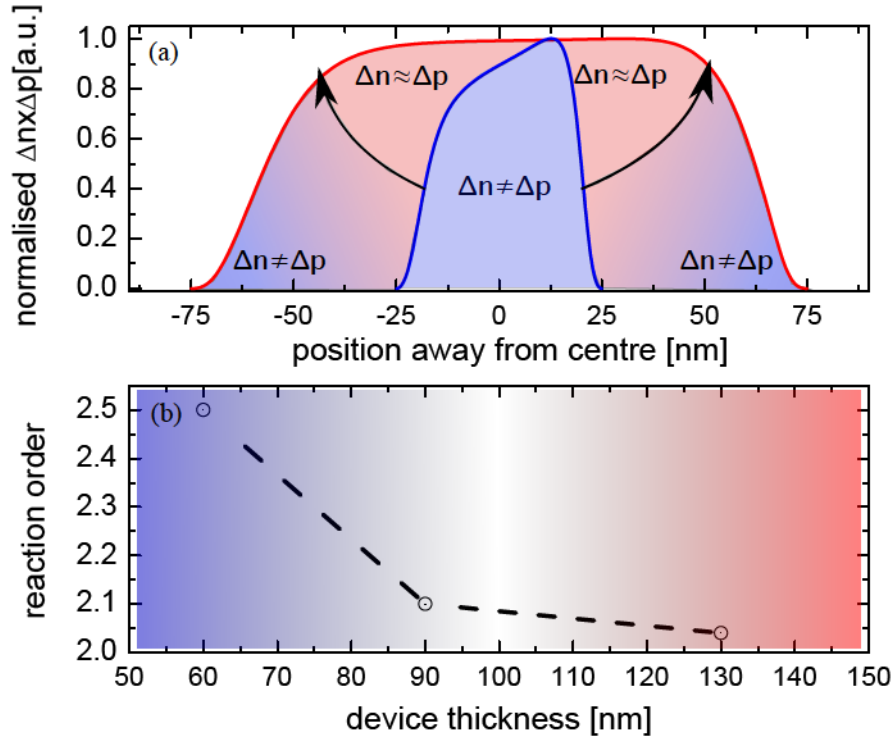


Figure 6.6: a) Simulated excess carrier density product $\Delta n \times \Delta p$ function of position with origin in the centre of the active layer for a thin 50 nm and thick 150 nm active layers. b) Experimental reaction order for the three different thickness of PTB7:PCBM. While for 150 nm thick devices, the simulated profile of opposite excess carrier densities have similar values for approximately 100 nm within the bulk, the assumption $n = p$ cannot be verified for thin active layer (here 50 nm) almost at any point within the active layer. As a result, the measured reaction orders for PTB7:PCBM devices starts high to decrease monotonically towards 2 the thicker the active layer becomes over the range 60-130 nm.

of non-geminate recombination has probably not changed in nature, contrary to what the apparent reaction order would suggest.

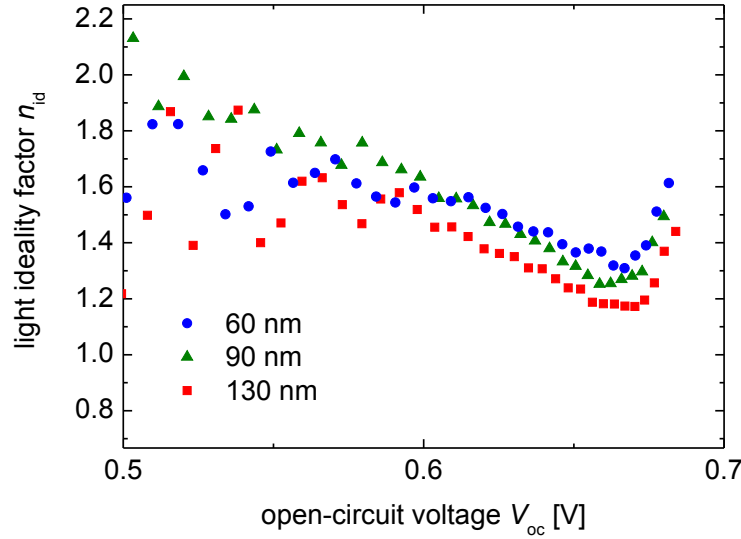


Figure 6.7: Light ideality factors function of illumination measured at room temperature of PTB7:PC₇₁BM devices at 60 nm, 90 nm and 130 nm thick. While the apparent reaction order is strongly dependent on the device thickness, the ideality factors stay within the same range confirming that the predominant non-geminate recombination mechanism has probably not changed over the range of thickness studied.

Ideally measurements of thick devices would be recommended to experimentally access the "bulk" reaction rate. Previous simulations predict a saturation of the reaction order at around 150 nm. (Kirchartz and Nelson, 2012) However, due to low mobility-lifetime products, charge extraction under short-circuit might be inefficient for thicker devices leading to an underestimation of the total excess carrier densities, or Bias Amplified Charge Extraction (BACE) mentioned in Chapter 4 is needed. Furthermore, unintentional doping might lead to small space charge region width even for thicker devices which would then also lead to high apparent reaction orders, which are not correlated to the recombination mechanism. Alternatively, the simulations show that higher overlaps of the spatial distributions of carriers are achievable even for relatively thin devices if measurements are done under higher illuminations. The challenge here would be to make sure these high illumination levels would still be representative of operating conditions. Overall, when the thickness or the doping concentration are a barrier to obtain meaningful insight into the exact recombination mechanism, the study of

the ideality factor derived from illumination dependent open-circuit voltage measurements would be a relevant alternative indicator of the recombination mechanism.(Kirchartz et al., 2013)

6.7 Conclusions

In conclusion, the hypothesis that at any point in the bulk heterojunction blend, the spatial gradients in holes and electrons can be neglected, has been often implicitly assumed in the studies of recombination dynamics. I have demonstrated here using modeling and experimental studies on blends of different crystallinity that the active layer thickness is a key determinant of the spatial distribution of carriers within the active layer and confirmed the predictions from recent simulations regarding the reaction order. This spatial distribution of carriers varies for thin devices where the assumption neglecting the spatial gradients in carriers breaks down, in particular at open-circuit condition. This in turn will have a fundamental impact on the way the recombination rate and carrier mobility will correlate with carrier concentration and is therefore crucial to be considered while attempting to identify the fundamental mechanism behind non-geminate recombination by studying the reaction orders or by applying the Langevin theory to carrier recombination. Since these shifts in the overlap of carriers spatial distributions are governed by the active layer thickness and the electrodes, it is valid for all the bulk heterojunction solar cells. This consequently cannot be ignored when trying to establish some general rules for improving charge transport in organic solar cells.

Unintentional doping in polymer:fullerene solar cells

7.1 Introduction

There is currently extensive research on the design and synthesis of low band gap semiconducting polymers to enhance the efficiency of such solar cells,(Luber and Buriak, 2013) and many families of polymers and synthesis routes are currently being explored.(Danieli et al., 1986; Heck, 2004; Miyaura and Suzuki, 1995; Sonogashira et al., 1975; Stille, 1986; Tieke et al., 2010) In this chapter, we focus upon one polymer design parameter which has received relatively little attention in such research to date, namely the impact of chemical doping. Doping is widely employed as one of the key design parameters in inorganic semiconductors to control the device electrostatics and carrier densities such that a desired functionality is achieved; it is for example used to generate the electric fields which separate photogenerated charges in p-n junction diodes used for inorganic photovoltaic devices.(Landsberg, 1991; Street, 1991)

In contrast, in solution processed organic solar cells, the built-in electric field is typically generated by appropriate contact materials like a low workfunction metal and a TCO or organic hole conductor. These electric fields drive photogenerated charges to the required device electrodes, with the initial charge separation being primarily a molecular process driven by a difference in the electronic energy levels of the donor and acceptor components of the photoactive layer. Molecular doping has been employed in such devices to enhance the performance of electron and hole collection layers and is generally perceived as beneficial.(Frohne et al., 2002; Lüssem et al., 2013; Nicht et al., 2014; Siebert-Henze et al., 2014)

However doping in the photoactive layer of OSCs has received relatively little attention to date. Such doping is nearly always unintentional,(Dicker et al., 2004; Ferguson et al., 2011; Gregg, 2009; Liang et al., 2009b; Liao et al., 2008; Meijer et al., 2003; Morfa et al., 2011; Mozer et al., 2005b) but has been shown to have a potentially large influence on the distribution of electric fields in the device by

Trukhanov et al. (2011); Kirchartz and Nelson (2012). Understanding how device performance, and in particular charge carrier transport and recombination dynamics, respond to changes in electric field distribution resulting from inadvertent photoactive layer doping is therefore a key consideration, both with regard to the synthetic and purification strategies employed to control such doping levels, and its impact on the choice of device architecture for optimum solar cell performance.

7.2 Background theory: depletion zone and charge collection in organic solar cells

In most models of organic solar cells, (Barker et al., 2003; Cuiffi et al., 2010; Hausermann et al., 2009; Kirchartz et al., 2008b; Koster et al., 2005a; Kotlarski et al., 2008; Lalic and Inganas, 2005; Marsh et al., 2007; Martin et al., 2007; Mottaghian et al., 2013; Shuttle et al., 2008c) the photoactive layer acceptor/donor blend sandwiched between two electrodes is considered as an intrinsic semiconductor. Contacting for instance a p-type semiconductor with a low workfunction contact, will lead to band bending and the formation of a space charge region. To illustrate the influence of doping on the electric field distribution in a device, we calculated band diagrams (at 0V applied bias in the dark) for a situation with low and high doping as shown in Figure 7.1, employing the Advanced Semiconductor Analysis (ASA) modeling detailed in the previous chapters. Figure 7.1 a) shows the case of a low p-type doping density ($1.5 \times 10^{16} \text{ cm}^{-3}$) leading, in this example of an active layer of 150 nm, to a relatively homogeneous electric field as a function of position in the active layer. In the case of a higher p-type doping concentration ($7 \times 10^{16} \text{ cm}^{-3}$), Figure 7.1 b) shows that the electric field is distributed such that it is high close to the cathode and much lower further away from the electrode. This is due to the width of the space charge region w :

$$w = \sqrt{\frac{2\epsilon_0\epsilon_r(V_{\text{BI}} - V)}{qN_A}} \quad (7.1)$$

which is much lower than the active layer thickness. Here $\epsilon_r\epsilon_0$ is the total permittivity of the active material, q the elementary charge, V_{BI} the built-in potential, V the applied voltage across the two electrodes and N_A the apparent doping density.

For the thick, 150 nm device, Figure 7.1b shows that while in the range $x \in [90;150]$ nm (i.e within the space charge layer according to equation 7.1 the steep bands at short circuit allow efficient carrier collection, the range $x \in [0;90]$ nm has

rather flat bands and low electric fields. Here the minority carriers (electrons) have to diffuse to the edge of the space charge region at $x = 90$ nm, while in presence of a large concentration of holes. In contrast, if the doping is such that width of the space charge region is comparable to the active layer thickness, the absorber will be fully depleted with or without that doping concentration and thus, the influence of the doping on the electric field is low as shown in Figure 7.1 a).

Simulations of band diagrams highlight a threshold of doping level reasonably accessible beyond which the active layer is partially depleted at thicknesses used for standard device fabrication and are consistent with previous modelling work. (Trukhanov et al., 2011; Kirchartz and Nelson, 2012) Substantial experimental evidence for the impact of inherent doping level on the optimization of carrier transport and analysis is still scarce in the current literature. This chapter is attempting to address this for one organic semiconductor system.

7.3 Methods

Even without the use of extra molecular dopants, the level of unintentional doping in typical efficient polymer batches can vary over an order of magnitude or more and have a large impact on fundamental optoelectronic properties of the device. These include the optimisation of transport and the typical analysis of non-geminate recombination. These points are discussed in the following paragraphs.

To attempt to study specifically the effect of doping on polymer:fullerene devices, while keeping everything else equal as far as possible, an efficient donor DPP-TT-T (Poly[[2,5-bis(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-alt-[[2,2'-(2,5-thiophene)bis-thieno[3,2-b]thiophen]-5,5'-diyl]]) was used. DPP-TT-T is a redshifted polymer (see the UV-Vis shown in Figure 7.6a) synthesised by microwave Stille coupling according to the recipe in Bronstein et al. (2011). When blended with [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM), high performance devices can be obtained, (Meager et al., 2013) as detailed previously in Chapter 4.

7.3.1 Mott-Schottky analysis of material doping

It appeared from preliminary research that depending on the purification process of the donor polymer, large variations in unintentional doping can be measured from batch to batch, while this doping was completely unintentional. The same group showed already the impact that a change in purification process could have

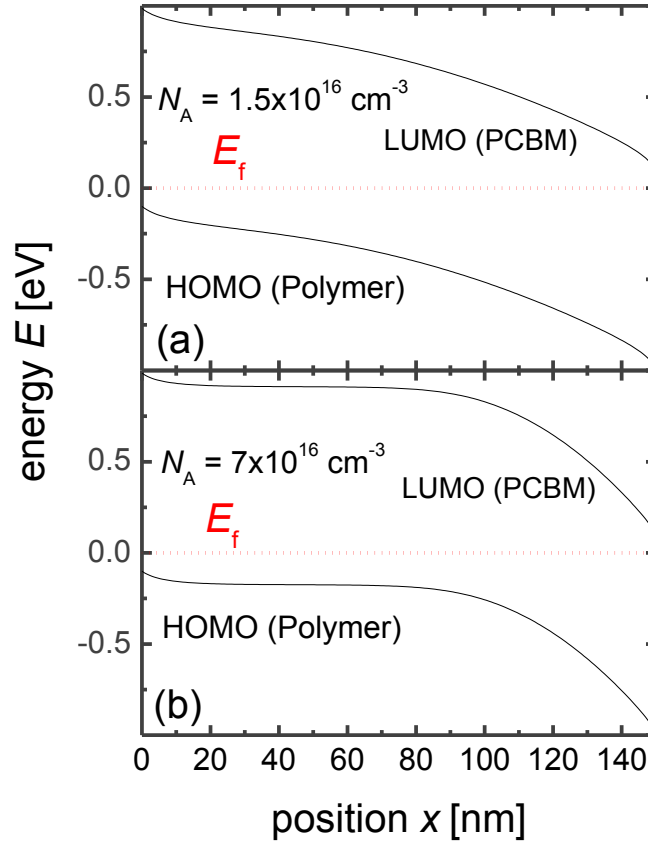


Figure 7.1: Band diagram using ASA modeling in the dark at short circuit for a 150 nm thick device (the anode is at the position $x=0$) at two doping levels: $1.5 \times 10^{16} \text{ cm}^{-3}$ (a) and $7 \times 10^{16} \text{ cm}^{-3}$ (b). The undoped device is fully depleted at 150 nm; a strong electric field across the entire active layer at short circuit allows a sufficient charge collection. However, for the same thickness, the change of doping level to $7 \times 10^{16} \text{ cm}^{-3}$ creates only a partial depletion of the active layer. The carriers can only drift within the space charge layer while in the quasi-flat band region, only a very weak electric field exists and carrier can only diffuse.

on device performance. (Ashraf et al., 2013) While the origin of the doping species here in this study is not certain, the doping levels were stable and stayed within 13% over one month. This was an unique opportunity to study the effect of doping while keeping the molecular content of the active layer constant. Figure 7.2 a) shows the measurements of capacitance at 1 kHz at different voltage bias V performed by Michelle S. Vezie and Prof. Dr. Thomas Kirchartz. The capacitance is varying by the change in space charge layer w controlled by the applied bias following the relation $C = \epsilon_0 \epsilon_r A / w$. Nevertheless, the space charge layer w is linked to the apparent doping level N_A by the Equation 7.1 above. Consequently, the level of doping can be deduced from the gradient of C^{-2} function of applied bias V according to:

$$C^{-2} = \frac{2(V_{BI} - V)}{q \epsilon_0 \epsilon_r A^2 N_A} \quad (7.2)$$

and presented in Figure 7.2 b). The reason why C^{-2} is plotted as a function of V_{dc} here is to highlight where the function is approximately linear as expected from Equation 7.2. At low and high applied biases (and consequently very high and low w respectively), the C-V plot is not dominated by the space charge region capacitance anymore. The use of Mott-Schottky does not assume that N_A is constant and the plot only shows the N_A obtained at every particular applied voltage, at the distance x to the junction. Furthermore, many artifacts can influence the profile obtained, as for example, when the trap densities are significant. As a result, the profile here should be used to obtain assessment of the differences in doping levels between different polymer:fullerene films instead of as a way to obtain the actual profile of doping through typical organic solar cells films.

In this study, the device fabrication process was strictly identical from one batch to the other and particular attention has been paid to evaporate the electrodes in the same run. This would enable ruling out major shifts in energetic barriers at the interface active layer electrodes which were unnecessary if not misleading in our present study. Furthermore, storage was also identical for both series of devices. According to Kirchartz et al. (2012b), the doping level N_A has been measured on devices whose active layer are not too thin (≥ 150 nm). The resulting apparent doping levels of the devices from the two batches made from different purification processes are ranging from $\approx 1.5 \times 10^{16}$ in open-triangles (labeled in what follows DPP-TT-T^u) to $\approx 7 - 9 \times 10^{16} \text{ cm}^{-3}$ in open squares (labeled in what follows DPP-TT-T^d). DPP-TT-T^d (has an average molecular weight in number: $M_n = 11$ kDa, in weight $M_w = 69$ kDa and a polydispersity index $PDI = M_w/M_n = 6.2$) and DPP-TT-T^u ($M_n = 24$ kDa, $M_w = 89$ kDa and $PDI = 3.7$). Previous work on π -conjugated polymers reported apparent doping levels ranging from

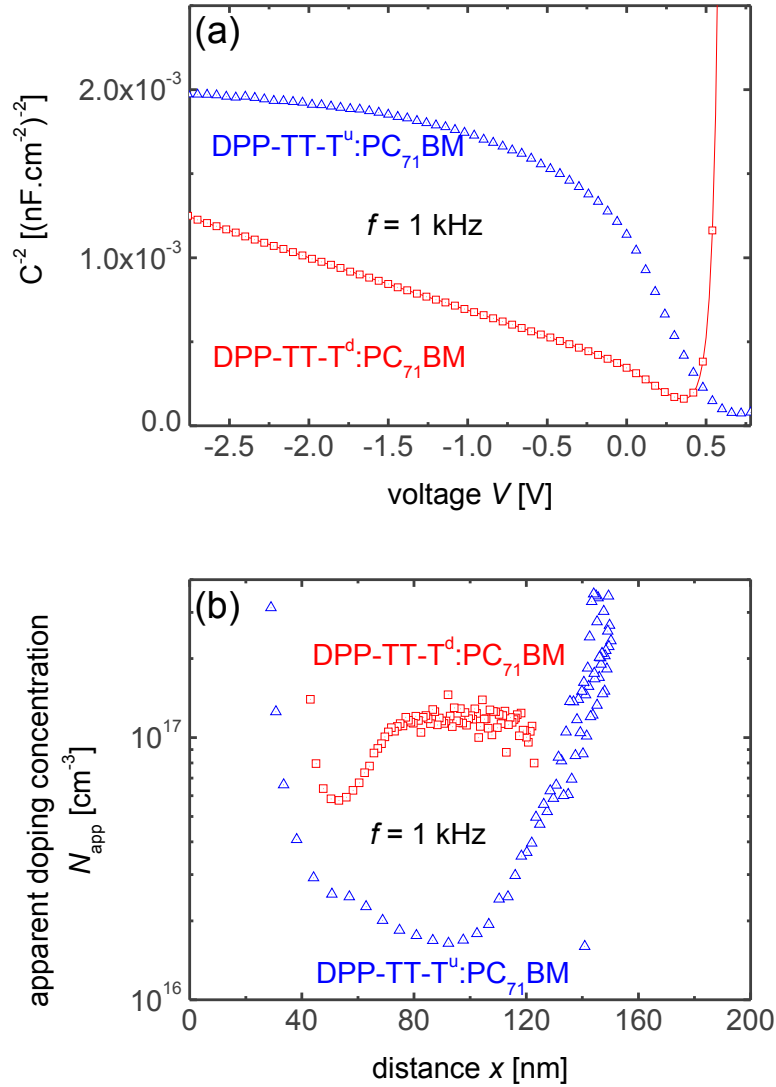


Figure 7.2: (a) Mott-Schottky plot in the dark at 1kHz for two thick devices of DPP-TT-T^u:PC₇₁BM (open up triangles) and DPP-TT-T^d:PC₇₁BM (open squares). The capacitance is inversely proportional to the space charge layer which is controlled by the applied bias. Nevertheless, the space charge layer is also governed by the doping level. (b) the gradient of C^{-2} function of V is inversely proportional to the apparent doping level N_A . There seem to have strong variations of the level of unintentional doping from one batch to another of yet the same molecular content. These measurements were conducted by Michelle S. Vezie and Prof. Dr. Thomas Kirchartz.

$[10^{14}; 10^{17}] \text{ cm}^{-3}$. (Dicker et al., 2004; Gregg, 2009; Mozer et al., 2005b; Kirchartz et al., 2012a; Jain et al., 2001; Mozer et al., 2005a; Wang et al., 2008) Here, assuming an homogeneous distribution of dopants N_A , these would be on average spaced by $N_A^{-1/3} \approx 25 \text{ nm}$ in the doped batch. Mott-Schottky analysis cannot determine the type of doping, in other words on which side the depletion region is located. Nevertheless, as will be developed below, the device behavior in conventional architecture lead us to conclude that the doping is p-type.

7.3.2 DPP-TT-T:PC₇₁BM devices fabrication

Details about purification process can be found in Ashraf et al. (2013). The solution used DPP-TT-T (Bronstein et al., 2011) and PC₇₁BM (Solenne) blended in 1:2 blend ratio in 4:1 chloroform (CF)/o-dichlorobenzene (ODCB) leading to a final concentration of 15 mg/mL. This was prepared 24 hours prior to spin coating and kept under stirring at room temperature in a sealed environment. Indium tin oxide (ITO) pattern glass substrates (Psiotech) were all precleaned with isopropanol and acetone, dried under nitrogen and further cleaned by plasma treatment (7 min at 2.5 mbar). Immediately following this treatment, a PEDOT:PSS solution was spin coated onto the substrate with an acceleration rate of 10k rpm/s and a plateau at 3500 rpm for 40 seconds. The films were annealed at 150°C for 15 minutes resulting in a thickness of $\approx 30 \text{ nm}$. After cooling, the photoactive films were deposited by spin coating the solution on preheated substrates at 80°C. The acceleration rate used was 10k rpm/s and the plateau speed ranged from 300 to 3500 rpm to obtain the thickness series. For both series, the calcium and aluminium cathodes were deposited by evaporation whose thickness was assessed to be 10 nm and 150 nm respectively. The evaporation was performed in one unique run so that variations in the electrode interface energetics could be neglected. Each pixel area was assessed to be 4.5 mm^2 . The devices were stored in a nitrogen glovebox and for all the measurements were confined in a nitrogen sample chamber. To attempt to bring answers to the objectives of this study stated above, two thickness series of DPP-TT-T:PC₇₁BM have been conducted using the two batches of DPP-TT-T which happened to have different doping levels. The protocol followed for device fabrication applied strictly the recipe in Bronstein et al. (2011). Moreover, the same blend ratios, same concentration, same spin speed and same metal electrode evaporation run for the two thickness series have been used for series. More details can be found just below. The device general conventional architecture is as follows: (glass/ITO/PEDOT:PSS/DPP-TT-T:PC₇₁BM/Ca/Al) with the donor being either DPP-TT-T^d or DPP-TT-T^u, respectively the higher and lower

doping level versions of the donor.

7.4 Results and discussions on thickness studies of doped and undoped DPP-TT-T:PC₇₁ BM devices

7.4.1 Current-voltage characteristics

As detailed in the theory section above, doping is expected to impact particularly on the space charge layer width w of the device, and therefore upon device performance as a function of photoactive layer thickness. As such, devices were fabricated as a function of photoactive layer thickness with a conventional architecture. The performances of the presented devices are summarised in Table 7.1. Although the thin devices of both the doped and undoped series generally show a good performance, in particular with high fill factors (58% and 62% for the doped and undoped devices respectively) indicative of efficient charge carrier collection, the trends observed while increasing the thickness are significantly different. While the current density under forward bias in the dark decreases with thickness according to the increase of the internal series resistance for thicker active layers, in the low doping version presented in Figure 7.3 a), the fill factor decreases drastically and the short-circuit current as well though to a lesser extent. Nevertheless, in the doped cases presented in Figure 7.3 b), the fill factor stays high while the short-circuit current decreases significantly even for films thicker than 300 nm.

In the first case, charge collection can be understood using the band diagram presented in Figure 7.1 a). Due to a low doping level and full depletion, the electric field is strong at short circuit and only decreases around the maximum power point resulting in strong voltage dependent losses. With increasing thickness, the drift component in charge transport is lowered due to an insufficient mobility-lifetime product and the fill factor is decreased substantially with the active layer thickness as the ratio $L_{\text{drift}}/d = \mu\tau(V_{\text{BI}}/d)/d$ decreases with the square of the active layer thickness d . This typical drop of cell performance with increasing device thickness has already been reported in different systems like by Ameri et al. (2008); Nam et al. (2010); Zeng et al. (2010) and addressed by Kirchartz et al. (2012a); Kotlarski et al. (2008); Dibb et al. (2013a); Dyakonov (2004a); Gupta et al. (2010); Koster et al. (2011); Kotlarski et al. (2011); Lenes et al. (2006); Pivrikas et al. (2005a); Vandewal et al. (2013). The thickness dependence of the impact of non-geminate recombination on the fill factor is further supported by the successful predictions of open-circuit voltages and current density-voltage responses at different light levels for fully depleted devices. These results can be found in Fig-

ure 7.4 and indicate negligible loss in the fourth quadrant due to field dependent generation for this blend ratio. Overall, the performance degradation will eventually be the results of the combined consequences of interference effects within the active layer and the competition between carrier sweep out and recombination dynamics. Applying now equation 7.1 for doping level of the order of $N_A \approx 7-8 \times$

Table 7.1: Overall performance of the two thickness series of DPP-TT-T^d:PC₇₁BM and DPP-TT-T^u:PC₇₁BM

Material donor/acceptor	Thickness [nm]	V_{oc} [mV]	J_{sc} [mA.cm ⁻²]	FF [%]	PCE [%]
DPP-TT-T ^u :PC ₇₁ BM	60±5	596±5	9.1±0.1	62±1	3.35±0.1
DPP-TT-T ^u :PC ₇₁ BM	160±10	575±5	8.3±0.1	47±1	2.24±0.1
DPP-TT-T ^u :PC ₇₁ BM	300±10	560±5	5.0±0.1	42±1	1.19±0.1
DPP-TT-T ^u :PC ₇₁ BM	375±10	557±5	4.0±0.1	40±1	0.91±0.1
DPP-TT-T ^d :PC ₇₁ BM	75±5	574±5	13.1±0.1	58±1	4.36±0.1
DPP-TT-T ^d :PC ₇₁ BM	81±5	572±5	12.9±0.1	55±1	4.07±0.5
DPP-TT-T ^d :PC ₇₁ BM	160±10	576±5	7±0.1	47±1	3.74±0.5
DPP-TT-T ^d :PC ₇₁ BM	390±30	505±5	2.3±0.1	46±1	0.55±0.5

10^{16} cm^{-3} , the width of the space charge region is estimated to be approximately $\approx 70 - 80 \text{ nm}$. In this second case, the field assisted collection is only happening partially through the active layer, as pictured in Figure 7.1 b). In this case, the common way of understanding charge collection explained earlier based on the carrier mobility-lifetime product throughout the entire active layer is not correct. Most charge carriers that contribute to the photocurrent are generated in the small space charge region, which does not change width with active layer thickness. Thus, the short-circuit current density will be reduced with thickness as less light is absorbed in the space charge region, but the FF will stay rather constant because the width of the space charge region stays constant and the diffusion of carriers generated out of the space charge is not voltage dependent, it will be subsequently constant between short circuit and open circuit. The measured increase in absorbance shown in Figure 7.6 a) did not result in more collected charges and subsequently in a higher J_{sc} consistent with previous simulations. (Dibb et al., 2013b) From the UV-Vis spectrum, it can be observed that the 0-1 absorption transition is slightly larger in thick films with respect to the 0-0, which could indicate that thin films might be slightly more crystalline. This observation could challenge the assumption that the microstructure of the blend film over the range of thickness 60 to 375 nm is constant and the resulting hole mobility could have

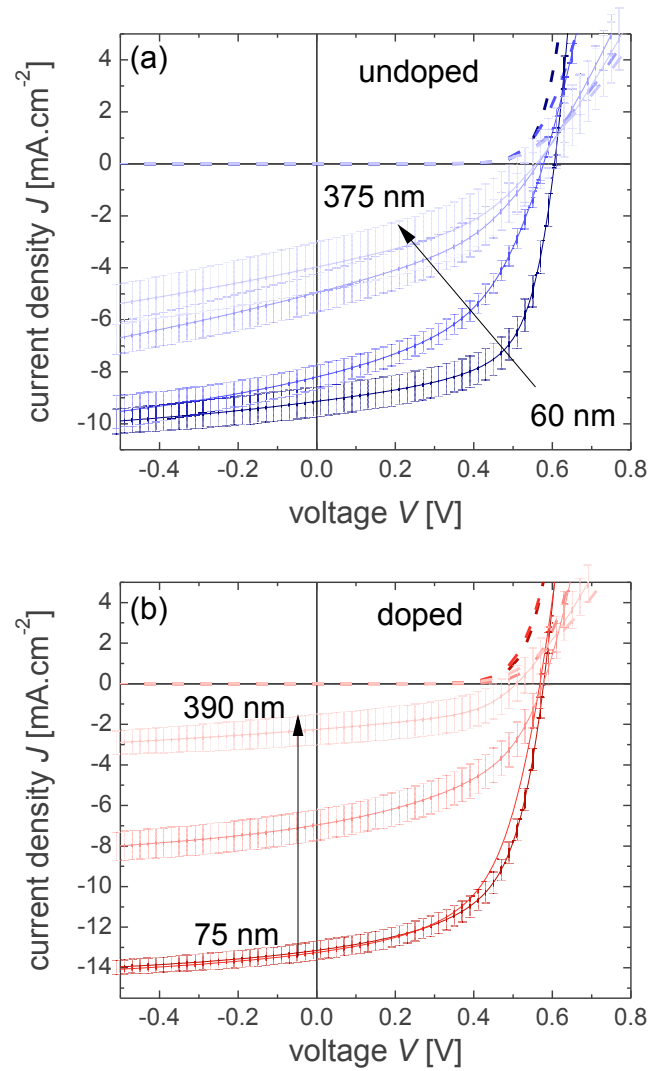


Figure 7.3: Experimental dark (dashed lines) and AM1.5 (solid lines) current-voltage responses of the devices from the two thickness series. (a) DPP-TT-T^u:PC₇₁BM ($N_A \approx 1.5 \times 10^{16} \text{ cm}^{-3}$) at 60, 160, 350 and 375 nm and (b) DPP-TT-T^d:PC₇₁BM ($N_A \approx 7 - 9 \times 10^{16} \text{ cm}^{-3}$) at 75, 81, 160 and 390 nm. The degradation of the carrier transport over the thickness range due to insufficient product mobility $\times$ lifetime in case (a) cannot explain the behavior of the doped counterpart (b) which have higher fill factor at comparative thicknesses due to efficient collection strictly within the space charge layer which is fixed (so constant here) by the doping level and not the device thickness.

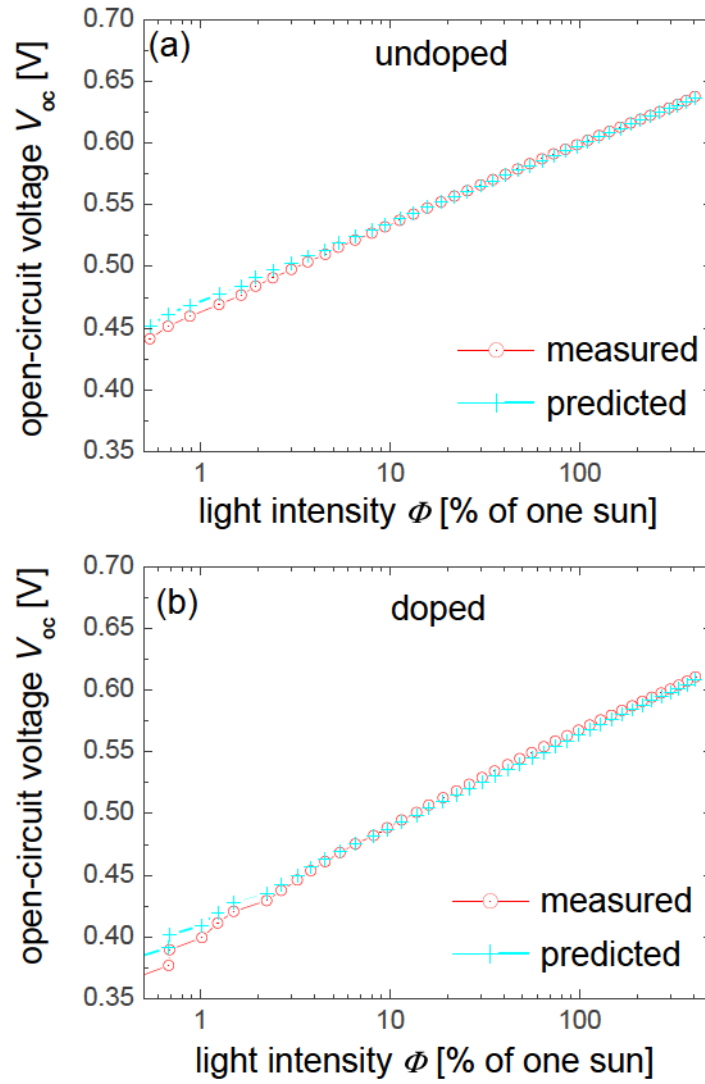


Figure 7.4: Prediction (crosses) and measured (open circles) of the open-circuit voltage V_{oc} for a range of light intensities for (a) 60 nm thick device with low doping level ($N_A \approx 1.5 \times 10^{16} \text{ cm}^{-3}$) and (b) 75 nm thick device at high doping level ($N_A \approx 7-9 \times 10^{16} \text{ cm}^{-3}$). The assumptions are non-geminate recombination as main loss process of photocurrent in the fourth quadrant and no field dependence generation. The accuracy of the predictions is within $\pm 5 \text{ mV}$.

consequently decrease over the thickness series. However, as shown previously with P3HT:PC61BM by Vanlaeke et al. (2006); Müller et al. (2008), the change in hole mobility was observed for substantially larger shifts in UV-Vis spectrum than the data presented here. Although the holes are the majority carriers in the case of p-type doping, those photogenerated within the space charge region will still need to be transported throughout the entire neutral region whose thickness increases with increasing total active layer thickness. This results in an increase of the internal series resistance for the holes and a slight decrease of fill factor with thickness as observed in this series. Eventually, towards to the second interference maximum, even with a density of dopants of the order of $N_A \approx 1.5 \times 10^{16} \text{ cm}^{-3}$, the width of the space charge region becomes smaller than the device thickness. Nevertheless, the fill factor of the low doping level devices has already substantially degraded before the active layer thickness starts to be partially depleted (beyond 150 nm).

The result of the shift in interference pattern which is supplying the effective collecting zone in carriers when the active layer thickness is increased was quantified. A calculation of the integrated generation rate within the space charge zone at different thicknesses of the total active layer is presented in Figure 7.5 b) based on ellipsometry data measured by Dr. Mariano Campoy-Quiles, ICMAB and shown in APPENDIX D. A calculation of the integrated generation rate within the space charge zone at different total thickness of active layer is presented in Figure 7.5 using the MMT modeling as detailed in Chapter 3, based on the measured refractive index n and extinction coefficient k following:

$$G_{\text{SCR}} = \frac{1}{d} \int_{d-w}^d G_x dx \quad (7.3)$$

In this definition, d is the thickness of the active layer, w is the space charge zone (which is here on the side of the cathode) and $x=0$ corresponds to the position of the anode. These calculations are consistent with the continuous decrease of J_{sc} with active layer thickness in case of high p-type doping level and quantitatively explains why the short-circuit current decreases with thickness for the series of doped devices.

7.4.2 Corrected photocurrent obtained in far reverse bias

Finally, to further support the idea that the loss of the extra carriers photogenerated in greater active layer thicknesses in doped and undoped batches has different fundamental origins, the corrected photocurrent $J_{\text{ph}}(V) = J_{\text{light}}(V) - J_{\text{dark}}(V)$ was

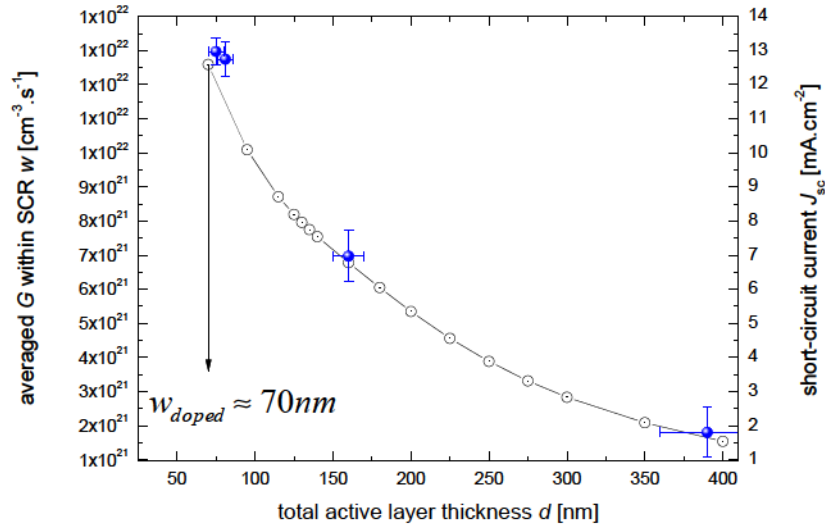


Figure 7.5: Spatial average over the width of the space layer of the generation G rate calculated by MMT modelling.

measured to explore the response to far reverse bias of a doped and an undoped device whose active layers were spin coated at 300 rpm. Although a slight change in viscosity is expected between the two batches, the resulting thickness was similar and measured to be ≈ 375 nm. Figure 7.6 b) shows the obtained corrected photocurrents for the doped (open squares) and the undoped (solid spheres) devices. The values of the obtained corrected photocurrents in far reverse bias [-30; -25] V are first substantially superior to their short-circuit currents even in the case of the doped device and then are very similar between the two levels of doping. The values of corrected photocurrent obtained at far reverse bias converge towards the values predicted by the J_{sc} assuming perfect collection calculated from Matrix Modelling Technique (MMT) as shown in Figure 7.7. According to equation 7.1, the width of the space charge region increases with negative bias since the increase in electric field leads to longer drift lengths L_{drift} at given $\mu\tau$ -product and therefore better collection. In case of the undoped device, which is much more depleted than the doped one at 0V, the sweep in reverse bias will continuously increase the collection efficiency with increasing negative bias. In case of the doped device, this increase will be much slower as initially only the width of the space charge region will increase while most of the device is still field neutral. Only once the doped device is fully depleted will it approach the same level of photocurrent than the undoped device.

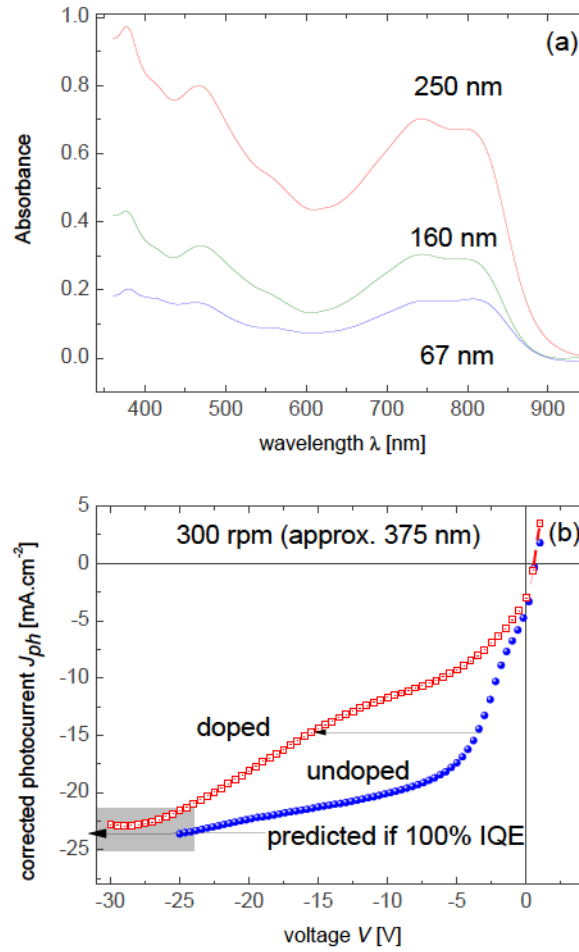


Figure 7.6: (a) UV-Vis spectra between 350 and 950 nm of a thickness series of doped ($N_A \approx 1 \times 10^{17} \text{ cm}^{-3}$) DPP-TT-T:PC₇₁BM devices at 67, 160 and 250 nm thick approximately. From 67 to 250 nm, the more absorber, the more light is absorbed despite the space charge layer being much smaller than 250 nm at this doping level. (b) corrected photocurrent $J_{ph} = J_{light} - J_{dark}$ of approximately the same thickness ($\approx 375 \text{ nm}$) at two different doping levels (open squares $N_A \approx 7 \times 10^{16} \text{ cm}^{-3}$ and solid sphere $N_A \approx 1.5 \times 10^{16} \text{ cm}^{-3}$). Despite differences at short-circuit conditions, the corrected photocurrents of both high and low doping levels devices converge at far reverse bias and match the theoretical value obtained from MMT modelling.

Figure 7.8 is representing the situation in both cases of charge transport in fully depleted (a) and partially depleted (b) devices.

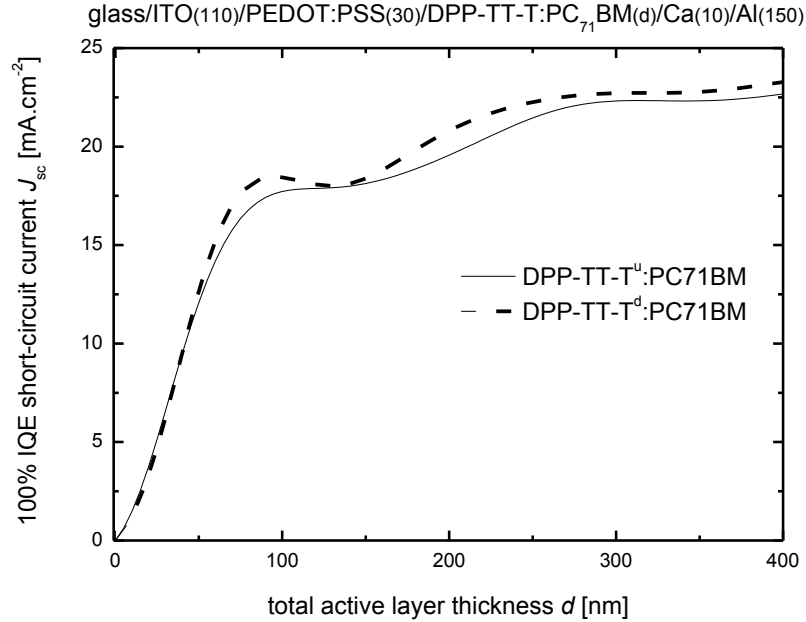


Figure 7.7: Theoretical short-circuit current J_{sc} assuming perfect collection calculated by MMT with the values $(n;k)$ measured by ellipsometry for a range of active layer thickness $d \in [0-400]$ nm for the following multilayers stack glass/ITO(110 nm)/PEDOT:PSS(30 nm)/DPP-TT-TPC₇₁BM(d)/Ca(10 nm)/Al(150 nm). At $d \approx 375$ nm, the theoretical value of the photocurrent is expected to be ≈ 22.7 mA.cm⁻².

7.4.3 Comparison of effective mobilities at two different doping levels

The effect of doping on current-voltage responses is crucial for device optimisation as it shows that although a promising OPV material might show very good transport properties, trying to optimise the devices towards the second interference maximum to obtain higher short-circuit current is doomed to failure if the material happens to be unintentionally doped. The previous results confirm that unintentional doping will be overall detrimental if thin devices show relatively well balanced transport as explained by Trukhanov et al. (2011). However, these modelling studies also show that doping can be beneficial for thin devices if the carrier mobilities were initially asymmetric. We measured here effective drift mobility of thin DPP-TT-T^u:PC₇₁BM and DPP-TT-T^d:PC₇₁BM devices using charge extraction at short circuit as described in Chapter 3. The drift effective mobilities

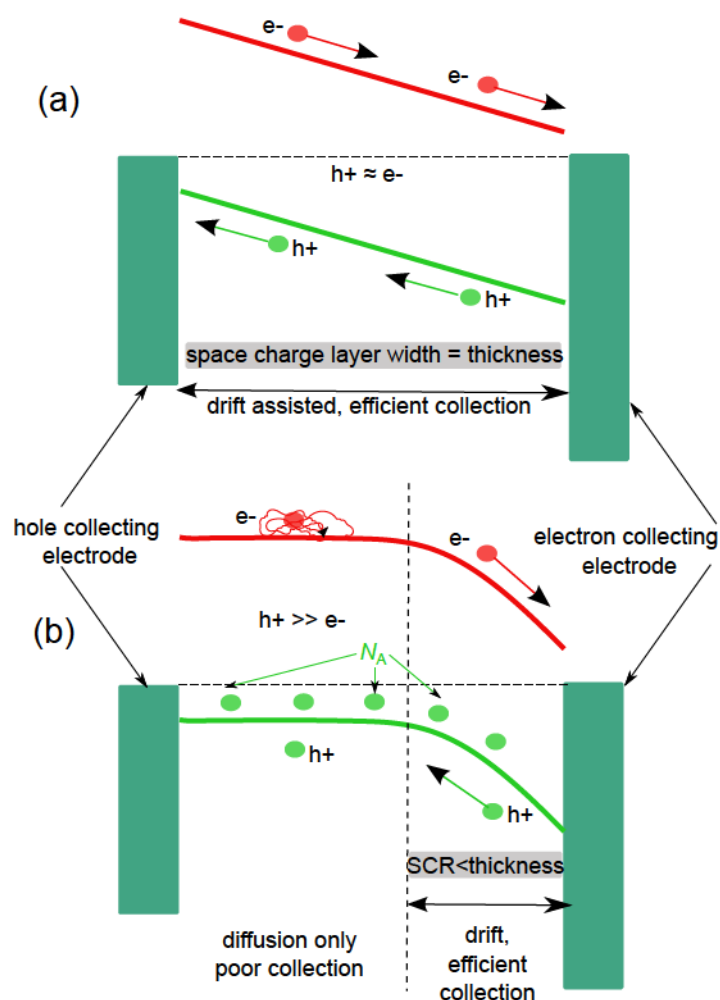


Figure 7.8: Schematics representing charge transport in fully depleted (a) and partially depleted (b) devices. In the second case, the electrons generated in the neutral region (close to the hole collecting electrode in case of p-type doping) can only diffuse and are in presence of a large excess of holes due to the presence of the p-type dopants on top of the photogenerated holes.)

obtained are represented in Figure 7.9. Both effective drift mobilities are at $1.2 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \pm 3 \times 10^{-5}$. This measurement suggests that transport (at least the drift components) between holes and electrons have not changed substantially upon the increase in doping and that transport has not been improved upon the increase in doping in this particular system (though some slight difference in the charge dependency can be observed).

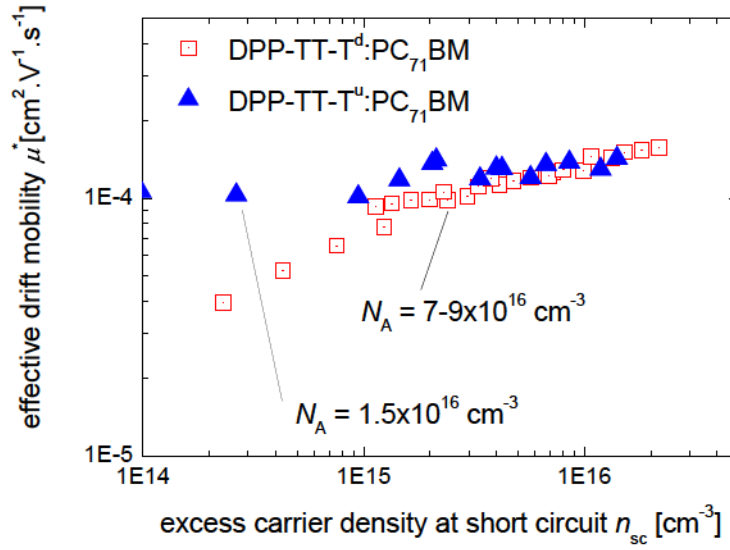


Figure 7.9: Effective drift mobility measured using charge extraction at short circuit on two fully depleted DPP-TT-T^u:PC₇₁BM (100 nm) and DPP-TT-T^d:PC₇₁BM (75 nm) devices.

7.4.4 Impact of doping on the analysis of the linearity of the short-circuit current with illumination

As explained above, the increase in the thickness of an undoped absorber resulted in a monotonic decrease of the fill factor which lead to a subsequent decrease in the short-circuit current. One quick assay of the development of bimolecular recombination at short circuit in the literature is the analysis of the linearity of J_{sc} as a function of illumination level Φ . Indeed, it has been well established that the short-circuit current in polymer:fullerene solar cells tend to show a power law ($J_{sc} \propto \Phi^\alpha$ with $\alpha \leq 1$; the sublinearity of J_{sc} with illumination has been well observed and interpreted as a consequence of the development of second order carrier loss processes at short circuit. (Dyakonov, 2004a; Koster et al., 2011; Gao et al., 1997; Riedel et al., 2004; Schilinsky et al., 2002; van Duren et al., 2004)

Figure 7.10 presents $d\ln(J_{sc})/d\ln(\Phi)$ at different light intensities as obtained experimentally and from simulation. The list of parameters used for these simulations can be found in Appendix D. In this case, the linearity of the short-circuit current is a correct assay of the degradation of carrier transport at 0V condition. The greater linearity of J_{sc} for the thin undoped device compared with a thicker undoped device is indeed synonymous of less bimolecular recombination at 0V.

However, we found experimentally that the trend was not followed in the doped thickness series as presented in Figure 7.10 b). Here, the linearity of J_{sc} stays high even for thick devices of 350 nm, for which the space charge layer is significantly thinner than the thickness of the absorber. In this case, the substantial number of carriers photogenerated outside of the space charge region, which are recombining with the excess of holes, is not translated into the degradation of the linearity of J_{sc} which is composed mostly of the carriers generated within the space charge region whose thickness is fixed by the doping level. Moreover, the recombination of minority carriers within the neutral region occurs with a large excess of holes, therefore, is pseudo-first order and consequently is unlikely to affect how J_{sc} scales with illumination. This change is captured in the simulation when the doping level is increased from $N_A = 1.5 \times 10^{16} \text{ cm}^{-3}$ to $N_A = 8 \times 10^{16} \text{ cm}^{-3}$ (all other parameters are kept constant). These data clearly show that a device with a relatively high fill factor and a very linear response of the short-circuit current with light intensity is not necessarily immune to major losses of photogenerated carriers if the active layer is not fully depleted.

7.4.5 Impact of doping on recombination dynamics

The importance of non-geminate recombination in many optimised organic solar cells has been emphasised over the last chapters of this thesis. In particular, attention is paid to the changes in reaction order which might hint to a change in fundamental recombination mechanism. (Shuttle et al., 2008c; Mozer et al., 2005a; Chen et al., 2011; Foertig et al., 2009; Garcia-Belmonte et al., 2010; Leong et al., 2011) In our study, the increase in total density of carriers will respond differently to illumination, especially at low light and voltage biases since the electrons will mostly originate from photon absorption while the holes originate from a combination of the ionisation of p-type dopants and photogeneration. This is likely to substantially change the way recombination dynamics is usually tackled.

Here charge extraction and transient photovoltage/photocurrent have been conducted on the two thickness series and the results are presented in the next two subsections.

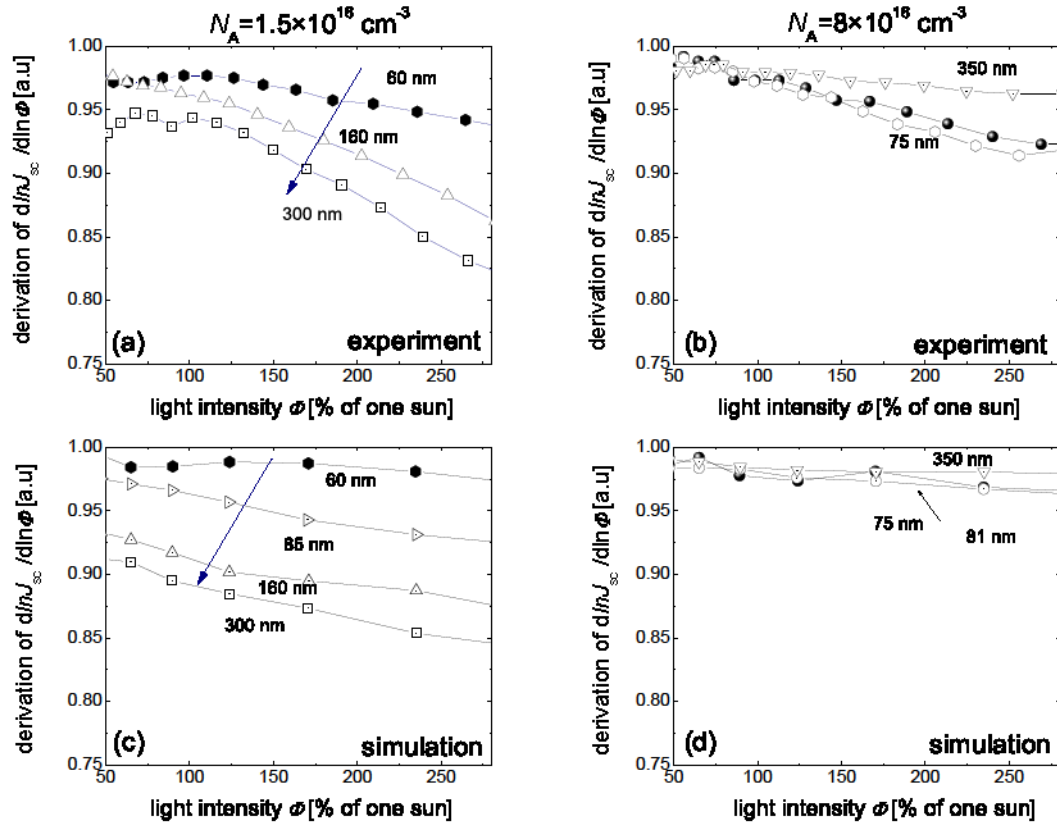


Figure 7.10: Linearity of the short-circuit current J_{sc} with illumination at different thicknesses for DPP-TT-T:PC₇₁BM devices with low level of doping (experimental a, simulation c) and high level doping (experimental b, simulation d). The loss of linearity is compatible with second order loss process. However, the linearity appears not degraded in the doped thickness series while there is substantial non-geminate recombination within the neutral region.

7.4.5.1 Impact of doping on charge extraction

Figures 7.11 a) and b) present experimental raw charge extraction data at open-circuit for the doped and undoped thickness series of DPP-TT-T:PC₇₁BM and show how they radically differ depending on the doping level. By collecting charges at 0V, the method is sensitive to excess carriers which managed to be swept out under short-circuit conditions. Since charge extraction measures the excess charge carriers relative to the dark short-circuit situation, the charge extraction will not see the holes created by the ionisation of the p-type dopants. The correction for geometric capacitance in our case would be inappropriate if the space charge region would be thinner than the total active layer thickness. Here, the chemical capacitance of the injected charges (diffusion capacitance), would be used instead, as detailed in Chapter 3. In the low doping level case where collection is made throughout the whole active layer, these experimental observations are confirming the predictions of Kirchartz and Nelson (2012) where at high thickness the change in spatially averaged excess carriers with voltage is higher than in the thin devices where the spatial distribution of carriers is more heterogeneous. If the excess carrier concentration Δn is following an exponential dependence on voltage (V_{oc}) according to the following:

$$\Delta n = \Delta n_0 \exp\left(\frac{qV_{oc}}{mk_B T}\right) \quad (7.4)$$

it becomes apparent that in the first case on Figure 7.11 a), m is decreasing with thickness while the spatial distribution of excess carriers becomes more homogeneous. This has been experimentally observed as well for polymers with low doping level such as PTB7:PC₇₁BM and PCDTBT:PC₇₁BM devices at different thicknesses as shown in Appendix C. On the other hand, in the doped case shown in Figure 7.11(b), all the devices presented here have actually the same effective space charge layer width (70 nm). The way the excess carriers scale with voltage is weak, similar to thin undoped devices. Basically, hardly any change in m is observed in the series of charge extraction data at open circuit for all the partially depleted devices since the charge extraction method is sensitive to excess carriers which only exist in the space charge region (fixed by the high doping level) and in the neutral region, the concentration of holes is mostly governed by the dopants, i.e. constant between the dark and under illumination. Furthermore, for the reason given above, the collection is only efficient in the space charge region so the charge extraction would not see the excess carriers in the neutral region anyway. Therefore, the data obtained are not going to change with the total active layer thickness as experimentally observed.

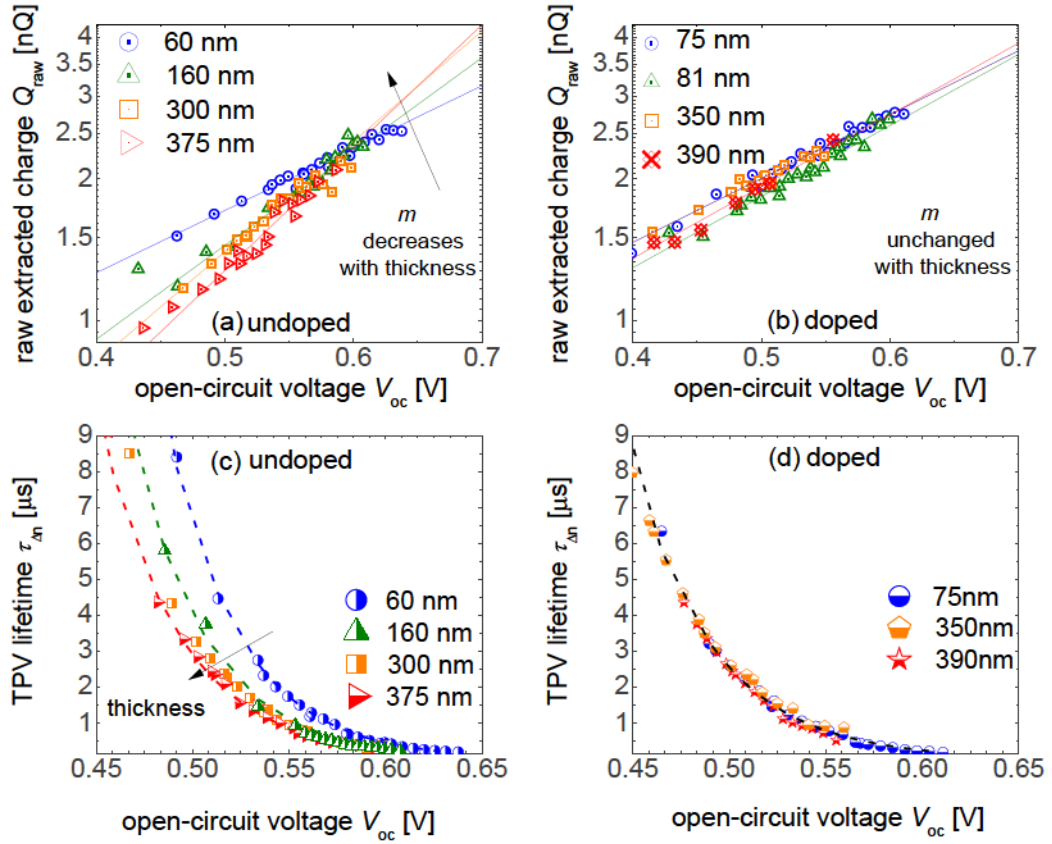


Figure 7.11: Charge extraction at open-circuit and TPV lifetimes for DPP-TT-T:PC₇₁BM devices. Raw charges at open-circuit extracted under short-circuit bias for different thicknesses for low level doping (a) and high level doping (b). The way extracted excess carriers scale with light intensity is radically different depending on the doping level. TPV lifetime at different open-circuit voltages and thicknesses for the low level doping (c) and the high level doping (d).

7.4.5.2 Impact of doping on transient photovoltage

Moreover, the observed TPV lifetimes in Figure 7.11 (c) and (d) of the thickness series have a unique response in the presence of doping. While the TPV lifetime versus V_{oc} in Figure 7.11 (c) changes with thickness at low doping level, no change is observed for all the partly depleted devices (one monoexponential is necessary to fit how the small perturbation lifetimes scale with V_{oc}). At open circuit, recombination via traps is typically largest in the space charge region, where electron and hole concentrations are roughly equal. This is confirmed by the fact that even in the doped systems the lifetime is still a monotonically decreasing function of open-circuit voltage and not just a constant as expected if recombination was dominated by the neutral zone. In this case, the space charge region dominates the lifetime. Since the doping keeps the width of the space charge region constant as a function of total active layer thickness, the TPV lifetime does not change appreciably with device thickness in the doped series. In this case, if the TPV lifetime has the following form:

$$\tau_{\Delta n} = \tau_{\Delta n 0} \exp\left(-\frac{q V_{oc}}{\vartheta k_B T}\right) \quad (7.5)$$

ϑ has a typical value of 1.73 ± 0.04 according to Figure 7.11 d), which was predicted to be obtained for doping levels of $\approx 9 \times 10^{16} \text{ cm}^{-3}$, consistent with our initial Mott-Schottky analysis (See Figure 7.12 for the comparison between prediction from Kirchartz and Nelson (2012) and our data presented here.)

7.5 Further discussion: high reaction orders, doping level and 2nd interference maximum

Consequently, given how insensitive the charge extraction data and the small perturbation lifetimes are regarding the thickness for doped devices and then how strongly the dark charges are involved in non-geminate recombination, the apparent reaction orders of doped devices are excessively high (here $\delta \approx 5$) due to the strong heterogeneity of carriers distribution within the active layer. Moreover, the reaction order does not change with the total active layer thickness since the effective layer of absorber, coinciding with the width of the space charge region, is fixed by the doping level. Figure 7.13 presents the calculated apparent reaction order of doped devices at two different thicknesses, namely 75 and 350 nm. For these doped devices, the width of the space charge was assessed to be approximately 70 nm.

While the spatial distribution of carriers changes substantially when the total

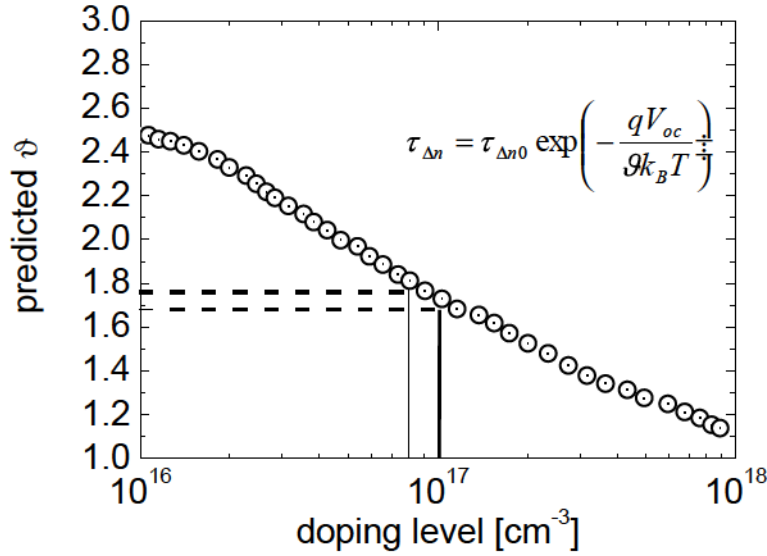


Figure 7.12: Comparison of the experimental value of fitting parameter ϑ and the predicted doping related to that value (open symbols) in Kirchartz and Nelson (2012).

active layer thickness is increasing from 75 nm to 350 nm, the apparent reaction order does not change at all. Obviously, the effective active layer in a 350 nm device is actually much reduced and if the apparent recombination rate is calculated with the width of the space charge region instead of the total active layer thickness, the obtained k_{rec} coincides with that of the thin 75 nm device. This highlights how similar the effects of the doping level and thin active layers are on the apparent recombination dynamics covered in the previous chapter.

7.6 Conclusions

To conclude, we discussed how the level of doping sites in the active layer affects the performance and the apparent recombination dynamics of polymer:fullerene solar cells. In the case of high doping levels, we see that charge transport is strongly affected due to band bending at short circuit which only allows efficient carrier collection within the space charge layer whose thickness is governed by the density of the dopants. Consequently, the highest optimal thickness of the active layer is limited by the intrinsic doping level and not only by the ability of the blend to transport charge carriers, which means that the efforts of molecular design aiming at fast charge transport as well as the potential of light absorption of the active

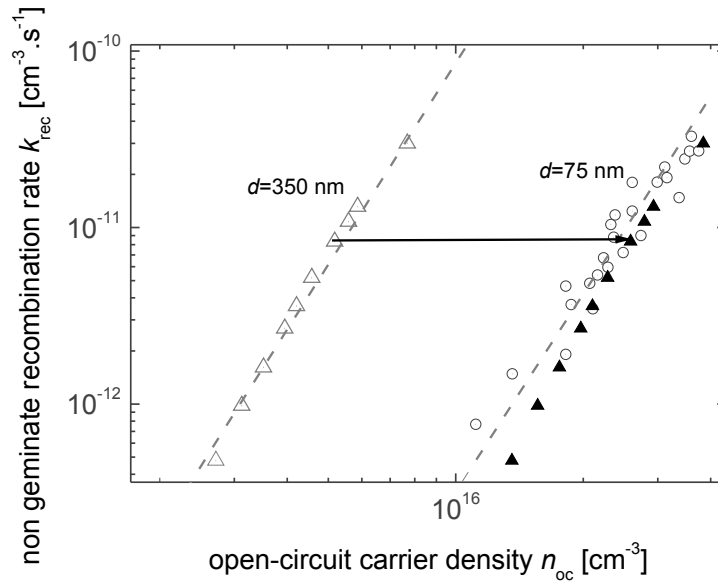


Figure 7.13: Measured recombination rate k_{rec} function of excess carrier concentrations at open circuit for two DPP-TT-T^d:PC₇₁BM at 75 nm (hexagons) and 350 nm (open up triangles). If the recombination rate of the device $d=350 \text{ nm}$ is calculated with the effective width w_{doped} of the space charge region instead of the total active layer, the recombination rate obtained (in solid up triangles) coincides with that of the thin device.

layer could be partially wasted. We emphasise in this study bringing intensive experimental evidence that, although the origin of doping in organic material might be very diverse (not only oxygen), the awareness of doping level from molecular synthesis to final device fabrication is crucial to make the most of the potential of every material proposed to attempt to push the overall performance of organic solar cells over 10 % power conversion efficiency.

This work shows that for a doping level as high as $7-9 \times 10^{15} \text{ cm}^{-3}$ and beyond, the usual way of understanding device carrier collection and recombination dynamics in organic bulk heterojunction solar cells is challenged. Due to the diverse origins of the dopants and the fact that n-type doping will have similar effect as p-type doping in the vicinity of the anode, the results presented hereby are likely to be relevant for a wide range of organic blends independent of their general architecture of the device used. It appears that the key for improving the performance of the blends will be i) to first and foremost control/find methods to decrease the unintentional doping level so that the active layer is still fully depleted at the second interference maximum around 200-250 nm. This can be insured by increasing the relative permittivity or decreasing the doping levels to values $\leq 6-7 \times 10^{15} \text{ cm}^{-3}$ as shown in Figure 7.14. Once this is fulfilled, ii) on the main target would be to obtain materials and nanomorphologies which enable sufficient mobility $\times$ lifetime product up to the second interference maximum while maintaining a substantial quenching of the excitons for photogeneration.

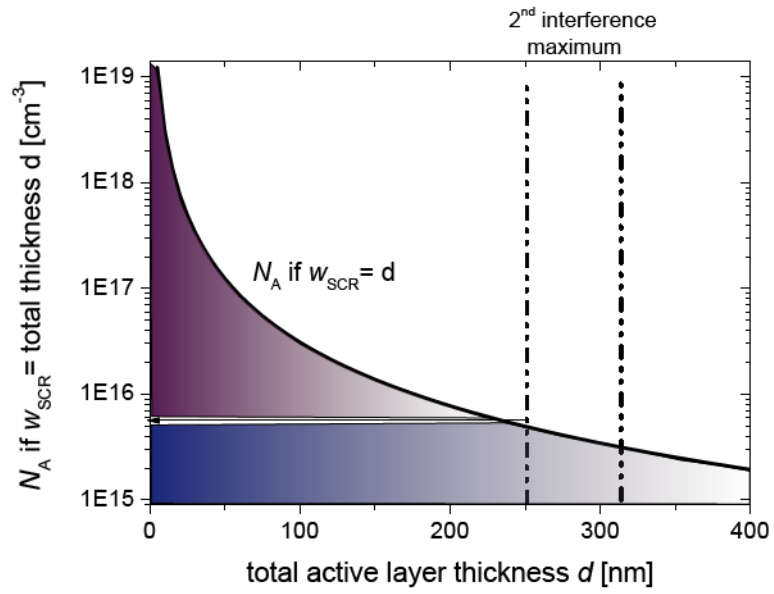


Figure 7.14: Calculation of the maximum doping level authorised N_A if the width of the space charge region is as thick as the total active layer thickness, for the range $[0;400]$ nm. If the device need to be fully depleted at the second interference maximum, the minimum doping level allowed is $N_A^{\max} \leq 6 - 7 \times 10^{15} \text{cm}^{-3}$.

Analysis of Langevin and non-Langevin recombination in organic solar cells

8.1 Introduction

In the previous chapters, we saw that when the active layer had a doping level as low as $7\text{--}9\times 10^{15}\text{cm}^{-3}$ and good contacts were fabricated, charge transport to the first and second interference maxima could be optimised by maximising the product mobility-lifetime. In other words, non-geminate recombination can be overcome with enough carrier mobility, or if the mobility of the carrier through the bulk heterojunction material is not that high, the recombination lifetime must be long enough to let the carriers to be collected.

We confirmed and validated that charge extraction and transient photovoltage can quantify non-geminate recombination in efficient polymer:fullerene solar cells. Also, we saw that the way the dependence of the recombination rate on carrier density was sensitive to the overlap of distributions of opposite carriers. Yet, even when the overlap of spatial distributions of electrons and holes is large enough, the apparent recombination rate is very often slower than the theoretical Langevin recombination rate. This has been observed and confirmed in many different experimental setups investigating non-geminate recombination in polymer:fullerene solar cells. (Pivrikas et al., 2005a; Juška et al., 2006; Koster et al., 2006; Sliaužys et al., 2006; Shuttle et al., 2008c; Deibel et al., 2008; Lungenschmied et al., 2009)

Understanding the reason why some polymer:fullerene systems show a non-Langevin behaviour (as was for instance the case in Chapter 5 with PBDTTT-C:PCBM with simultaneous improvement in carrier mobility and lifetime) and not others, is crucial, as ultimately, enhancing further performance of these systems will require further reduction of non-geminate losses in thicker active materials. Langevin recombination rate is often used in modeling and is implicitly assumed

when formulating some design rules for performant organic solar cells. Yet, there is still no consensus on whether crystalline blends should be favored to amorphous blends for high efficiency polymer:fullerene solar cells. In this last chapter, we propose a method to quantify the degree to which the bulk recombination is similar to Langevin predictions for a wide range of systems. Then, different explanations for observing recombination rate slower than predicted by Langevin recombination are reviewed. Finally, the discussion is extended by further considering the underlying assumptions behind these different suggested explanations.

8.2 Degradation of the fill factor with thickness

As shown previously in this thesis or in the following Figure 8.1, efficient polymer:fullerene systems fabricated around their first interference maximum will not necessarily be able to transport the charges beyond that point. In Chapter 7, we addressed the effect of doping on the optimisation of transport for one particular efficient blend. Except when the devices are limited by their doping level, the ability of transporting carriers through larger thicknesses and lower drift force will govern whether or not a polymer:fullerene blend will continue to operate efficiently at higher thicknesses.

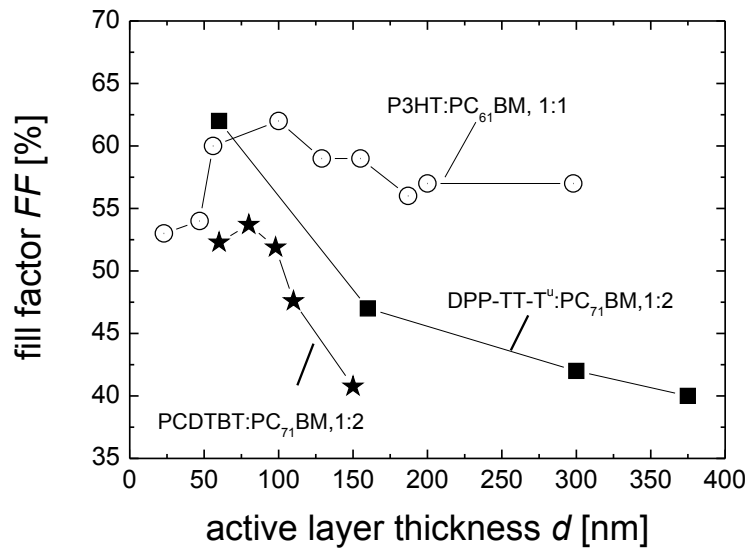


Figure 8.1: Measured fill factor at different thicknesses of P3HT:PC₆₁BM, DPP-TT-T':PC₇₁BM and PCDTBT:PC₇₁BM. Substantial differences in transport properties lead to different fill factor around the second interference maximum.

We saw in the last chapters, in particular with the $\mu\tau$ concept, that in fully

depleted devices, there will be a threshold thickness of the active layers beyond which either the imbalance of transport will enhance the build-up of a space charge reducing the electric field inside the device, which will impede further the carrier to drift, or simply the polaron lifetime will be insufficiently short compared with the typical time needed for the carrier to sweep away from the bulk. Goodman and Rose (1971) for instance showed in particular by simulation that a difference of carrier mobilities of one order of magnitude is sufficient to result in a degradation of the fill factor due to the formation of space charge beyond active layer thickness of ≈ 150 nm. In this case, the space charge limited photocurrent would follow the relation:

$$J_{\text{ph}} = (qG)^{0.75} (9/8 \epsilon_0 \epsilon_r \mu_{\text{slowcarrier}})^{0.25} \sqrt{V} \quad (8.1)$$

In other words, in the extreme case of space charge limited devices, the reverse bias corrected photocurrent would scale with the generation rate of carrier G with the power 0.75.

If the device is thin enough or the transport of opposite carriers is balanced enough, the only barrier to carrier sweep out will be the actual non-geminate recombination. Although Langevin recombination is commonly used to describe the recombination in the bulk of polarons in polymer:fullerene solar cells, attempting to compare the recombination rate and carrier mobility is not an easy task inspite of the abundance of techniques available to quantify them. There are indeed a large range of techniques investigating the recombination dynamics, such as Montanari et al. (2002); Westerling et al. (2003); Pivrikas et al. (2005a,b); Mozer et al. (2005a); Sliauzys et al. (2006); Dennler et al. (2006); Pivrikas et al. (2007); Koster et al. (2006); Shuttle et al. (2008b) and as many are focusing on carrier transport such as Juška et al. (2006); Shuttle et al. (2010a); Clarke et al. (2011); Wehrenfennig et al. (2014). The question becomes which recombination rate and which carrier mobility need to be considered, similarly to what has been done in DSSC over the last few years. (Barnes et al., 2013) In the next section, a method to compare recombination rate and carrier mobility in a few efficient polymer:fullerene solar cells is suggested.

8.3 Method

8.3.1 Polymer:fullerene devices used for comparison

For the comparison between apparent bulk recombination rate and effective drift mobility, high fill factor polymer:fullerene devices were chosen. These are the

same as the one detailed previously in Chapter 4. In particular, the device preparation is detailed in the before-mentioned chapter. The comparison is restricted to high fill factors devices to limit the deviation from pure drift driven mobilities at short circuit.

8.3.2 Recombination dynamics and effective mobility

As detailed previously in Chapters 3 and 4, the measurements of recombination dynamics were undertaken using a combined use of charge extraction at open circuit and transient photovoltage. Effective drift mobilities were measured using charge extraction at short circuit.

8.4 Results

8.4.1 Comparing measured bulk recombination rate and Langevin prediction

In Chapter 6, precisions were added suggesting the observed recombination rate obtained with these techniques is free from the variations in spatial distribution of carriers once the device thickness is reaching approximately 150 nm or equivalently at high illumination. Figure 8.2 presents the recombination lifetimes as a function of excess carrier density for the different systems presented previously in Chapter 4. The recombination rate is then selected at high illumination (several suns, depending on what is accessible), in order to make sure that the obtained excess carrier density can be reproduced during mobility measurement as explained just above. Although these data correspond to devices with relatively high fill factor ($FF \geq 57\%$ as shown in Table 4.1), the observed recombination lifetimes are substantially different.

To compare the recombination rate obtained as explained above with the Langevin prediction, the measurement of carrier mobility is necessary. Since the recombination rate corresponds to a macroscopic, bulk recombination rate in an operating device, it is necessary to measure an effective transverse mobility across the whole active layer representative of operating devices, which probably rules out data obtained using techniques such as Time of Flight or TeraHerz spectroscopy. Although obtaining drift mobility data from charge extraction at short circuit, as explained previously in Chapter 3, is limited by the fact that it only gives access to an effective mobility without being able to differentiate both types of carriers, this method is chosen so that it can still offer a consistent comparison on all the systems studied, rather than trying to obtain data from the literature origi-

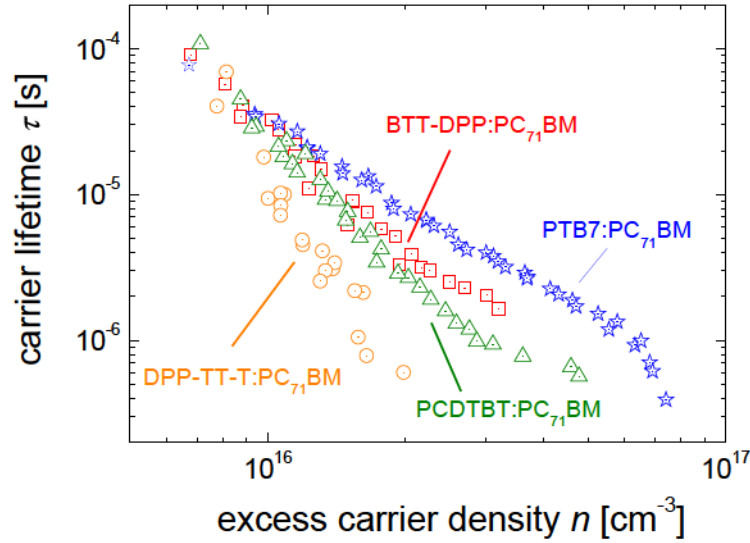


Figure 8.2: Total lifetime at different charge densities obtained by combined charge extraction and transient photovoltage experiments of different polymer:fullerene blends.

nating likely from different techniques. Figure 8.3 presents different short-circuit current densities measured at different light intensities as a function of the corresponding excess carrier densities. According to equation 3.6, the slope is directly governed by the effective carrier density assuming the transport is drift driven. It appears that although the difference in mobility is not ranging over more than 2 decades, the obtained mobilities are indeed substantially different from one another. The carrier mobility is then selected at the same excess carrier density that the recombination rate is measured.

8.4.2 Comparison obtained for some efficient polymer:fullerene solar cells

By applying the method exposed above on different systems of different morphologies, and with its own limit of applicability, interesting variations are observed. Figure 8.4 presents the ratio of the apparent recombination rate obtained by combined charge extraction and transient photovoltage to the rate predicted with Langevin expression using the effective mobility obtained by charge extraction at short circuit. To allow fair comparison and counter the effect that thickness has on the variation in spatial distribution (as presented in Chapter 5), the values were obtained at high light intensities (a few suns giving $n \approx 2.5 \times 10^{16} \text{ cm}^{-3}$).

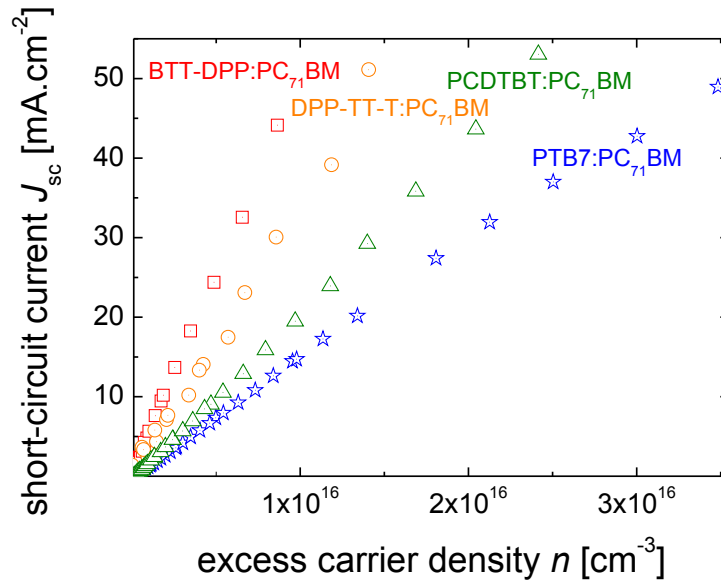


Figure 8.3: Short-circuit current and their related excess carrier densities measured by charge extraction at short-circuit for the same blends BTT-DPP:PC₇₁BM, DPP-TT-T:PC₇₁BM, PCDTBT:PC₇₁BM and PTB7:PC₇₁BM. The ratio will lead to the calculation of the drift effective mobility.

The P3HT device data is extracted from Shuttle et al. (2010a) and was obtained with the same techniques. From this figure, it appears there are some deviations to different degrees from the Langevin prediction as defined in equation 2.17. As mentioned earlier in this chapter, this non-Langevin behaviour has been observed using different techniques.(Pivrikas et al., 2005a; Juška et al., 2006; Koster et al., 2006; Sliaužys et al., 2006; Shuttle et al., 2008c; Deibel et al., 2008; Lungenschmied et al., 2009)

In Chapter 5 of the thesis, we saw that the charge transport properties of PBDTTT-C:PCBM blend improved with PCBM loading with simultaneous improvement of drift mobility and carrier lifetime was observed. Interestingly, Table 8.4.2 presents the values obtained using the method detailed above at the excess carrier density of $n=2.5 \times 10^{16} \text{ cm}^{-3}$ corresponding to relatively high illumination.

To guarantee the space charge limited photocurrent is not established at these thicknesses ($\leq 100 \text{ nm}$), the corrected photocurrent was measured and the value obtained in reverse bias (-1.25 V) was measured at different illumination levels. Figure 8.5 presents the reverse bias corrected photocurrent obtained for the three blends ratios. The power law appears to be linear and consequently much higher than the theoretical 0.75 which would be synonymous of space charge limited

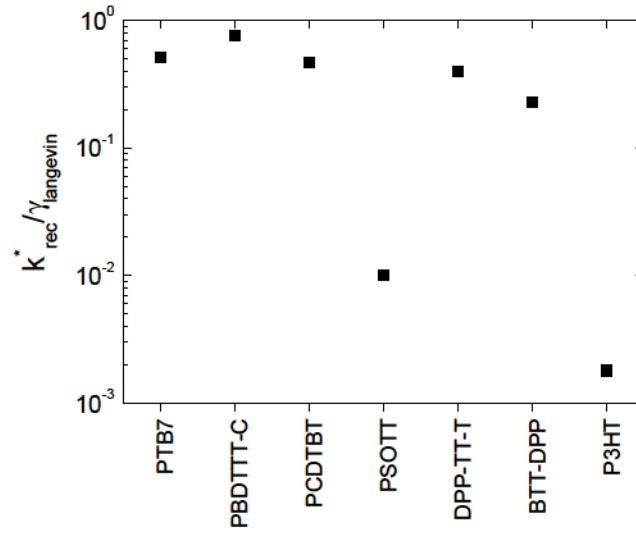


Figure 8.4: Ratio between apparent recombination rate k_{rec}^* taken at relatively high charge density ($n \approx 2.5 \times 10^{16} \text{ cm}^{-3}$) over the predicted recombination with Langevin expression based on drift mobility measured using charge extraction at short circuit.

photocurrent as explained just above.

Table 8.1: PBDTTT-C:PC₇₁BM, comparison apparent recombination rate and Langevin prediction

Blend ratio [% w]	$\mu_{\text{drift}}(n=2.5 \times 10^{16} \text{ cm}^{-3})$ [cm ² /Vs]	$k_{\text{rec}}^*(n=2.5 \times 10^{16} \text{ cm}^{-3})$ [cm ³ s ⁻¹]	γ_{Langevin} [cm ³ s ⁻¹]
1:1	2.6×10^{-5}	1.2×10^{-11}	1.25×10^{-11}
1:1.5	3.7×10^{-5}	7.2×10^{-12}	1.75×10^{-11}
1:2	4.9×10^{-5}	4.3×10^{-12}	2.25×10^{-11}

As can be observed from Figure 8.6, at the 1:1 blend ratio, it is remarkable that the apparent recombination rate is actually very close to the one predicted by the case of ideal Langevin recombination. As PBDTTT-C:PCBM is very amorphous, one could think that no specific ordering in the blend makes overall the transport quite isotropic. (Hou et al., 2009) Nevertheless, as the PCBM proportion is slightly increased, the effective mobility is increased and in parallel, the ratio of effective mobility to the one predicted by the case of ideal Langevin decreases. It could be argued that the PCBM loading increased the phase separation, however, over this narrow range of blend ratio, the blends are amorphous. In this particular system, it seems that the PCBM load improved the recombination lifetime, not directly affecting $\gamma_{\text{transport-limited}}$.

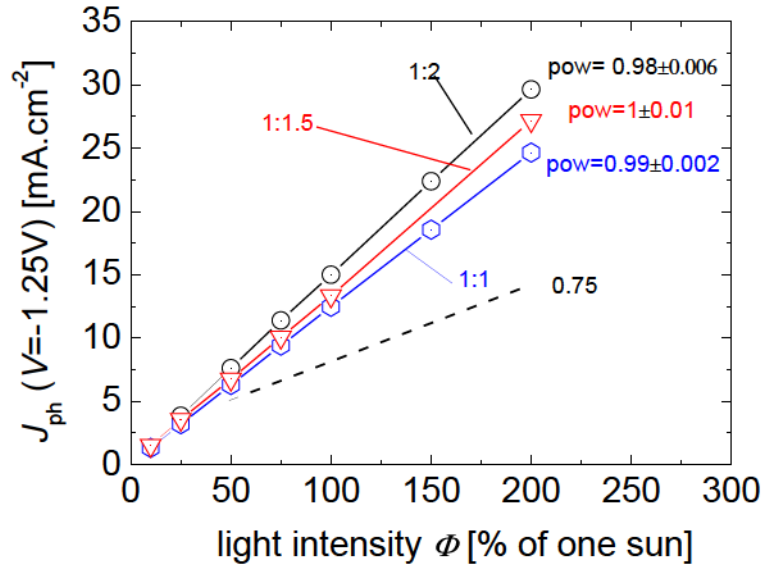


Figure 8.5: Reverse bias ($V=-1.25$ V) value of the photocurrent for the three blend ratios of PBDTTT-C:PC₇₁BM at different illumination levels ranging from [10;200]% sun.

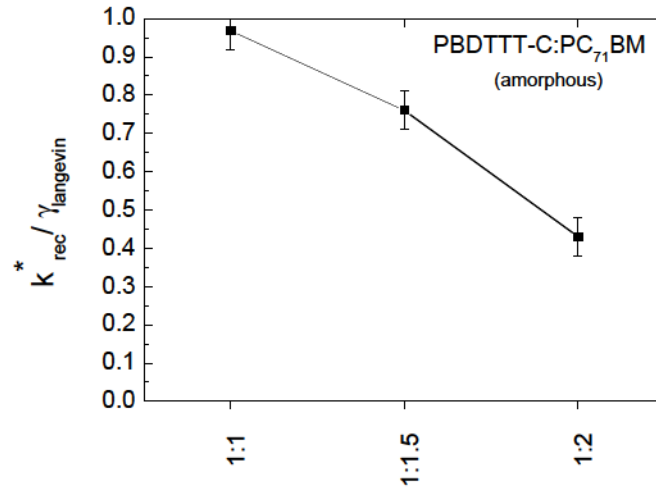


Figure 8.6: Ratio of apparent recombination rate at ($n \approx 2.5 \times 10^{16} \text{ cm}^{-3}$) and prediction from Langevin expression using the effective drift mobility at the same macroscopic density obtained by charge extraction at short circuit for PBDTTT-C:PC₇₁BM at three different blend ratios. The improvement of the quality of transport (at higher PCBM loading) by improvement of mobility and carrier lifetime were possible by decreasing the efficiency of recombination when "collision" occurs. The ratio recombination over collision decreased upon PCBM loading. We note that 1:1 blend was very close to extreme case of Langevin recombination.

8.5 Discussion: Non-Langevin recombination in the literature

Four main different explanations have been proposed to account for the slower observed recombination rate compared with predictions from Langevin's definition. Deibel et al. (2009) previously reviewed a few alternative explanations and these form a part of the review. Very often, recombination rate is compared to carrier mobility. However, the first and common difficulty resides in the fact that every recombination event is local while local variables are generally impossible to access.

8.5.1 The slower of the two

With the general definition of the Langevin recombination rate in Equation 2.17, if the two carriers have substantially different local mobilities, the recombination rate is determined by the fast carrier. However, Koster et al. (2006) noted that despite the intimate mixing of donor and acceptor in the bulk heterojunction, the bulk recombination event had to happen at the interface donor/acceptor. In this context, the limiting step for the two oppositely charged polarons to meet was actually governed by the slow carrier joining the heterojunction.. Consequently, it was suggested that the observed recombination rate $K^* < \gamma_{\text{langevin}}$ was less than that predicted by Langevin theory due to the phase separation of the two semiconductors and the fact that the two carriers might evolve into their relative phases with different mobilities. They suggested a correction of the Langevin recombination rate as follows:

$$\gamma = \frac{e \cdot \min(\mu_e; \mu_h)}{\epsilon_0 \epsilon_r} \quad (8.2)$$

8.5.2 Phase separation

Another explanation that considers the spatial separation of the carriers uses the concept of random potential landscape in disordered semiconductors introduced by Adriaenssens and Arkhipov (1997). In this approach, the band gap is constant, however, the electrons and holes in disordered media will accumulate in the local minima of potentials, as represented in Figure 8.7. In this way, the opposite carriers are physically separated, evolving separately from one minimum to another in their respective bands. To recombine, the energy barrier ΔE representing the spatial fluctuations of potential energy needs to be overcome. Consequently

Adrianssens suggested correcting the Langevin recombination rate as follows:

$$\gamma = \exp\left(-\frac{\Delta E}{k_B T}\right) \frac{e\mu_T}{\epsilon_0 \epsilon_r} \quad (8.3)$$

This expression is, in particular, consistent with some observations of the temperature dependence of the recombination rate observed in some polymer systems. (Koster et al., 2006; Juška et al., 2006)

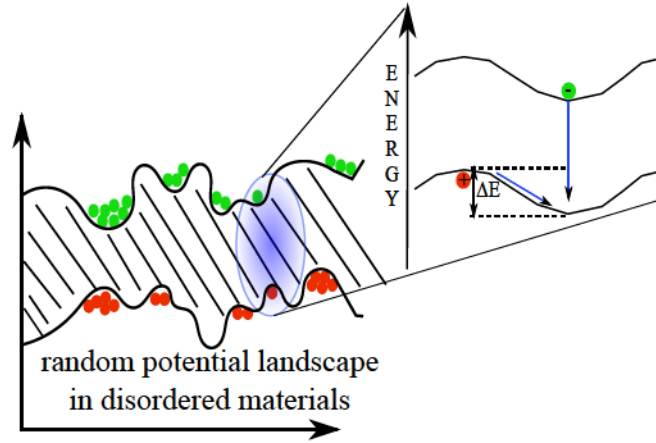


Figure 8.7: Depiction of the effect of random potential landscape in disordered media on the recombination rate.

8.5.3 Spatial distribution

As presented in Chapter 6 of this thesis, the spatial distributions of carriers are not always homogeneous, in particular when the recombination rate is assessed (at open circuit) for light levels that are not excessively high (in thin devices $\leq 100\text{nm}$). Consequently, especially at low light levels, the carriers are more sheltered from the opposite carriers due to uneven spatial distributions, making the apparent recombination rate lower than predicted by Langevin rate, assuming that all the charges can explore the same 3D-space. Deibel et al. (2009) suggests the inclusion of the prefactor ζ in front of the Langevin expression such that $\zeta = K_{\text{langevin}}/K^*$ where:

$$\zeta = \frac{\frac{1}{d} \int_0^d n(x)p(x) dx}{\bar{n}(x) \cdot \bar{p}(x)} \quad (8.4)$$

In practice, a mismatch between the corrected expression and the apparent recombination rate can be observed: $\zeta = \zeta_{\text{concentrationgradient}} \times \zeta_{\text{static}}$ where ζ_{static} was thought to represent the effects of differences between the dielectrics constants of

the two acceptor/donor phases as suggested by Szmytkowski (2009). The latter could even represent the potential presence of deep traps within the band gap, too deep to be able to be thermally activated or to let a free opposite carrier recombine with a carrier sitting in one of these states.

8.5.4 Deep trap states within the band gap

Finally, as previously mentioned, the presence of localised states within the band gap will slow down the recombination rate and is generally responsible for the carrier density dependence of the mobility and recombination rate. In effect, the trapped carrier is temporarily protected from meeting opposite charge carriers. TAS measurements usually probe at much higher excitations densities and a transition from a trap limited to a free-to-free recombination mechanism has been previously observed. (Clarke et al., 2009) The higher excitation densities will also suppress problems of variation in spatial distribution of carriers.

8.5.5 The common assumption

Comparing macroscopic values to local events is a particularly difficult task in the disordered media that are polymer:fullerene bulk heterojunctions. Variations from one system to another are expected to be substantial and not only sensitive to the specific blend morphology but also to deposition techniques. All the different cases explained above are likely to be present to varying extents in the different solar cells found currently in the literature. However, conceptually, these four points share a common fundamental assumption: that in the process of non-geminate recombination in polymer:fullerene blends, the carriers finding each other is the limiting step. With this in mind, it seems logical that faster carriers are more likely to recombine, as the process of finding each other is faster. Following the same logic, every event that prevents the opposite carriers from finding each other will slow down the apparent recombination rate. However, within the current literature, there is no proof that the ratio recombination over collision is generally unity. For instance, as pictured in Figure 8.8, once a carrier is under an electric interaction with an opposite carrier which is stronger than thermal energy, the likelihood of escape is probably higher if the carrier is very mobile in its phase than if it is slow or even "waiting" at the interface. Furthermore, at the scale of capture radius, the spatial extent of wavefunctions could be probably more appropriate to describe the charges similarly to how charge separation is usually tackled, with charge transfer states and the Onsager-Braun theory. Moreover, if entropy is sometimes mentioned as an extra driving force to enhance charge separation at the

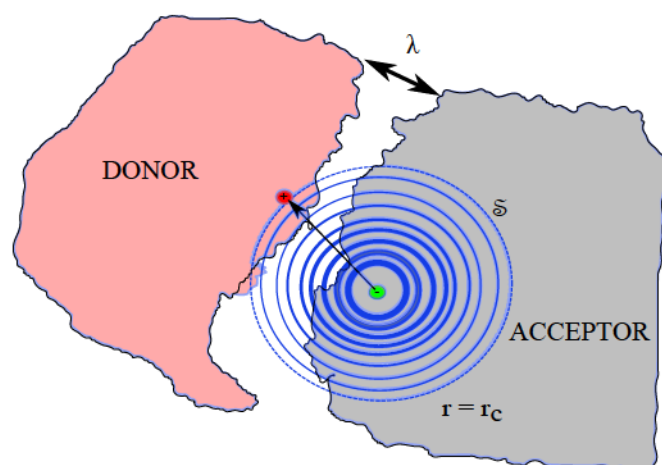


Figure 8.8: Depiction of two opposite carriers at a heterojunction. While the hole (red spot) can be well within the coulomb capture radius of the electron (green spot), it is far from obvious that the recombination efficiency will be unity: the mobility of the hole might be large enough to escape from the coulomb attraction of the electron, though the distance between the two phases l can be small enough locally; ballistic recombination might not be sufficient to describe recombination event and the charge transfer state might be necessary. The reorganisation energy necessary to make the recombination occur could be critical.

heterojunction, non-geminate recombination is definitely not assisted by entropy effects.

8.5.6 Langevin's work on recombination of ions in gas phase

Langevin recombination rate was used and verified experimentally in different organic systems. However, in its original context of recombination of ions in gas phase, Langevin's statement was slightly different from how it is used today: if we assume $p = eP$ and $n = eN$ and the recombination of ions α such as:

$$\frac{dp}{dt} = \frac{dn}{dt} = -\alpha pn \quad (8.5)$$

Langevin states that the ratio ε , which defines the number of recombinations over collisions between two ions of opposite charges, is always smaller or equal to unity

$$\varepsilon = \frac{\alpha}{4\pi(k_1 + k_2)} \quad (8.6)$$

In the original paper, the demonstration was conducted in GCS units and given that:

- the Gauss law in vacuum in CGS system is $\nabla \cdot E = 4\pi\rho$ while it is $\nabla \cdot E = \rho/(\varepsilon_0)$ in SI system.
- that the material is a real dielectrics and not vacuum.
- in Langevin's demonstration the number of charge per unit volume is N and P .

One can easily come back to the Langevin recombination rate γ_{langevin} as it is traditionally used today. Experience confirms that this ratio ε is always smaller than 1 and tends toward this value when the pressure in the gas increases. (Langevin, 1903)

8.6 Further discussion

Langevin type recombination was proposed and verified to explain non-geminate recombination in organic materials very early in the research in organic semiconductors. (Karl and Sommer, 1971). However, in these early cases, the media were usually very homogeneous (like anthracene) and not always very representative of a bulk heterojunction.

Indeed, in our system, transport is rarely 3D and isotropic. Once in the Onsager sphere, the drift of one charge into the electric field created by a neighbour opposite charge was taken into account to establish the Langevin expression (see Chapter 2). However, this assumed a very isotropic transport. If the morphology of the blend is such that the transport is non 3D and some specific directions are favored, the diffusion term must be taken into account, as has been suggested by Nenashev et al. (2010); Greenham and Bobbert (2003). In particular, it is argued that a high degree of ordering is likely to impose some specific anisotropy in the transport of polarons.

To mirror Langevin's work adapted to non-geminate recombination in bulk heterojunctions, two classes of arguments must be taken into account: all the arguments which will influence the extreme case of Langevin recombination with "the carriers finding each other" being the limited step ($\gamma_{\text{transport-limited}}$) and on the other end, the ratio ε , also termed 'recombination efficiency' by Groves and Greenham (2008).

$$k_{\text{eff}}^* = \varepsilon * \gamma_{\text{transportlimited}} \quad (8.7)$$

In the light of the previous section, it is difficult to bring definitive answer to the phenomenon responsible for the observed non-Langevin behaviour of the devices presented herein. Regarding P3HT:PCBM and PSOTT:PCBM, the non-Langevin behaviour is most likely driven by phase segregation (so a transport limited argument) as these two systems show generally low photoluminescence quenching, high crystallinity and evidence of large domains. (Subramaniyan et al., 2011; Shoaee et al., 2010) Interestingly, DPP-TT-T which is crystalline according to Chapter 4, is showing a much closer match to the Langevin prediction than the other crystalline materials especially for BTT-DPP (with the same blend ratio and crystallinity level). Regarding the blend ratio perturbation study with PBDTTT-C, no morphology study indicated any degree of crystallinity and the CT emission was shown in Chapter 5 to shift with the slight fullerene loading. Further measurements would be necessary to probe the energetics at the heterojunction prior to a recombination event in the bulk and this goes beyond the scope of this thesis. No evidence can exclude the non unity of the recombination efficiency ε in some of the systems presented. Nevertheless, it becomes apparent that a shift away from a macroscopic approach of recombination might be necessary to attempt to understand further the nature of the recombination events. The consideration of the spin of the polarons prior to recombination and the formation of singlet and triplet charge transfer states and their influence on the recombination efficiency ε in OPV is for example a step towards a more molecular view of non-geminate

recombination.(Rao et al., 2013; Lakhwani et al., 2014)

8.7 Conclusions

Carrier mobility is usually accessed experimentally at short circuit. Investigating charge transport in different systems requires a comparison between mobility and lifetime in the same net field conditions. Furthermore, the highly disordered nature of polymer:fullerene solar cells makes the link between macroscopic measurements and local physical events in the blend difficult to establish. Nevertheless, many techniques showed that non-geminate recombination rate was substantially lower than the one predicted by the ideal case of Langevin recombination.

We reviewed different explanations in the literature to account for these observations. The underlying assumption that the recombination is transport limited is highlighted and discussed. This analysis suggests that the non-geminate recombination rate should be considered as a product between transport limited recombination rate (called Langevin type of recombination) times the efficiency of recombination (once the carriers are in strong electrostatic interaction).

Conclusions and Future Work

The main focus of this thesis was to investigate the non-geminate recombination by combined experimental and modeling studies in bulk heterojunction solar cells. A range of different polymer:fullerene systems were studied to obtain an insight into the fundamental parameters which would eventually enable these losses to be reduced. The conclusions of each chapters are briefly summarised before suggesting future works on this topic.

9.1 Conclusions

After a description of the optoelectronic techniques used regularly in this thesis, we saw in Chapter 4 that charge extraction and transient photovoltage techniques are robust experimental techniques to quantify non-geminate recombinations not only in polythiophene devices but also in many different types of polymer:fullerene solar cells with various levels of crystallinity. Charge transport seems to be critical for device performance in the power generating quadrant once these devices have been optimised and further improvement of these solar cells requires more precise understanding of the exact dominant loss process which can be, in principle, numerous. Light ideality factor measured by the way the open-circuit voltage scales with many illumination levels allowed, when the dark shunt resistance is sufficiently high, the investigation of the different types of dominant non-geminate losses in more details. In particular, a consistent transition from bulk (either trap mediated or free-to-free) recombination to surface recombination at higher light levels was observed. This indicates that transport and contacts are equally important.

In Chapter 5, the resulting shifts in electronic properties of an amorphous blend upon blend ratio perturbation was investigated. The method employed proved, in this case, to allow powerful quantification of the clear variations in energetics at the heterojunction and carrier dynamics with yet a slight change in fullerene content and allowed understanding the overall devices performance observed for three blend ratios. In particular, the effective mobility of the carriers and lifetimes were observed to be simultaneously improved with increasing

PCBM loading, which goes against the concept of transport limited recombination (Langevin type recombination) proposed regularly in the literature. Furthermore, a quantitative agreement between charge extraction at open circuit and electroluminescence probing the energetics at the heterojunction was demonstrated.

In Chapter 6 and 7, two challenges relating to the experimental techniques for investigating non-geminate recombination were tackled. First, in Chapter 6, the effect of variations in spatial distribution of carriers on the quantification of the non-geminate recombination rate were studied by combined drift-diffusion modeling and experiments. The results confirm previous modeling studies of open-circuit recombination dynamics. In particular, we find that the reaction order can substantially increase in thin devices, while the actual recombination mechanism is not changed. Moreover, using the same approach, the effects of the variations in doping level from batch-to-batch on device performance and the analysis of recombination dynamics were investigated in depth. It was eventually demonstrated that optimised polymer:fullerene solar cells have to have a maximum doping level of $N_A^{\max} \leq 6 - 7 \times 10^{15} \text{cm}^{-3}$ to maximise power conversion efficiencies and make the most of the absorption of the active layer.

Finally, in the final chapter, the different interpretations of reduced Langevin recombination in the literature were briefly reviewed. Based on experimental data, the common underlying assumption that the ratio collision over recombination should be unity is seriously questioned as this neglects the way Langevin stated his initial results and some rare experimental results. An alternative way to formulate Langevin recombination is needed, knowing that its impact on proposed design rules for improved organic solar cell performance is substantial.

9.2 Suggestions for future work

First, from a pure experimental viewpoint, it would be useful to be able to implement the charge extraction technique on devices with poor collection or with deep trap states. To do this, a change in the way the sweep out of excess carriers is required. Instead of conducting this sweep at short circuit, reverse bias could be employed. A few experimental pitfalls will also have to be avoided, such as carrier injections while the sweep out is conducted under reverse bias.

Although many investigations of non-geminate recombination are focusing on bulk recombination, surface recombination seems as critical in some systems, even at operating illuminations. More work is needed today on optimising the interface electrode/active layer and see how different experimental techniques allow fine investigations of these surface recombinations.

The potential sources of unintentional doping in polymer:fullerene blends are many, from the synthesis, to device fabrication, storage or even operation. However, methods to control and (if possible) to reduce it irreversibly, to values enabling device optimisation at the second interference maximum, are strongly needed.

While we saw that increased fullerene content resulted in higher effective mobility in one system, more device optimisation for systems where PCBM is the major absorber could potentially be interesting, as the loss of absolute absorption can be compensated by thicker active layer due to enhanced charge transport properties with higher fullerene loading.

Finally, a more detailed understanding of why non-geminate recombination in some polymer:fullerene systems is transport limited (extreme case of Langevin recombination) while in others, it is limited by the efficiency of recombination is of particular interest. This eventually could lead to finer rules on optimal molecular structures and film deposition techniques to enhance the mobility-lifetime product for thicker active layers and allow optimal light harvesting in the organic solar cells.

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Appendix A

Table A.1: Parameters used for the PCDTBT:PCBM thickness series.

Name	Symbol	65nm	85nm	158nm
Generation rate	$G [\text{cm}^{-3}]$	8.9×10^{21}	6.3×10^{21}	3.2×10^{21}
Parallel resistance light	$R_{plight} [\Omega \text{cm}^2]$	120	88	180
Parallel resistance dark	$R_{pdark} [\Omega \text{cm}^2]$	5×10^5	4×10^6	7×10^6
electron mobility	$\mu_n [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	5×10^{-4}		
hole mobility	$\mu_p [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	5×10^{-4}		
effective DoS-cb	$N_C [\text{cm}^{-3}]$	1×10^{19}		
effective DoS-vb	$N_V [\text{cm}^{-3}]$	1×10^{19}		
conduction band tail	$N_{Ctail} [\text{cm}^{-3}]$	2.2×10^{18}		
valence band tail	$N_{Vtail} [\text{cm}^{-3}]$	2.2×10^{18}		
tail slope cb	$E_{chC} [\text{meV}]$	110		
tail slope vb	$E_{chV} [\text{meV}]$	110		
capture coefficients	$\beta_n^+ [\text{cm}^3 \cdot \text{s}^{-1}]$	2×10^{-13}		
capture coefficients	$\beta_p^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	1.2×10^{-10}		
capture coefficients	$\beta_p^- [\text{cm}^3 \cdot \text{s}^{-1}]$	2×10^{-13}		
capture coefficients	$\beta_n^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	1.2×10^{-10}		
band gap	$E_g [\text{eV}]$	1.3		
Ext serie resistance	$R_s [\Omega \text{cm}^2]$	0		
surface recombination	$S [\text{cm}^2 \cdot \text{s}^{-1}]$	10^5		
contact barrier front	$\varphi_{bf} [\text{meV}]$	200		
contact barrier back	$\varphi_{bb} [\text{meV}]$	50		
temperature	TT [K]	300	300	300

The shape of tail states in the band gap assumed in the ASA modelling used in this thesis was previously described with Equation 2.1 using E_{chC} , E_{chV} , $N_{0CBtail}$ and $N_{0VBtail}$ as parameters.

Furthermore, μ_p and μ_n are the band mobilities.

In the simulations about the influence of the surface recombination on the light ideality factor presented in Chapter 4, the recombination velocity is proportional to the density of surface states active in recombination at the interface between the active layer and the electrode as well as the capture cross section of these states. At this interface, the accumulation of minority carriers (here holes at the cathode)

Table A.2: Parameters used for the PCDTBT:PCBM CaAl comparison.

Name	Symbol	Ca/AL	Al
Generation rate	$G [\text{cm}^{-3}]$	8.3×10^{21}	6.1×10^{21}
Parallel resistance light	$R_{plight} [\Omega \text{cm}^2]$	1300	1300
Parallel resistance dark	$R_{pdark} [\Omega \text{cm}^2]$	3000	10^4
Ext series resistance	$R_s [\Omega \text{cm}^2]$	0	60
contact barrier back	$\varphi_{bb} [\text{meV}]$	100	240
surface recombination	$S [\text{cm}^2 \cdot \text{s}^{-1}]$	10^5	10
electron mobility	$\mu_n [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	7×10^{-4}	
hole mobility	$\mu_p [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	7×10^{-4}	
effective DoS-cb	$N_C [\text{cm}^{-3}]$	1×10^{19}	
effective DoS-vb	$N_V [\text{cm}^{-3}]$	1×10^{19}	
conduction band tail	$N_{Ctail} [\text{cm}^{-3}]$	1.1×10^{18}	
valence band tail	$N_{Vtail} [\text{cm}^{-3}]$	1.1×10^{18}	
tail slope cb	$E_{chC} [\text{meV}]$	110	
tail slope vb	$E_{chV} [\text{meV}]$	110	
capture coefficients	$\beta_n^+ [\text{cm}^3 \cdot \text{s}^{-1}]$	1.5×10^{-12}	
capture coefficients	$\beta_p^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	1.2×10^{-10}	
capture coefficients	$\beta_p^- [\text{cm}^3 \cdot \text{s}^{-1}]$	1.5×10^{-12}	
capture coefficients	$\beta_n^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	1.2×10^{-10}	
band gap	$E_g [\text{eV}]$	1.29	
temperature	$TT [\text{K}]$	300	300

depends on the ease with which the holes are diffusing against any built-in electric field. However, the measurements of light ideality factors are conducted at open circuit. Consequently, the built-in field is weak and the diffusion of holes at the cathode will be only controlled by their mobility according to the Einstein relation between diffusion coefficient and mobility. On the other hand, The majority carrier at the contacts are fixed by the workfunctions and the related band edges according to Equation 2.9.

The surface recombination flux J_S is directly proportional to density of minority carriers (hence an ideality factor of 1) and it is assumed that the surface recombination velocity does not depend on the density of minority carriers:

$$J_S = qS_{\text{minority}}\Delta n_{\text{minority}} \quad (\text{A.1})$$

In practice, only a difference between S_{minority} being low (typically $1\text{-}10\text{ cm}^2.\text{s}^{-1}$) and high (typically $10^4\text{-}10^6\text{ cm}^2.\text{s}^{-1}$) is observable, which means beyond a certain value of surface recombination velocity, every minority carrier arriving at a surface state active in recombination is considered to recombine necessarily.

Moreover, the trap assisted recombination is considered in the model based on Shockley-Read-Hall statistics. In Figure A.1, the four capture and emission processes involving a single trap interacting with both the valence and conduction bands are depicted. In the case of a single trap captures both one electron and one hole, there is trap-assisted recombination. On the other hand, if one trap captures first and then emits one same carrier, the trap participates to slow down the carrier transport. In quasi-equilibrium, these four rates are connected and the calculation of the occupation probability of this trap f_{SRH} can be calculated as shown in more details for example in Kirchartz and Nelson (2013). Overall, the net recombination rate via any distribution of traps $N_t(E)$ is given by :

$$R = \int_v^c N_t(E) \beta_n^+ \beta_p^- \frac{np - n_i^2}{n\beta_n^+ + p\beta_p^- + \beta_n^0 + \beta_p^0} dE \quad (\text{A.2})$$

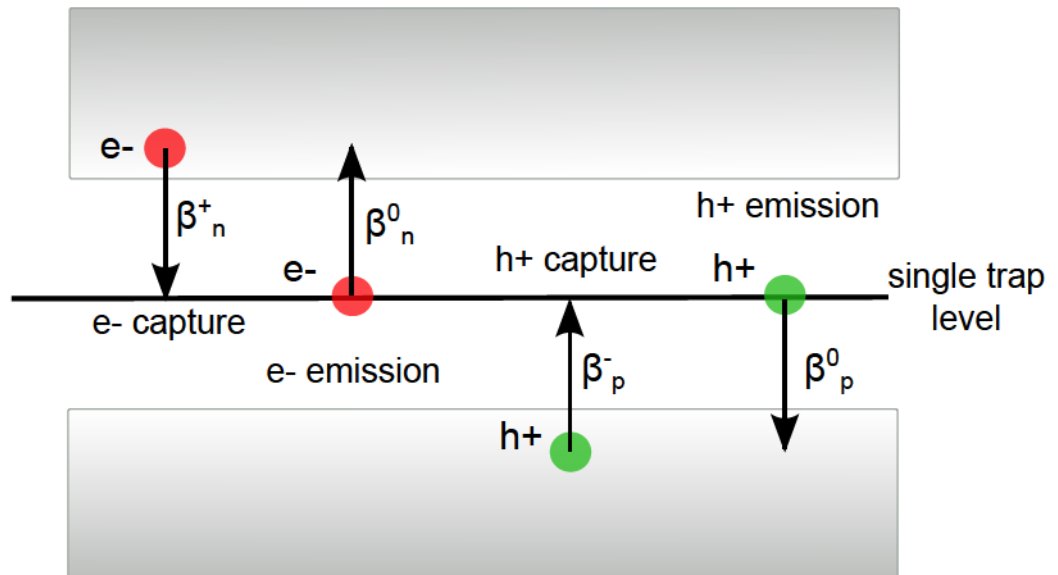


Figure A.1: Depiction of electron and hole capture and emission coefficients used in ASA modelling.

Appendix B

Table B.1: Parameters used for the PTB7:PCBM thickness series.

Name	Symbol	PTB760nm	PTB790nm	PTB7130nm
Generation rate	$G [\text{cm}^{-3}]$	2×10^{22}	9×10^{21}	6×10^{21}
electron mobility	$\mu_n [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	1.37×10^{-3}		
hole mobility	$\mu_p [\text{cm}^2 \cdot (\text{Vs})^{-1}]$	1.37×10^{-3}		
effective DoS-cb	$N_C [\text{cm}^{-3}]$	1×10^{19}		
effective DoS-vb	$N_V [\text{cm}^{-3}]$	1×10^{19}		
conduction band tail	$N_{Ctail} [\text{cm}^{-3}]$	2.8×10^{20}		
valence band tail	$N_{Vtail} [\text{cm}^{-3}]$	2.8×10^{20}		
tail slope cb	$E_{chC} [\text{meV}]$	110		
tail slope vb	$E_{chV} [\text{meV}]$	110		
direct recombination	$R_{direct} [\text{cm}^3 \cdot \text{s}^{-1}]$	7.3×10^{-16}		
capture coefficients	$\beta_n^+ [\text{cm}^3 \cdot \text{s}^{-1}]$	3.9×10^{-13}		
capture coefficients	$\beta_p^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	11×10^{-10}		
capture coefficients	$\beta_p^- [\text{cm}^3 \cdot \text{s}^{-1}]$	3.9×10^{-13}		
capture coefficients	$\beta_n^0 [\text{cm}^3 \cdot \text{s}^{-1}]$	1×10^{-10}		
band gap	$E_g [\text{eV}]$	1.03		
surface recombination	$S [\text{cm}^2 \cdot \text{s}^{-1}]$	10^5		
contact barrier front	$\varphi_{bf} [\text{meV}]$	0		
contact barrier back	$\varphi_{bb} [\text{meV}]$	0		
temperature	TT [K]	300	300	300

Table B.2: Parameters used for the P3HT:PCBM thin device.

Name	Symbol	85nm
Generation rate	G [cm^{-3}]	7×10^{21}
electron mobility	μ_n [$\text{cm}^2 \cdot (\text{Vs})^{-1}$]	8×10^{-1}
hole mobility	μ_p [$\text{cm}^2 \cdot (\text{Vs})^{-1}$]	1×10^{-1}
effective DoS-cb	N_C [cm^{-3}]	2.3×10^{18}
effective DoS-vb	N_V [cm^{-3}]	9.8×10^{19}
conduction band tail	N_{Ctail} [cm^{-3}]	7.9×10^{20}
valence band tail	N_{Vtail} [cm^{-3}]	7.6×10^{20}
tail slope cb	E_{chC} [meV]	59
tail slope vb	E_{chV} [meV]	29
direct recombination	R_{direct} [$\text{cm}^3 \cdot \text{s}^{-1}$]	2.5×10^{-9}
capture coefficients	β_n^+ [$\text{cm}^3 \cdot \text{s}^{-1}$]	1.75×10^{-11}
capture coefficients	β_p^0 [$\text{cm}^3 \cdot \text{s}^{-1}$]	1.97×10^{-10}
capture coefficients	β_p^- [$\text{cm}^3 \cdot \text{s}^{-1}$]	6.44×10^{-11}
capture coefficients	β_n^0 [$\text{cm}^3 \cdot \text{s}^{-1}$]	9.35×10^{-10}
band gap	E_g [eV]	1.17
surface recombination	S [$\text{cm}^2 \cdot \text{s}^{-1}$]	6×10^6
contact barrier front	φ_{bf} [meV]	69
contact barrier back	φ_{bb} [meV]	13
temperature	TT [K]	300

Appendix C

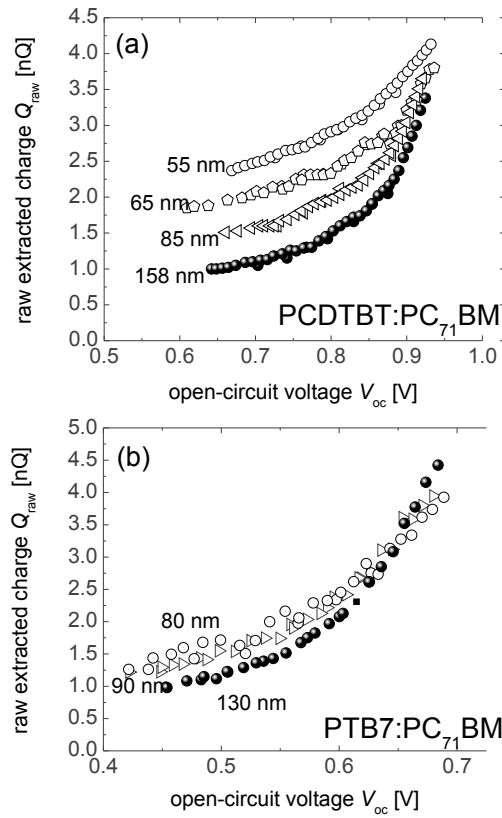


Figure C.1: Raw extracted charges from charge extraction at open circuit for two others thickness series of low doping level (a) PCDTBT:PC₇₁BM at 55, 65, 85 and 158 nm and (b) PTB7:PC₇₁BM at 80, 90 and 130 nm.

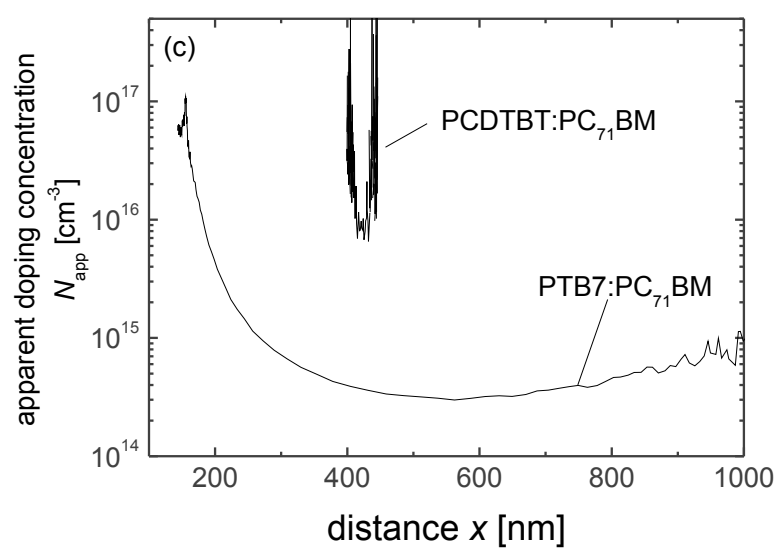


Figure C.2: Mott-Shottky analysis of drop cast films of (a) PCDTBT:PC₇₁BM and (b) PTB7:PC₇₁BM.

Appendix D

Table D.1: Parameters used for the DPP-TT-T:PCBM thickness series.

Name	Symbol	DPP75nm	DPP160nm	DPP300nm
Generation rate	$G [\text{cm}^{-3}]$	1.21×10^{22}	6.55×10^{21}	4.34×10^{21}
electron mobility	$\mu_n [\text{cm}^2 \cdot (\text{Vs})^{-1}]$		4.6×10^{-3}	
hole mobility	$\mu_p [\text{cm}^2 \cdot (\text{Vs})^{-1}]$		4.6×10^{-3}	
effective DoS-cb	$N_C [\text{cm}^{-3}]$		3.1×10^{19}	
effective DoS-vb	$N_V [\text{cm}^{-3}]$		1×10^{19}	
conduction band tail	$N_{Ctail} [\text{cm}^{-3}]$		1.12×10^{16}	
valence band tail	$N_{Vtail} [\text{cm}^{-3}]$		2.36×10^{18}	
tail slope cb	$E_{chC} [\text{meV}]$		330	
tail slope vb	$E_{chV} [\text{meV}]$		330	
direct recombination	$R_{direct} [\text{cm}^3 \cdot \text{s}^{-1}]$		6.8×10^{-8}	
capture coefficients	$\beta_n^+ [\text{cm}^3 \cdot \text{s}^{-1}]$		3.8×10^{-13}	
capture coefficients	$\beta_p^0 [\text{cm}^3 \cdot \text{s}^{-1}]$		1.6×10^{-10}	
capture coefficients	$\beta_p^- [\text{cm}^3 \cdot \text{s}^{-1}]$		4.5×10^{-11}	
capture coefficients	$\beta_n^0 [\text{cm}^3 \cdot \text{s}^{-1}]$		1.3×10^{-11}	
band gap	$E_g [\text{eV}]$		1.08	
surface recombination	$S [\text{cm}^2 \cdot \text{s}^{-1}]$		1.3×10^5	
contact barrier front	$\varphi_{bf} [\text{meV}]$		7	
contact barrier back	$\varphi_{bb} [\text{meV}]$		7	
temperature	TT [K]		300	

N_A was varied from 1.5×10^{16} to $8 \times 10^{16} \text{ cm}^{-3}$ between the two different batches.

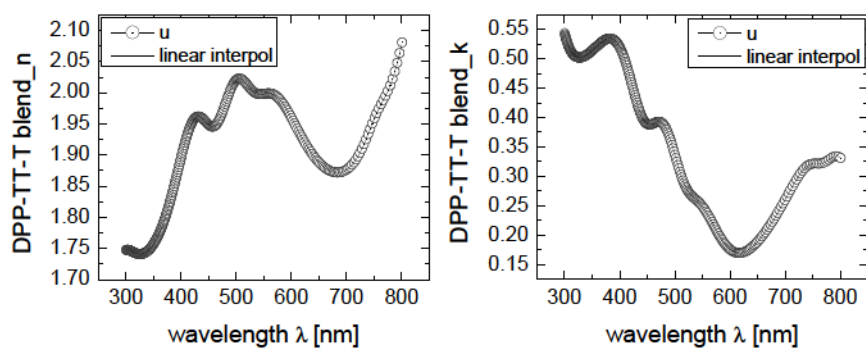


Figure D.1: Ellipsometry data on DPP-TT-T^u:PC₇₁BM 88 nm films deposited on quartz.

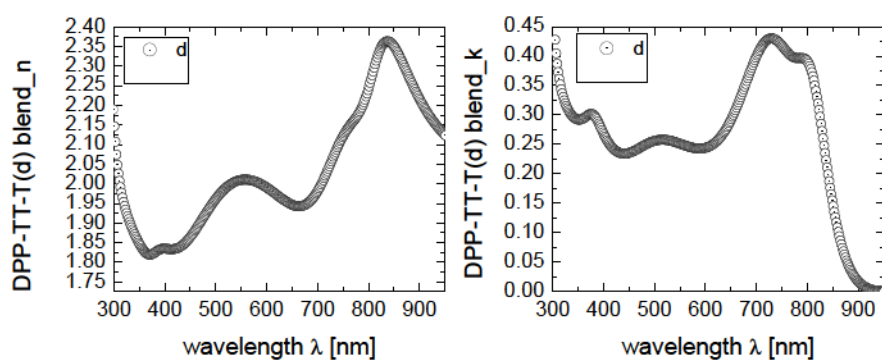


Figure D.2: Ellipsometry data on DPP-TT-T^d:PC₇₁BM $\approx$ 80 nm films deposited on quartz.