DESIGNING THIN FILM SOLAR CELLS
FOR OPTIMUM PHOTOVOLTAIC PERFORMANCE

by

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(BSc. Physics, MSc. Solid State Physics)

A thesis submitted in fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Faculty of Engineering, Health, Science and the Environment
Charles Darwin University

January 2017
Thesis declaration

I hereby declare that this submission towards the degree of Doctor of Philosophy of the Charles Darwin University is the result of my own investigations and all references to ideas and work of other researchers have been specifically acknowledged. I hereby certify that the work embodied in this thesis has not already been accepted in substance for any degree and is not being currently submitted in candidature for any other degree.

David Ompong

January, 2017
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Appendix C Copyright permissions
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air Mass 1.5</td>
</tr>
<tr>
<td>BCP</td>
<td>Bathocuproine, or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>Bis-PCBM</td>
<td>Bisadduct of phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CBP</td>
<td>4,4′-bis(9-carbazolyl)-1,1′-biphenyl</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium telluride</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium di-selenide</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>CuPc</td>
<td>Copper phthalocyanine</td>
</tr>
<tr>
<td>D-A</td>
<td>Donor acceptor</td>
</tr>
<tr>
<td>DDO-PPP</td>
<td>Poly (p-phenylene)</td>
</tr>
<tr>
<td>DIP</td>
<td>Di-indenoperylene</td>
</tr>
<tr>
<td>ESOI</td>
<td>Exciton-spin-orbit interaction</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>F8BT</td>
<td>Poly(9,9-dioctylfluorene-cobenzothiadiazole)</td>
</tr>
<tr>
<td>F8TBT</td>
<td>poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2’,2’”-diyl)</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonance energy transfer</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>Ir(ppy)3</td>
<td>Fac-tris-(phenylpyridine) iridium</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene)</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)</td>
</tr>
<tr>
<td>nc-ZnO</td>
<td>Zinc oxide nanoparticles</td>
</tr>
<tr>
<td>NPD</td>
<td>N,N'-bis (naphthalen-1-yl)-N, N'-bis(phenyl)-benzidine</td>
</tr>
<tr>
<td>OAAM</td>
<td>Optical admittance analysis method</td>
</tr>
<tr>
<td>OHSC</td>
<td>Organic hybrid solar cells</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PBDTBDD</td>
<td>poly(((4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethyl)) co-(5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c’]dithiophene-4,8-dione))</td>
</tr>
<tr>
<td>PCBM</td>
<td>1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-phenyl C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>Poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PCPs</td>
<td>(\pi)-conjugated polymers</td>
</tr>
</tbody>
</table>
PDHFHPPV  Poly(dihexylfluorenedihexoxyphenylenedivinylene)
PDHFV  Poly(dihexylfluorenevinylene)
PEDOT:PSS  Poly (3, 4-ethylenedioxythiophene):poly(styrenesulfonate)
POV  Poly(triphenylmethoxytriazinediethyldiethylhexyloxyphenylenedivinylene)
PPV  Poly (1,4-phenylene-vinylene)
Pt  Platinum
PTB7  Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexy)carbonyl]thieno[3,4-b]thiophenediyl]]
PTCDA  3,4,9,10-perylenetetracarboxylic dianhydride
PTCBI  3,4,9,10-perylene tetracarboxylic-bis-benzimidazole
PTEH  Poly(triphenyltriazinediethylhexyloxyphenylenedivinylene)
PtOEP  Polycrystalline 2,3,7,8,12,13,17,18-octaethyl-21H23H-porphine platinum II
Si NCs  Silicon nanocrystals
Si-PCPDTBT  Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta2,1-b:3,4-b’]dithiophene-siloe 2,6-diyl]]
SubPc  Boron subphthalocyanine chloride
T  Temperature
TCO  Transparent conducting oxide
TIR  Total internal reflection
Voc  Open-circuit voltage
List of Symbols

$\varepsilon_o$ Absolute permittivity

$A_l(\lambda)$ Absorbance in the $l$th layer

$\alpha_{ab}$ Absorption coefficient

$y$ Admittance of a medium

$I_e(I_h)$ Angular momentum of electron (hole)

$Z$ Atomic number

$L$ Average length of a molecular orbital

$k_B$ Boltzmann constant

$N$ Complex refractive index

$k$ Coulomb constant

$\varepsilon$ Dielectric constant or relative dielectric permittivity

$R_{da}$ Donor acceptor distance of separation

$E_g$ Effective band gap

$N_e(N_h)$ Effective density of states for LUMO (HOMO) of acceptor (donor) material

$y_{\text{eff}}$ Effective optical admittance

$\vec{E}$ Electric field

$\nabla U(\nabla C)$ Electrical (chemical) potential gradient

$n(p)$ Electron (hole) concentration

$J_n(J_p)$ Electron (hole) current density

$m_e(m_h)$ Electron (hole) mass

$\mu_e(\mu_h)$ Electrons (hole) mobility

$E_{F,e}(E_{F,h})$ Electron (hole) quasi Fermi level
$P$  Electron: hole mobility ratio

$s_e(s_h)$  Electron (hole) spin

$e$  Electronic charge

$|0\rangle$  Electronic vacuum state

$\Delta$  Energy loss due to energetic term

$D$  Exciton diffusion coefficient

$L_D$  Exciton diffusion length

$\tau_h$  Exciton hopping time

$a_x$  Excitonic Bohr radius

$k$  Extinction coefficient

$\hat{\psi}_e(\hat{\psi}_h)$  Field operator for an electron(hole) in the LUMO (HOMO)

$R_f(R_d)$  Förster (Dexter) radius

$k_f(k_d)$  Förster (Dexter) transfer rate

$\nabla E_{F,e}(\nabla E_{F,h})$  Gradient of the electron (hole) quasi-Fermi level

$g$  Gyromagnetic ratio

$\tau_s(\tau_f)$  Lifetime of singlet (triplet) exciton

$\vec{H}$  Magnetic field

$\alpha$  Material-dependent parameter representing the ratio of the magnitude of the Coulomb and exchange interactions between the electron and hole in an exciton

$|v_i\rangle$  Molecular vibrational occupation state

$p_e(p_h)$  Orbital momentum of electron (hole)

$\delta$  Phase difference
\( \hbar \omega \) Photon of energy

\( k_{isc} \) Rate of intersystem crossing

\( \beta \) Recombination coefficient

\( \mu_x \) Reduced mass of exciton

\( \mu \) Reduced mass of the electron in a hydrogen atom

\( h \) Reduced Planck’s constant

\( n \) Refractive index

\( c \) Speed of light

\( \Phi(\lambda) \) Spectral density of the photon irradiance

\( \psi_j \) Time average numerical magnitude of the Poynting’s vector at the \( j \)th and the \( (j+1) \)th boundaries

\( A(\lambda) \) Total absorbance

\( J \) Total angular momentum

\( R(\lambda) \) Total reflectance

\( T(\lambda) \) Total transmittance

\( \rightarrow \) Unit vector

\( b_{nv}^\dagger(b_{nm}) \) Vibrational creation (annihilation) operator

\( \phi_{LUMO}(\phi_{HOMO}) \) Wavefunctions of the electron (hole) in the LUMO (HOMO)

\( \lambda \) Wavelength
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Abstract

In this thesis, theoretical studies on the various operation mechanisms of bulk heterojunction solar cells have been carried out, with the view of enhancing their photovoltaic performance. The processes considered in this thesis include mechanism of intersystem crossing of excitons, diffusion of excitons, probability of recombination of free charge carriers into their excitonic states, and charge carrier transport. The results obtained from the above theoretical works have inspired the optimisation of two types of bulk heterojunction solar cells by simulation, using the optical admittance analysis method (OAAM). After the introduction in chapter 1, the mechanism of intersystem crossing in organic materials is described and the rate of intersystem crossing is derived in chapter 2, by using the first order perturbation theory and Fermi’s golden rule. A newly derived exciton-spin-orbit-vibrational interaction operator which depends on the atomic number of the constituent atoms in the material is used as a perturbation operator. Thus, the influence of incorporation of heavy metal atoms on the rate of intersystem crossing is also studied. The diffusion length and diffusion coefficient of excitons, and recombination of free charge carriers into their excitonic states are presented in chapter 3. In chapter 4, an analytical expression for charge carrier mobility dependent open-circuit voltage in organic and hybrid solar cells is derived by optimising the current density obtained using the drift-diffusion model. By using the derived expression, the calculated open-circuit voltage in organic and hybrid solar cells is used to illustrate the effects of charge carrier mobilities on the open-circuit voltage. In chapter 5, the optimisation of design of two BHJ OSCs of structures: (1) ITO/PEDOT:PSS /P3HT:PCBM/LiF/Al and (2) ITO/ZnO/PTB7:PCBM /LiF /Ag is carried out. The thicknesses of the active layers and metal electrodes are optimised using OAAM simulation. It is found that by
optimising the thicknesses of the two BHJ OSCs structures, one can increase the short-circuit current density of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al BHJ OSC by 4.8% and that of ITO/ZnO/PTB7:PCBM /LiF/Ag by 13.3%. Thus, an increase of more than 2 and 6 % in power conversion efficiency can be achieved in ITO/PEDOT:PSS/ P3HT:PCBM/LiF/Al and ITO/ZnO /PTB7:PCBM /LiF /Ag OSCs, respectively. The results of this investigation are expected to be useful in the fabrication of high-efficiency bulk heterojunction solar cells.
List of publications contributing to this thesis

Chapter 2:


Chapter 3:


Chapter 4:


Chapter 5:

List of conference presentations contributing to this thesis


Chapter 1 Introduction

Mankind use energy for various domestic and industrial needs. Aside the chemical energy from food, we also need other forms of energy for our homes, offices, transportation, etc. Spurred on by the industrial revolution, we can now find a myriad of electrical gadgets around us; this is because electrical energy is the most versatile form of energy as it can be easily converted to other forms of energy [1]. Global energy demand is increasing at an unprecedented rate. The demand for energy is expected to increase further in the coming decades due to population growth and rising standards of living in all parts of the world. In countries outside the Organization for Economic Cooperation and Development, demand for energy is predicted to rise by 71% from 2012 to 2040 [2]. Currently, the majority of electrical energy is generated from conventional energy sources such as fossil fuels, in the form of coal, crude oil, and natural gas, hydroelectric power generators, and nuclear power plants [1], and a greater percentage of the energy being consumed is from fossil fuels.

Today, the availability, sustainability and environmental impacts of using conventional fossil fuel derived energy are being questioned. The widespread combustion of fossil fuels for energy generation is partly responsible for the gradual warming of the Earth’s atmosphere, which leads to global climate changes that can threaten the survival of humans, plant and animal species on Earth [3]. The use of nuclear energy is also hazardous as the nuclear power plants can have serious safety problems, including safe disposal of the radioactive wastes produced in the process of generating power. Although the spent reactor fuels cannot generate electricity, they are still radioactive and thus can pose health risks to living organisms. There are
limits on the number of hydroelectric plants that can be constructed as they rely on suitable geographic features like valleys behind large rivers for their construction [1]. In addition, these conventional sources of energy are available within the confines of our planet and hence they are conservative and limited, which means they are being depleted as we are using them.

In view of these problems, there is a strong research interest to develop new sources of energy which are renewable and sustainable. There are many such options, for example, generating power from alternative energy sources such as energy from the sun, wind, tides, biomass, etc., which are all variants of solar energy. Although solar energy is free its conversion to electricity is not free and it requires a device called photovoltaic cell or solar cell.

1.1 Photovoltaic cells: From inorganic to organic

1.1.1 Solar cells

The device that converts solar energy directly into electrical energy is called a solar cell, and it operates on the basis of the photovoltaic effect, as a result it is also referred to as photovoltaic (PV) cell. A solar cell is a semiconductor device. The most popular semiconductor material used in the solar industry is silicon (Si), both crystalline (c-Si) and noncrystalline (amorphous) forms are used [4], in addition, monocrystalline and polycrystalline GaAs, CdTe, etc., are also used in fabricating solar cells [5]. Although the photovoltaic action was first discovered by the French physicist A. E. Becquerel in early 1839, it was not until 1954 when Chapin and his colleagues at Bell Laboratory invented the first practical silicon single crystal based p-n junction solar cell with 5.7% power conversion efficiency (PCE) [6], which has
now been improved to around 26% [7]. Today, solar cells are made from many different semiconductor materials both organic and inorganic. In the context of organics, solar cells are fabricated from small molecules and polymers [8].

A crystalline silicon solar cell is basically a p-n junction as shown in Figure 1.1. A silicon atom has four valence electrons in the outermost shell. A silicon crystal is formed through sp$^3$ hybridisation of silicon bonds in the form of tetrahedrals, as a result a silicon atom can form covalent bonds with four other silicon atoms. Since pure c-Si cannot be used as a device, this led to the invention of a p-n junction. A p-n junction is formed by doping a wafer of c-Si from one side with boron (B) and the opposite side by phosphorous (P) atoms. A boron atom has only three valence electrons, this means it can accept an electron from a neighbouring silicon atom and gets ionised. Upon ionisation of the boron atom, a free hole is created in the valence band. The hole is a vacant electronic state in the valence band of the semiconductor. The region of silicon crystal doped with boron thus has excess number of holes and it is called p-region (p for positive charge). A phosphorus atom has five valence electrons in its outer orbital, this means it can get ionised by donating an electron to a neighbouring silicon atom. When a phosphorus atom is thus ionised, an electron is donated to the conduction band, which leads to an excess free electron in the lattice. Thus, the opposite side of a silicon crystal doped with phosphorous has excess number of free electrons and it is called the n-region (n for negative charge). Although these holes and electrons are bound to the B and P atoms in silicon, their binding energies ($\approx ke^2/4\pi \varepsilon r$; $k = 9 \times 10^9$ is a constant, $e$ electron charge, and $r$ is the average electron-nucleus or hole-nucleus distance) [5], reduces due to the dielectric constant ($\varepsilon$) of silicon, which
is nearly 12 and hence these charge carriers become relatively free to move within the crystal. A crystal of silicon prepared with one side made of p-region and the other side made of n-region is called a p-n junction. A p-n junction causes diffusion of electrons from the n-region to the p-region and holes from the p-region to the n-region where they recombine at the p-n junction. Due to the recombination process, the region close to the junction becomes almost completely depleted of free electrons and holes. It contains only immobile ionized atoms, positively charged ionized P atoms in the n-region and negatively charged ionized B atoms in the p-region. This region of space charge is called depletion region because no free charge carriers exist here; only immobile ionised dopants of opposite charges on each side of the junction, which maintain a built-in electric field and acts like an open-circuit battery [5, 6]. Thus a p-n junction made from pure silicon becomes a device.

When a photon of energy $\hbar \omega \geq E_g$, where $E_g$ is the band gap energy, is incident on a p-n junction, it is absorbed and the absorbed energy excites an electron...
from the valence band to the conduction band, leaving a hole behind in the valence band. Thus, absorption of a photon in the junction creates a pair of electron (e) and hole (h). The excited photo-electrons created in the space charge region move to the positively charged ions in the n-region and free holes move to the negative ions in the p-region (Figure 1.1) and give rise to a potential difference between the two sides. When these opposite sides are connected externally through a conducting wire, current flows to provide electricity [5].

Most of the manufactured solar cells at present are p-n junctions made from silicon wafers, known as the first generation solar cells. This technology involves growing single crystals of silicon and then cutting them in thin slabs to prepare p-n junctions. The process is relatively expensive due to the high cost of silicon wafers. Also, more silicon material is needed, about 200 μm in fabricating each cell. Therefore, a second generation thin film silicon solar cells were fabricated from hydrogenated amorphous silicon (a-Si:H), which use less active layer material. There are other types of thin film solar cells prepared from different materials, such as, copper indium gallium di-selenide (CIGS), gallium arsenide (GaAs), cadmium telluride (CdTe), etc. [9]. Among the thin film solar cells there is an increased research interest in organic and hybrid solar cells which form a category of third generation solar cells. The objectives of the third generation solar cells are to have increased PCE, be less toxic, and of low cost [9]. The focus of this project is to study the operation of organic solar cells with a view to achieve an optimal photovoltaic performance as described in the rest of the thesis.
1.1.2 Organic solar cells

Organic solar cells (OSCs) have many potential advantages, such as preparation on flexible substrates, thinness, large area applications, simple manufacturing process and ability to integrate them into other devices and structures such as computers, mobile phones, watches, bags, buildings etc. [10]. OSCs are fabricated from organic semiconductor material(s) whose optical properties are different from those of inorganic semiconductors, like Si. It is therefore very important to understand the properties of organic semiconductors relative to inorganic ones first before understanding the operation of OSCs. In this regard, the relevant properties of organic semiconductors are briefly described below.

The generation of photo-excited electron and hole pairs in organic semiconductors is different from that in inorganic semiconductors. Organic semiconductors consist of molecules which possess π-conjugated chemical structure. The bond between neighbouring molecules in an organic semiconductor is due to the weak van der Waal’s forces, which are much weaker than covalent and ionic bonds in inorganic semiconductors. This bonding structure gives organic semiconductors their unique flexibility, light weight, and low sublimation points which allow easy processing [11]. As the intermolecular interaction is weak in organic semiconductors, the energy bands become very narrow behaving like molecular energy levels of individual molecules called molecular orbitals. In this way, comparing with the band formation in inorganic semiconductors, the highest occupied molecular orbital (HOMO) of constituent molecules behaves like the valence band and the lowest unoccupied molecular orbital (LUMO) as the conduction band in organic semiconductors [12]. As shown in Figure 1.2, upon
absorption of a photon of energy $\hbar \omega \geq E_{\text{LUMO}} - E_{\text{HOMO}}$, where $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ are respectively, the energies of the LUMO and HOMO levels of molecules in an organic semiconductor, an electron is excited from the HOMO to the LUMO by creating a hole in the HOMO, similar to the excitation of an electron and hole pair from the valence to the conduction band in inorganic semiconductors. However, due to the small dielectric constant (3-4) the binding energy between the excited e and h is relatively large in organic semiconductors [13, 14], which binds them in a hydrogenic state called exciton, having a binding energy $E_b = \frac{k e^2}{\alpha} , \alpha$ is the average electron-hole distance. The exciton thus formed has, a binding energy of about 0.1-1.4 eV [13] in organic semiconductors. There are two types of excitons

![Figure 1.2 Schematic diagram of Frenkel exciton formation in an organic solid.](image)
that can be formed in nonmetallic solids upon photon absorption: Wannier or Wannier–Mott excitons and Frenkel excitons. The concept of Wannier–Mott excitons is valid for inorganic semiconductors like Si, Ge, and GaAs, where a large overlap of interatomic electronic wave functions enables electrons and holes to be far apart but bound in an excitonic state and hence they are also known as the large radius orbital excitons. Excitons formed in organic solids are such that the electrons and holes are excited on the same molecule and bound in an excitonic state. These excitons are called Frenkel excitons [8, 15], or small radius orbital excitons.

Depending on the electron and hole spins, an exciton can be formed in a singlet or triplet spin configuration as shown in Figure 1.3. [16, 17]. The properties of excitons responsible for the operation of OSCs, such as, binding energy, lifetime, diffusion coefficient, diffusion length, recombination etc. are different for singlet and triplet excitons. For instance, singlet excitons have smaller binding energy and hence can dissociate easily than triplet excitons. The drawback of generating singlet excitons in OSCs is that they can readily recombine to the ground state. It is well known that the transition from a triplet excited state to the singlet ground state is spin forbidden and therefore cannot take place without the involvement of the spin-orbit interaction. The lifetime of triplet excitons is therefore much longer than that of singlet excitons. Consequently it may be advantageous to convert the photogenerated singlet excitons into triplet excitons for efficient transport of excitons to the interface before quenching and subsequently increasing the PCE. Singlet-to-triplet exciton conversion through intersystem crossing has been used to enhance photovoltaic response by incorporating transition metal complexes [11, 15, 17].

The generation of Frenkel excitons by photon absorption is not advantageous
for the operation of an OSC. These excitons need to be dissociated into free charge carriers, that is, free electrons and holes which are drawn to the opposite electrodes to give rise to the photocurrent; this is the primary role of all solar cells.

![Figure 1.3 Schematic diagrams of (a) spin configuration for the singlet and (b) three spin configurations for triplet.](image)

Therefore, unlike inorganic solar cells where free e and h are generated by photon absorption, an OSC has to first dissociate Frenkel excitons before it can act as a solar cell.

### 1.1.2.1 Single layer OSC

Following the p-n junctions solar cell approach, the first generation of OSCs was fabricated from a single layer of organic semiconductor sandwiched between two electrodes, a transparent conducting oxide (TCO) as an anode [18, 19] and
Figure 1.4 (a) Schematic diagram and (b) Operation principles of a single layer OSC: 1. photon absorption, 2. exciton formation, 3. exciton dissociation and 4. charge transport; electron moves to cathode and hole moves to anode.

a metal such as aluminium (Al), silver (Ag), calcium (Ca), etc., as cathode, as shown in Figure 1.4. Unlike inorganic semiconductors, organic semiconductors cannot be doped to create a p-n junction, as a result OSCs lack the strong built-in electric field that is created by the p-n junction to separate the electrons and holes generated by light absorption. Thus, both the dissociation of excited excitons and transport of e and h to the opposite electrodes in a single layer OSC have to rely mainly on the electric field generated by the difference in the work functions between the anode and cathode given by [18,19]:

$$F = \frac{\phi_c - \phi_a}{d}$$  \hspace{1cm} (1.1)

where $\phi_c$ and $\phi_a$ are the work functions of cathode and anode, respectively, and $d$ is the separation between them, which is about the total active layer thickness of an
OSC. However, as the exciton is an electrically neutral entity the built-in-electric field is expected to have little contribution in the exciton dissociation. This built-in electric field can only contribute in charge transport and collection after the excitons have dissociated [18]. As a result the single layer OSCs had very poor PCE, which led to the development of bilayer OSCs described below.

1.1.2.2 Bilayer OSC

To dissociate excitons excited in the single layer more efficiently, Tang [14] replaced the single layer with a bilayer structure (Figure 1.5); where the first layer consists of a donor material and the second layer is an acceptor material and thus a donor-acceptor (D-A) interface was introduced in the structure. A donor organic material has its LUMO and HOMO energies higher than those of the acceptor material, which creates LUMO and HOMO energy off-sets at the D-A interface, given respectively, by:

\[
\Delta E_{\text{LUMO}} = E_{\text{LUMO}}^D - E_{\text{LUMO}}^A
\]

\[
\Delta E_{\text{HOMO}} = E_{\text{HOMO}}^D - E_{\text{HOMO}}^A
\]

(1.2)

(1.3)

where \(E_{\text{LUMO}}^j\) and \(E_{\text{HOMO}}^j\) are energies of LUMO and HOMO of \(j = D\) (donor) or A (acceptor). On the above bilayer structure, if photons of energy \(\hbar \omega \geq E_{\text{LUMO}}^j - E_{\text{HOMO}}^j\) are incident, then depending on the thickness of the donor and acceptor layers, excitons may be excited in both the layers, as shown in Figure 1.4(b). Theses excitons need to travel to the D-A interface to form charge transfer (CT) excitons by transferring the electron to the acceptor’s LUMO from excitons excited in the donor or by transferring the hole to the donor’s HOMO from excitons
excited in the acceptor [20].

The process of the formation of CT excitons releases some excess energy in the form of molecular vibrations and if this excess energy is equal or more than the binding energy of excitons and if it impacts back to CT excitons then CT excitons can dissociate into free charge carriers as it has recently been modelled [16, 19, 21]. After the dissociation of CT excitons the generated free e and h charge carriers may be drawn to the opposite electrodes by the built-in electric field in Eq. (1.1) created by the difference between the work functions of the two electrodes. If such a cell is connected externally to any load a photocurrent will flow. Thus, the operation of a bilayer OSC can be described by the following four processes in sequence: 1) photon absorption from the sun in the donor or acceptor excites electron-hole pairs which instantly form neutral Frenkel excitons, 2) diffusion of the excitons to the
donor-acceptor (D-A) interface and formation of charge transfer (CT) excitons at the D-A interface by transferring the electron to the acceptor, from excitons excited in the donor and by transferring the hole to the donor from excitons excited in the acceptor [20], 3) dissociation of the CT excitons at the D-A interface and 4) transport and collection of the dissociated free charge carriers at their respective electrodes to generate photocurrent [19].

In a bilayer structure, excitons are required to diffuse to the D-A interface to form CT excitons leading to the subsequent dissociation. It may be noted that an exciton being an electrically neutral entity it cannot be directed to move in any particular direction by any external or built-in electric field. Therefore, an exciton can only diffuse from one point to another in a random motion and when it reaches the D-A interface, it will form a CT exciton. This requires that the exciton diffusion length $L_D$ must be larger than the thickness of the donor or acceptor layers. In organic semiconductors $L_D$ is short ~ 10 nm and this short $L_D$ presents a significant drawback in a bilayer structure [11, 14]. A thicker layer is preferable since that will enhance absorption and hence the number of excitons generated, however, in such a layer, the excitons generated far from the interface may recombine and not reach the interface to be dissociated. Therefore, due to the $L_D$ constraint the bilayer structured OSCs have very poor PCE [11]. To solve this problem in the bilayer OSCs, the bulk heterojunction OSC was introduced.

### 1.1.2.3 Bulk Heterojunction OSC

Bulk heterojunction (BHJ) OSC, shown in Figure 1.6 is formed by inter-mixing donor and acceptor materials in a solution, and then spin-coating the mixer on a
substrate. The resulting film is an interpenetrating nanoscale network of donor and acceptor materials, as such, generated excitons do not need to travel to a particular D-A interface to get dissociated; a donor molecule is likely to have an acceptor molecule next to it. Otherwise, a BHJ OSC also operates through the four processes described above. In BHJ OSCs, the D-A separation within the film is commonly 10-20 nm, which is within the exciton diffusion length of many organic semiconductors [8]. Consequently, nearly 100 % internal quantum efficiency can be achieved in most BHJ OSCs, which means that nearly all photo-generated excitons can be dissociated. This, however, does not mean that the entire photo-generated carriers will contribute to the generation of current in the device since recombination, traps, and contact barriers at the interfaces may still hinder the performance of OSCs [8, 19]. Some BHJ OSCs architecture have a hole transport layer (HTL) and an electron transport layer (ETL) between the anode and donor, and the acceptor and cathode interfaces, respectively. These interfacial layers may be of organic or inorganic origin, the purpose of the HTL is to reduce the potential barrier between the donor’s HOMO and anode’s valence band and that of the ETL is to reduce the barrier between the LUMO of acceptor and cathode’s conduction band for efficient collection of free charge carriers to take place at the electrodes [11, 22].

Currently, there are two types of BHJ OSCs that are fabricated depending on the material used for the active layer: 1) from small molecule organic materials and 2) from polymer organic materials. BHJ OSCs fabricated from polymers is the most successful device architecture because exciton dissociation becomes near-perfect by creating a highly folded architecture such that all excitons are formed near a heterojunction [13].
As a result, the PCE of polymeric BHJ OSCs have increased during the last 18 years up to 10.61% in laboratory scale [10] and 8.7% for solar modules [7]. Figure 1.7 shows how PCE of the different types of solar cells has increased in the past 41 years.

**Figure 1.6** (a) Schematic diagram and (b) Operation principles of a bulk heterojunction OSC: 1. photon absorption, 2. exciton diffusion, 3. exciton dissociation and 4. charge transport; electron moves to cathode and hole moves to anode.
Figure 1.7 Illustration of the best research-solar cell efficiencies of the different kinds of solar cells records by the US National Renewable Energy Laboratory (NREL).
1.1.2.3.1 Theoretical Studies on Operation Mechanism of BHJ OSC

Over the years, some theoretical studies have been conducted on the operation principles of BHJ OSCs in order to understand the device physics, which is essential for further improvement of the photovoltaic performance of OSCs. Here we review some of the theoretical works done.

The effect of exciton-spin-orbit-photon interaction on the absorption process in OSCs has been studied by Narayan and Singh [23]. Using the exciton-photon interaction and exciton-spin-orbit-photon-interaction as perturbation operators, expressions for rate of absorption of singlet and triplet excitons have been derived, respectively. The exciton-spin-orbit-photon-interaction is a new time-dependent perturbation operator, obtained as a function of the square of the atomic number of the heaviest atom. Therefore, by incorporating heavy metal-organic complexes in the active layer it has been found that the direct absorption rate to the triplet exciton states increases, which increases the total absorbance in the active layer, leading to enhanced photocurrent and hence higher PCE. Also, to improve photon absorption in OSCs, a variety of plasmonic and light trapping structures have been modelled [8, 24]. In this study [24], diffractive nanostructures are modelled on top of ITO layer in BHJ OSCs to influence light distribution inside the active layer. The design predicted 14.8% increase in absorption. Also, the concept of redistributing the photon density-of-states by inserting dielectric mirrors in the device structure of OSCs has been used to enhance the absorption in the active layer [25]. In this work, a numerical optimisation has been carried out to design a multilayer dielectric stacks capable of achieving 40% increase in photocurrent by shifting the photon density-of-states from spectral region where it is not needed to spectral region where
absorption enhancement would lead to enhanced photocurrents [25]. After enhanced absorption, efficient exciton diffusion and charge carrier collection are needed for optimal photovoltaic performance.

An efficient diffusion of excitons is required for achieving higher internal quantum efficiency in OSCs. The exciton diffusion can take place via the interaction between an excited molecule and a ground-state molecule. For diffusion and transport of excitations in solids there are two old theories which also used for the diffusion of excitons in organic semiconductors. One is Förster’s resonance energy transfer (FRET) mechanism [26], illustrated in Figure 1.8, where an excited molecule A* gets de-excited due to the Coulomb interaction by transferring the energy released non-radiatively to excite another molecule B. In this mechanism, the energy of excitation gets transferred to excite another molecule and hence it is also known as the energy transfer mechanism. FRET is applied to the diffusion of singlet

![Figure 1.8](image-url)  
**Figure 1.8** Schematic representation of the Förster resonance energy transfer mechanism for singlet excitons.
excitons such that a Frenkel singlet exciton excited on a molecule recombines and transfers its energy to excite another identical molecule in the system. As it involves recombination of excitons to the ground state, FRET is applicable only to singlet excitons (see Figure 1.8). The second mechanism is called the Dexter mechanism, illustrated in Figure 1.9 [27], where an exciton excited on a molecule A* transfers its excited electron to an unexcited nearby molecule B which transfers one of its ground state electrons to the molecule A* and thus the exciton gets transferred to molecule B, as A* gets de-excited. The Dexter mechanism involves transfer charge carriers between molecules, thus it is also known as the carrier transfer mechanism and it applies to both singlet and triplet excitons (see Figure 1.9).

![Diagram](image)

**Figure 1.9** Dexter transfer mechanism due to the exchange interaction: (a) for singlet excitons and (b) for triplet excitons.
The Dexter mechanism occurs due to the interaction of electronic wavefunctions of neighbouring molecules and hence this mechanism is known to be short range [27]. When the excitons are transferred to the D-A interface by either Förster or Dexter mechanism, the process that follows is the formation of CT excitons which serves as a precursor to dissociation of excitons.

Braun [28] has extended Onsager’s theory of recombination to the mechanism of dissociation of Frenkel excitons in organic solids, the so called Onsager-Braun model. In this model of exciton dissociation which depends on external electric field is one of the widely used exciton dissociation models in BHJ OSCs [29, 30]. However, it is increasingly becoming evident in recent years that electric field might play very little role in exciton dissociation because excitons are neutral charge excited entities and so are the CT excitons. Therefore, the built-in electric field due to the difference in work functions of electrodes is not considered to be effective in the dissociation of CT excitons [21]. In addition, a CT exciton is a discrete quantum state holding a quantum of solar energy, the distance between the bound electron-hole is also fixed as exciton Bohr radius. In this regard, it is debatable whether the Onsager-Braun electric field dependent exciton dissociation model is applicable in the dissociation of CT excitons in BHJ OSCs [11, 19]. The exciton dissociation and charge recombination dynamics have also been theoretically investigated by using electronic structure calculations together with Marcus formula [31]. The results reveal that the exciton dissociation is a barrierless reaction in some organic blends. This supports the high internal quantum efficiencies found in BHJ OSCs [31]. Narayan and Singh [16] have proposed a molecular vibrational energy assisted exciton dissociation model. In this model, exciton dissociation depends on
the mechanism of formation of CT excitons. The formation of a CT exciton releases excess energy in the form of molecular vibrations, which may impact back on the CT exciton to dissociate it, provided the excess energy released is equal or greater than the binding energy of the CT exciton [16, 21]. This might explain why formation of a CT exciton is considered as a prerequisite to the dissociation of excitons [16]. This model is appealing from device physics point of view because it shows that exciton dissociation is field independent.

The function of the built-in electric field is to transport the charge carriers arising from the dissociation of CT excitons to their respective electrodes for collection. To be able to extract charge carriers effectively at the active layer/electrode interface, the potential barrier at the active layer/electrode interfaces has to be minimum. This means the work function of the anode is ideally expected to match the donor HOMO level, whilst the work function of the cathode is expected to match the acceptor LUMO level. When these conditions are met, the contacts become ohmic, leading to highly efficient charge collection [8].

1.1.2.4 Hybrid Solar Cells

As described above, the organic materials have low charge carrier mobilities in comparison with inorganic materials, a hybrid of organic and inorganic materials may be expected to give a better performance. Such solar cells fabricated from the hybrid of organic and inorganic materials are called hybrid solar cells and are able to benefit from both, the high mobility of charge carries in inorganic and the easy fabrication techniques and flexibility of organic materials [32].

The device fabrication and fundamental operating principles of organic and
hybrid solar cells are identical, and their structures are similar to Figure 1.5 except that the acceptor material in the hybrid structure is an inorganic semiconductor, instead of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} (PCBM) or other fullerene derivatives. The inorganic acceptor materials are usually used as quantum dots dispersed in a polymer matrix and also are used in complex shaped nanoparticles, like nanorods, nanowires or tetrapods, mixed with a polymer [11, 20]. The inorganic semiconductors may have high absorption coefficients and particle size induced tunability of the optical band gap. Hybrid solar cells can overcome the inefficient hopping charge transport in organic solar cells as charge transfer is favoured between inorganic semiconductors of high electron affinity and organic molecules of relatively low ionization potential [32].

The morphology of the D-A interface has a major influence on the efficiency of exciton dissociation, charge transport and charge collection, hence, nanostructured hybrid solar cells have been developed with the view of controlling the donor and acceptor domain sizes. Until recently nanostructured hybrid solar cells have shown performances far below the standard BHJ OSCs. Recently, the PCE of state-of-the-art hybrid solar cells has reached 13.7% [33]. Currently, most nanostructured hybrid solar cells have domain sizes larger than 50 nm, it is expected that when the size of the donor and acceptor domains become much smaller, comparable to the diffusion length of excitons \( \approx 10 \) nm, the performance of nanostructured hybrid solar cells will improve significantly [34].

### 1.2 Aim and organisation of thesis

The work done in this thesis is theoretical, the aim is to design thin film bulk
heterojunction OSCs with enhanced photovoltaic performance. In order to achieve this aim, the operation principles of BHJ OSCs are studied comprehensively. The admittance analysis method is used to optimised the structure of BHJ OSCs. The course of study presented in this thesis consists of study of the: 1) mechanism and rate of intersystem crossing from singlet to triplet excited state to reduce recombination losses, 2) exciton diffusion to the D-A interface for dissociation, and 3) influence of charge mobility on the open-circuit voltage, and 4) optimisation of active layer thickness to enhance absorption and subsequent photocurrent generation.

Accordingly the thesis is organised as follows: chapter 1 presents the introduction. Chapter 2 describes the mechanism of intersystem crossing of excitons from singlet to triplet state and the derivation of such rate of transfer. Intersystem crossing has been studied for many years but no attempt has yet been made to derive the transition matrix element due to the spin-orbit interaction in calculating the intersystem crossing rates. The rate of intersystem crossing is derived by using the first order perturbation theory and Fermi’s golden rule, where a newly derived exciton-spin-orbit-vibrational interaction operator is used as a perturbation operator to flip the spin of the singlet exciton to triplet exciton. Incorporation of a heavy metal atoms enhances the spin-orbit interaction and hence the intersystem crossing rate because it depends on the square of the heaviest atomic number. The content of this chapter is based on the journal article published by D. Ompong and J. Singh, Physica Status Solidi C, 13, 89–92 (2016). Chapter 3 presents the study of diffusion and Langevin recombination of excitons in BJH OSCs. The Förster and Dexter transfer processes are used to derive the diffusion coefficients and diffusion lengths of singlet and triplet excitons, respectively. It is shown in this chapter that the diffusion lengths
of singlet and triplet excitons are comparable. This is because triplet excitons have lifetime about three orders of magnitude larger than singlet excitons while the transfer rate of singlet excitons is about the same orders of magnitude larger than that of triplet excitons. Also, using the Langevin recombination theory, it is shown that the rate of recombination of dissociated free charge carriers back into their excitonic states before possible direct recombination is different for singlet and triplet excitons. The content of this chapter is based on the journal article published by D. Ompong and J. Singh, A European Journal of Chemical Physics and Physical Chemistry, 16, 1281-1285 (2015). Chapter 4 presents the derivation of open-circuit voltage ($V_{oc}$) as a function of the charge carrier mobilities by optimising the current density obtained using the drift-diffusion model. The derived expression is used to calculate $V_{oc}$ in BHJ OSCs and hybrid solar cells. It is shown that when the difference between the electron and hole mobilities is small, then the $V_{oc}$ of the solar cell is not affected much by charge carrier mobilities and the most important factor contributing to the $V_{oc}$ is the energy levels of the D-A materials of the OSC. The contents of this chapter are based on the journal article published by D. Ompong and J. Singh, Frontiers in Nanoscience and Nanotechnology, 2, 43-47 (2016). Chapter 5 presents the application of the optical admittance analysis method (OAAM) to optimise the thickness of the active layer in BHJ OSCs with two different structures: (1) ITO/PEDOT:PSS /P3HT:PCBM/LiF/Al and (2) ITO/ZnO /PTB7:PCBM /LiF /Ag. The optimisation is carried out by maximising the absorbance in the photoactive layer. The photon absorption is the first process of operation of solar cells and knowledge of the absorbance and the spatial distribution of the absorption in the active layer is the starting point for the optimisation. For photovoltaic devices, high absorption involves
maximisation of the overlap of the solar photon flux with the absorbance spectra of the active layers, in order to maximise the photo-generated currents in the device. The simulated short-circuit current density \( J_{sc} \) is found to be maximum at the thicknesses of 75 nm and 115 nm in P3HT:PCBM and PTB7:PCBM blend layers, respectively. The simulated results are found to be comparable with the experimental ones. The optimal thickness of Al cathode from the simulation is found to be 40 nm for both P3HT:PCBM and PTB7:PCBM blends. The content of this chapter is based on the journal article by D. Ompong and J. Singh, Journal of Material Science: Materials in Electronics (Submitted for publication). Chapter 6 is devoted to conclusions drawn from the work presented in chapters 2 - 5 is presented and recommendations are made for future research directions. It may be noted that the chapters 2-5 present the original published work in the corresponding journal articles by modifying the contents only for consistency and continuity of the presentation in the thesis. For example, the numbering of equations, sections, references, etc., has been modified.
Chapter 2 Study of intersystem crossing mechanism in organic materials

This work has been published in the following paper:


Statement of contribution of each author:

The candidate D. Ompong has carried out all the research activities to obtain the results presented in this chapter under the supervision of J. Singh.
Abstract

Intersystem crossing rate from singlet excited state to triplet excited state of an organic molecule has been derived using exciton-spin-orbit-molecular vibration interaction as a perturbation operator. Incorporation of heavy metal atom enhances the spin-orbit interaction and hence the intersystem crossing rate because it depends on the square of the heaviest atomic number. We found that in the presence of heavy atom the singlet-triplet energy difference still plays an influential role in the intersystem crossing process. The derived exciton-spin-orbit-molecular vibration interaction operator flips the spin of the singlet exciton to triplet exciton after photo-excitation from the singlet ground state with the assistance of molecular vibrational energy. From this operator an expression for the intersystem crossing rate is derived and calculated in some organic solids.
2.1 Introduction

Excitons excited in organic semiconductors can be in singlet (S) and triplet (T) spin configurations and as a consequence, both singlet and triplet excitons can be excited in OSCs. In organic materials the selection rules for the electronic dipole transitions allow generation of only singlet excitons by exciting an electron from the singlet ground state. To excite triplet excitons, one needs to flip the spin to triplet configuration in the excited state, which is achieved through the strong exciton-spin-orbit interaction (ESOI) [23, 35]. This is how ESOI also helps in creating triplet excitons via intersystem crossing (ISC). In organic solids, the triplet exciton state usually lies below the singlet exciton state and their vibronic states overlap in energy. In this case, first a singlet exciton is excited by the photon absorption to a higher vibronic energy level which is iso-energetic with the vibronic level of the triplet state. As a result, if the ESOI is strong it flips the spin of the excited electron to triplet and it crosses to the triplet exciton state[36]. As ESOI is proportional to the atomic number \( Z_n \) [23], it is expected to be weak in organic materials which are composed mainly carbon and hydrogen [37]. To enhance ESOI, therefore, one needs to incorporate heavy metal atoms in organic solids and polymers.

The incorporation of iridium (Ir) and platinum (Pt) into the active layer of OSCs results in the phosphorescent sensitizer, fac-tris(2-phenylpyridine) iridium [Ir(ppy)₃][38, 39] and platinum-acetylide \( [p-\text{PrTh}] \)[40] and has been found to increase the PCE [36, 39] of OSCs. Although this improvement has been attributed to the increase in the triplet exciton concentration with higher diffusion length [38, 39, 41], the mechanism of such a process has never been fully understood.

In this paper, our objective is to study the effect of spin-orbit interaction on
the mechanism of ISC in organic semiconductors and polymers. It is known that the
spin-orbit coupling flips the singlet spin configuration to triplet and vice versa and
hence facilitates ISC. [35, 36, 42]. ISC from a singlet excited state to a triplet excited
state has been studied theoretically[43-45] and as well as experimentally [40, 41].
Theoretical models have so far been limited to either numerical calculation of ISC
rates [43-45] or estimation of the spin-orbit interaction transition matrix element [46].
To the best of the authors’ knowledge no attempt has yet been made to derive the
transition matrix element due to the spin-orbit interaction in calculating the ISC rates.
Here, an exciton-spin-orbit-molecular vibration interaction operator suitable for ISC
in organic solids is derived. Using this operator, an expression for ISC rate is derived
and calculated in some organic solids. The effects of incorporation of heavy atom on
the ISC rate are explored and the results are compared with their experimental values.

2.2 Exciton-spin-orbit-molecular vibration interaction operator

The stationary part of the spin-orbit interaction for an exciton in a molecule
consisting of \( N \) atoms can be is written as [35]:

\[
H_{so} = -\frac{e^2 g k}{2 \mu_e c^2} \sum_n \left( \frac{x_{en}}{r_{en}} s_e \cdot l_{en} + \frac{x_{hn}}{r_{hn}} s_h \cdot l_{hn} \right)
\]  
(2.1)

where \( g = 2 \) is the gyromagnetic ratio, \( k = 1/4\pi \varepsilon_0 \) is the Coulomb constant, \( \mu_e \) is the
reduced mass of exciton: \( \mu_e^{-1} = m_e^{-1} + m_h^{-1} \), \( c \) is the speed of light, \( s_e(s_h) \) is the
electron (hole) spin, \( l_{en} = r_{en} \times p_e \) is electron angular momentum and \( r_{en}(p_e) \) is the
position vector (orbital momentum) of the electron from the nth nucleus. Similarly,
\( l_{hn} = r_{hn} \times p_h \) is the hole angular momentum and \( r_{hn}(p_h) \) is the position vector (orbital
momentum) of the hole from the nth nucleus. For a non-rigid structure, Eq. (2.1), can
be expanded in Taylor series about the equilibrium position of molecules. Terminating the expansion at the first order, we get:

$$H_{so} = H_{so}^0 + H_{so}^{1}$$  \hspace{1cm} (2.2)$$

where $H_{so}^0$ is the zeroth order term and represents the interaction in a rigid structure and $H_{so}^{1}$ is the first order term which gives the interaction between exciton-spin-orbit interactions and molecular vibrations and it is obtained as:

$$H_{so}^{1} = -\frac{3e^2gkZ}{2\mu e^2c} \sum_{v,\nu} \left( \frac{s_e \cdot l_{\nu} R_{\nu} + s_h \cdot l_{\nu} R_{\nu}}{r_{e}^4 + r_{h}^4} \right)$$ \hspace{1cm} (2.3)$$

where $R_{\nu}$ is the molecular displacement from the equilibrium position due to the intramolecular vibrations. The quantity within parentheses in Eq. (2.3) depends on $r_{e}^{-4}$ and $r_{h}^{-4}$ thus the nearest nuclei to the electron and hole is expected to play the dominant influence and as such the presence of other nuclei may be neglected as an approximation. This approximation helps in reducing the summation to only one nucleus for each electron and hole. In carrying out the Taylor series expansion, it is further assumed that the distances $r_{e}$ and $r_{h}$ of the electron and hole with reference to the individual nuclei of a molecule can be replaced by their distances $r_{e}$ and $r_{h}$, respectively, with reference to the equilibrium position of the individual molecules. This approximation may be regarded to be quite justified within the Born-Oppenheimer approximation regime. In second quantization $R_{\nu}$ can be expressed as [16]:

$$R_{\nu} = (q_{\nu} - q_{\nu}^0)(b_{\nu}^* + b_{\nu})$$ \hspace{1cm} (2.4)$$

where $b_{\nu}^*$ ($b_{\nu}$) is the vibrational creation (annihilation) operator in vibrational mode $\nu$. For expressing the operator in Eq. (2.3) in second quantisation, we can write
the field operator for an electron in the LUMO and that of a hole in the HOMO, respectively, as:

\[
\hat{\psi}_e = \sum_{\sigma_e} \phi_{LUMO} a_L(\sigma_e) \\
\hat{\psi}_h = \sum_{\sigma_h} \phi_{HOMO} d_H(\sigma_h) \quad d_H(\sigma_h) = a_H(-\sigma_h)
\]  

(2.5a)

(2.5b)

where \( \phi_{LUMO} \) and \( \phi_{HOMO} \) are the wavefunctions of the electron in the LUMO and hole in the HOMO, respectively. It may be clarified here that we are dealing with molecules, hence, the valence and conduction bands wavefunctions are those of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. Using Eq. (2.5) the interaction operator given in Eq. (2.3) can be expressed in second quantization as:

\[
\hat{H}_I \approx \frac{-4e^2 \hbar k Z}{\mu_e c^2 r_x^4} \sum_{v,\sigma_v,\sigma_d} (q_{vo} - q_{md}) a_L^\dagger(\sigma_v) d_H(\sigma_h) \delta_{\sigma_v,\sigma_d} (s_e \bullet 1_v + s_h \bullet 1_h) (b_{mv}^\dagger + b_{mv})
\]  

(2.6)

where \( r_x \) is the average separation between the electron and hole in the exciton and it is approximated as  

\[ \langle \phi_{HOMO} (r_m^{-4}) \phi_{LUMO} \rangle \approx \langle \phi_{HOMO} (r_m^{-4}) \phi_{LUMO} \rangle \approx \left( \frac{r_x}{2} \right)^{-4}. \]

To evaluate the spin and orbital angular momentum operators in the interaction operator Eq. (2.6), we can use [47]

\[
s \bullet l = \frac{J^2 - l^2 - s^2}{2}
\]  

(2.7)

where \( J \) is the total angular momentum. Equation (2.7) can be re-arranged as:

\[
J^2 = I^2 + s^2 + 2(s I_x + s Y + s I_y)
\]  

(2.8)

Defining \( s_i \) and \( l_i (i = x, y) \) in Eq. (2.8) in terms of orbital angular momentum raising (lowering) operator as \( L_i = I_i + i l_i \) (\( L_i = I_i - i l_i \)) and spin angular momentum raising
(lowering) operator as \( S_+ = s_x + is_y \), \( S_- = s_x - is_y \), respectively, we get

\[
J^2 = l^2 + s^2 + 2 \left( \frac{S_+ L_z + S_- L_z + S_+ L_z + S_- L_z}{4} \right) - 2 \left( \frac{S_+ L_z - S_- L_z - S_+ L_z + S_- L_z}{4} \right) + 2s \cdot l_z
\]

\[ (2.9) \]

Using Eq. (2.8) in Eq. (2.6) we obtain

\[
s \cdot l = s \cdot l_z + \frac{S_+ L_z}{2} + \frac{S_- L_z}{2}
\]

\[ (2.10) \]

It is this term in the interaction operator Eq. (2.6) that flips the spin of the exciton from the singlet to triplet configuration. Using Eq. (2.10) in Eq. (2.6) we get

\[
\hat{H}_I = \frac{12\hbar^2 g k Z e^2}{\mu e^2 r_i} \sum_{\nu, \sigma_\nu, \sigma_s}(q_{\nu \nu} - q_{\omega \omega}) a_{\nu}^\dagger(\sigma_\nu) d_{\mu}(\sigma_\omega) \delta_{\sigma_\nu, \sigma_\omega}(b_{\nu}^+ + b_{\nu})
\]

\[ (2.11) \]

here we assume \( l_{ez} \approx l_{hz} = l_z = \hbar \), which is the angular momentum associated with first excited state with the magnetic quantum number 1. A detailed derivation of Eq. (2.11) is provided in appendix A.

### 2.3 Intersystem crossing rate

Assuming that the initial state \( |i\rangle \) consists of an exciton in the singlet spin configuration and molecular vibrations and the final state \( |f\rangle \) consists of a triplet exciton and molecular vibrations. Using occupation number representation the initial state can be written as:

\[
|i\rangle = \frac{N^{3/2}}{\sqrt{2}} \sum_{n_1, m_1, \nu_1, \sigma_\nu, \sigma_\nu} \sum_{n_\nu, m_\nu} \left[a_{m_\nu}^+(+\sigma_\nu)d_{m_\nu}^+(\sigma_\nu) + a_{n_\nu}^-(\sigma_\nu)d_{n_\nu}^+(+\sigma_\nu)\right] |0\rangle |\nu_1\rangle
\]

\[ (2.12) \]

where the electron is created in the LUMO at site \( n_1 \) and a hole in the HOMO at site \( m_1 \). \(|0\rangle\) represents the electronic vacuum state and \(|\nu_1\rangle\) is the initial molecular
vibrational occupation state. Likewise, the final state can be expressed as:

$$|f\rangle = \frac{N \sqrt{2}}{2} \sum_{n_1,n_2,v_2} \sum_{a_i,a_f} \left[ a_{n_1,v_2}^+ (+\sigma_v') d_{m_2,c_2}^+ (-\sigma_h') - a_{n_2,m_2}^+ (-\sigma_v') d_{m_2,c_2}^+ (+\sigma_h') \right] |0\rangle |v_2\rangle$$  \hspace{1cm}(2.13)

where the electron is located in the LUMO at site $n_2$ and a hole in the HOMO at site $m_2$, and $|v_2\rangle$ is the final molecular vibrational occupation state after the spin flip into the triplet excited state.

Using Fermi the usual anticommutation relation for fermions and commutation relations for boson operators, the transition matrix element is obtained from Eqs. (2.11)-(2.13) as:

$$\langle f|\hat{H}_f|f\rangle = -\frac{12gke^2\hbar^2n_v}{\mu^2c^2r_s^2} (q_{\omega_0} - q_{\omega_0})$$  \hspace{1cm}(2.14)

where $n_v$ is the effective number of vibrational levels taking part in the transition process.

Using Fermi’s golden rule then the rate of intersystem crossing $k_{isc}$ can be written as:

$$k_{isc} = \frac{2\pi}{\hbar} \left| \langle f|\hat{H}_f|f\rangle \right|^2 \delta(E_f - E_i)$$  \hspace{1cm}(2.15)

Here $E_f = E_T + n_\omega \hbar \omega_0$ is the final triplet state energy and $E_i = E_S + n_\omega \hbar \omega_0$ is the initial singlet state energy including the energy of corresponding vibrational energies. $E_S$ and $E_T$ are the singlet and triplet exciton energies, respectively.

Substituting Eq.(2.14) into Eq.(2.15), we get $k_{isc}$ as:

$$k_{isc} = \left[ \frac{12gke^4kZe^2\hbar^2n_v}{\mu^2c^2\alpha_s^2} (q_{\omega_0} - q_{\omega_0}) \right]^2 \delta(-\Delta E + n_\omega \hbar \omega_0)$$  \hspace{1cm}(2.16)
where \( r_s = \frac{a_r}{\varepsilon} \) is used to express the rate in terms of the excitonic Bohr radius \( a_r \) and \( \varepsilon \) is the dielectric constant. Expressing \( E_j - E_i = -\Delta E + n_i \hbar \omega, \) where \( \Delta E = E_s - E_T, \)
\( n_e = n_2 - n_1, \) and the square of the molecular displacement due to excitation as:
\[
(q_{wo} - q_{wo})^2 = \frac{8\pi^2}{3} \quad [16], \quad k_{isc} \text{ is obtained as:}
\]
\[
k_{isc} = \frac{3072\pi^2 \varepsilon^6 k^2 Z^2 e^4 \hbar^3}{\mu_e^4 \varepsilon^4 a_x^8 (\hbar \omega_v)^3} (\Delta E)^2.
\]

(2.17)

### 2.4 Results and Discussions

The rate derived in Eq. (2.17) depends on excitonic Bohr radius, molecular vibrational energy, the atomic number of the heaviest atom and \( \Delta E, \) the exchange energy between the singlet and triplet excited states. Although ISC is very well known process, the interaction operator derived here in Eq. (2.6) is the first one known to the best of our knowledge. The above derivation also clarifies how the phenomenon of ISC occurs. An exciton is first excited to the singlet exciton state which is higher in energy than the triplet state. The higher energy of the singlet excited state provides the required exciton-spin-orbit-molecular vibration interaction energy to flip the spin to triplet state before the transfer can take place. This is the reason that \( k_{isc} \) in Eq. (2.17) vanishes when \( \Delta E \) is equal to zero.

The rate in Eq. (2.17) is calculated in several known molecules used in the fabrication of organic solar cells and listed in Table 2.1, along with material parameters used in the calculation.
According to Table 2.1, the calculated rates are found to be in reasonable agreement with experimental results and the minor discrepancies may be attributed to the approximations used in deriving Eq. (2.17). The rate in Eq. (2.17) can be applied to calculate the ISC rate in any molecular solid. It is therefore expected that the results...
of this paper will provide a simple way to study ISC in any organic device.

### 2.5 Conclusions

In summary, we have derived an expression for the exciton-spin-orbit-molecular vibration interaction operator which has been used to calculate the rate of ISC from singlet excited state to triplet excited state in organic molecules. The rate is sensitive to spin-orbit coupling and the singlet-triplet energy difference. This study may help in designing OSCs with enhanced triplet exciton concentration.
Chapter 3 Diffusion length and Langevin recombination of singlet and triplet excitons in organic heterojunction solar cells

This work has been published in the following paper:


Statement of contribution of each author:

The candidate D. Ompong has carried out all the research activities to obtain the results presented in this chapter under the supervision of J. Singh.
Abstract

We derived new expressions for the diffusion length of singlet and triplet excitons by using the Föster and Dexter transfer mechanisms, respectively, and have found that the diffusion lengths of singlet and triplet excitons are comparable. By using the Langevin recombination theory, we derived the rate of recombination of dissociated free charges into their excitonic states. We found that in some organic polymers the probabilities of recombination of free charge carriers back into the singlet and triplet states are approximately 65.6% and 34.4 %, respectively, indicating that Langevin-type recombination into triplet excitons in organic semiconductors is less likely. This implies that the creation of triplet excitons may be advantageous in organic solar cells, because this may lead dissociated free charge carriers that can be collected at their respective electrodes, which should result in better conversion efficiency.
3.1 Introduction

When an organic molecule absorbs a photon, a pair of electron and hole is excited on the same molecule to form an exciton [17]. Excitons are usually excited in singlet (S) and triplet (T) spin configurations. An exciton consists of a pair of excited electron and hole bound in a hydrogenic state due to their Coulomb interaction. When the electron and hole in an exciton have opposite spins [↑↓ + ↓↑], it is a singlet exciton with multiplicity 1 and when the electron and hole have parallel spins [↑↑, ↓↓, ↑↓ - ↓↑] then it is a triplet exciton with multiplicity 3 [17, 53]. In organic materials, the selection rules for the electronic dipole transitions allow generation of only singlet excitons by exciting an electron from the singlet ground state. Therefore, the probability of generating a triplet exciton by spin inversion is extremely low in most molecules and mostly singlet excitons are created first in organic photovoltaic (OPV) cells when light is absorbed [36, 53-55].

Although each of the processes involved in the operation of OSCs has an influence on the overall conversion efficiency of an OSC, the efficiency of exciton dissociation and subsequent charge separation to the respective electrodes plays the most important role [40]. A mechanism for exciton dissociation at the D-A interface has been proposed [16] in which exciton relaxes first to a CT exciton state by transferring its electron from the LUMO of the donor to the LUMO of the acceptor, which is at a lower energy and thus the excess energy is released in the form of molecular vibrational energy. The excess vibrational energy, if larger than the exciton binding energy, may impact back to the CT exciton to dissociate it into a pair of free electron and hole. It is therefore critically important that all generated excitons reach the interface to form CT exciton and dissociate into free charge carriers. As such, any
recombination of CT excitons prior to their dissociation into free charge carriers will have a negative impact on the performance of an OSC.

In low-mobility materials such as π-conjugated polymers (PCPs), the diffusion-controlled bimolecular recombination or the so-called Langevin recombination dominates. This type of recombination occurs when opposite charge carriers approach each other within the Coulomb radius, given by

\[ r_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \]

at a temperature \( T \), where \( \varepsilon \) is the relative dielectric permittivity, \( \varepsilon_0 \) is absolute permittivity, and \( k_B \) is Boltzmann’s constant [56].

Previous approaches involving the application of Langevin theory to study the recombination of CT excitons, prior to charge separation in OSCs [30, 57], have not considered the spin; as such, no distinction is made between the recombination of singlet and triplet excitons. The introduction of spins to distinguish between the process of recombination of singlet and triplet excitons has been considered only recently [55].

In this paper, we have calculated the diffusion lengths of singlet and triplet excitons to study the influence of exciton diffusion lengths on the fraction of excitons that reaches the D-A interface in a heterojunction organic solar cell. Furthermore, by using the Langevin recombination theory, we have derived the rates of recombination of dissociated free charges back into their excitonic states. We have calculated the probability of recombination into singlet and triplet excitonic states in some organic polymers. It is expected that the present work will advance the understanding of the roles of singlet and triplet excitons in OSCs. The results also show that the generation of not only singlet excitons but also triplet excitons can be useful in the operation of OSCs.
3.2 Exciton generation in OSCs

When a photon is absorbed, an electron in the organic semiconductor is excited from HOMO to the LUMO of a molecule. However, because of the low dielectric constant ($\varepsilon \approx 3 - 4$) in organic solids, a strong Coulomb attraction exists between a photo-excited electron–hole (e-h) pair [13, 58], which binds them in a Frenkel exciton [17]. The excitonic Bohr radius is the radius of the orbital formed between the excited e-h pair in an exciton and it is different for singlet and triplet excitons as given by [59]:

$$a_s(S = 0) = a_s = \frac{\alpha^2 \varepsilon \mu}{(\alpha - 1)^2 \mu_s} a_o$$  \hspace{1cm} (3.1)

and

$$a_s(S = 1) = a_r = \frac{\varepsilon \mu}{\mu_s} a_o$$  \hspace{1cm} (3.2)

in which $\alpha$ is a material-dependent parameter representing the ratio of the magnitude of the Coulomb and exchange interactions between the electron and hole in an exciton, $S$ is the spin of the exciton ($S = 0$ for singlet and $S = 1$ for triplet), $\mu$ is the reduced mass of the electron in a hydrogen atom, $a_o$ is the Bohr radius, and $\mu_s$ is the reduced mass of an exciton, given by $\mu_s = 0.5m_e$, with $m_e$ being the free electron mass [60]. Singlet excitons have relatively smaller binding energy and larger excitonic Bohr radius compared with the triplet excitons [15]. Due to their favourable spin configuration, singlet excitons can easily recombine radiatively to the singlet ground state without reaching the interface.

3.3 Exciton diffusion

An exciton can move throughout the material as a neutral quasi particle. There
are two general mechanisms by which excitons can diffuse in organic semiconductors
and PCPs: 1) Förster resonance energy transfer (FRET) and 2) Dexter carriers
transfer. In Förster transfer, an excited electron in an exciton on a molecule
recombines with the hole and the energy is transferred nonradiatively to excite an
exciton on another molecule. Such a recombination is only possible for singlet
excitons due to their favourable spin configuration and hence FRET is applicable only
to the transfer of singlet excitons. In the Dexter transfer mechanism, the excited
electron and hole are transferred to excite a nearby molecule due to the overlap of
electronic wavefunctions. Therefore, the Dexter transfer mechanism can occur only at
short range and it applies to both singlet and triplet excitons. In Dexter’s approach, the
exciton transfer rate decays exponentially with distance [54]. The Förster and Dexter
transfer rates are given, respectively, as [15]:

\[
k_f = \frac{1}{\tau_s} \left( \frac{R_f}{R_{da}} \right)^6
\]  

(3.3)

and

\[
k_d = \frac{1}{\tau_T} \exp \left( \frac{2R_d}{L} \left( 1 - \frac{R_{da}}{R_d} \right) \right)
\]  

(3.4)

where \( \tau_s \) is the lifetime of singlet excitons, \( \tau_T \) is the lifetime of triplet excitons, \( R_{da} \) is
the D-A distance of separation (NB: the donor-acceptor used here is from one
molecule to another molecule, this is different from donor-acceptor materials which
are layers of organic solid), \( R_f(R_d) \) is the Förster (Dexter) radius, and \( L \) is the
average length of a molecular orbital which is found to be 0.11 nm [61] in Ir(ppy)_3.
We have assumed the same value here for all triplet exciton calculations. As stated
above, the rate in Eq. (3.4) applies also to singlet excitons with the singlet lifetime;
However, in this work we have applied it only to triplet excitons. The diffusion coefficient \( D \) of an exciton of lifetime \( \tau \) is given by \[15\]:

\[
D = \frac{L_D^2}{\tau} = \frac{R_{da}^2}{6\tau_H}
\]

where \( \tau_H \) is the exciton hopping time, \( L_D \) is the exciton diffusion length. By using Eqs. \(3.3\)\(-\)\(3.5\) the diffusion lengths of singlet (S) and triplet (T) excitons are, respectively, obtained as:

\[
L_D(S) = \frac{R_f \sqrt{\tau_S k_f}}{\sqrt{6}}
\]

and

\[
L_D(T) = \sqrt{\frac{\tau_T k_T}{6} \left[ R_d - \frac{L}{2} \ln(\tau_T k_d) \right]}
\]

and the corresponding diffusion coefficients are obtained as:

\[
D(S) = \frac{R_f^2 \sqrt[k_f]{\tau_S^2}}{6 \sqrt{\tau_S}}
\]

and

\[
D(T) = \frac{k_T}{6} \left( R_d - \frac{L}{2} \ln(\tau_T k_d) \right)^2
\]

Notably, in both Eqs. \(3.6\) and \(3.7\), the diffusion length is dependent on the product of the lifetime and the respective transfer rate.

### 3.4 CT exciton recombination dynamics

Three main processes need to be considered from the time an exciton at the D-A interface generates a CT exciton to the time when charges are collected at the electrodes: geminate recombination, bimolecular recombination, and charge transport
The geminate recombination phase starts when the electron of an exciton is transferred from a donor to an acceptor molecule at the interface to form a CT exciton. A singlet CT exciton can decay to the ground state with a rate constant $k_q$ or separate into free charge carriers with rate constant $k_d$; the latter can occur for both single and triplet excitons. Once separated, some fraction of the charge carriers may return to form CT excitons with a rate constant $k_r$, as shown in Figure 3.1. Therefore, long-lived CT excitons can act as a precursor for free charge carriers [30, 63]. Among the fraction of reformed CT excitons, some may recombine and others may separate again. This can be repeated many times. When some fraction have already recombined and some separated to sufficiently long distances, the geminate recombination phase ends and the bulk recombination phase starts [63].

![Diagram](image)

**Figure 3.1** Charge carrier transfer processes in organic solar cells. CT exciton may either decay to the ground state with a rate constant $k_q$ or dissociate with a rate $k_d$. $k_r$ is the recombination rate of the charge carriers to form the original CT exciton after dissociation.
Recombination between electrons and holes is an energy loss process for the efficiency of OSCs, whether it occurs through geminate recombination or bulk recombination. Therefore, it is very important to suppress these recombinations in OSCs [63].

According to the Langevin theory, in an organic system, charge recombination occurs when an electron and a hole come close to each other within $r_c$. In the Langevin bimolecular process, the recombination coefficient is given as [56]:

$$\beta = e \frac{\mu_e + \mu_h}{\varepsilon \varepsilon_o} \ (3.10)$$

where $\mu_e (\mu_h)$ is the mobility of electrons (holes). The recombination rate is given by [55]:

$$k_r = \beta np \ (3.11)$$

where $n$ and $p$ are electron and hole concentrations, respectively. The recombination coefficients are evaluated by substituting the relative dielectric permittivity from Eqs. (3.1) and (3.2) into Eq. (3.10), thereby giving the singlet (S) and triplet (T) recombination coefficients, respectively, as:

$$\beta_S = e \frac{(\mu_e + \mu_h)\mu a_o}{a_S \mu_s \varepsilon_o} \frac{\alpha^2}{(\alpha - 1)^2} \ (3.12)$$

and

$$\beta_T = e \frac{(\mu_e + \mu_h)\mu a_o}{a_T \mu_s \varepsilon_o} \ (3.13)$$

By using the coefficient of Eqs. (3.12) and (3.13) in Eq. (3.11), we can obtain the rates of recombination of singlet ($k_S$) and triplet ($k_T$) excitons, which give the
corresponding probability of recombination:

\[
\frac{k_s}{k_s + k_T} = \frac{a'_s \alpha^2}{a'_s \alpha^2 + a'_t (\alpha - 1)^2} = \frac{1}{1 + \frac{a'_t}{a'_s} \left(\frac{\alpha - 1}{\alpha}\right)^2}
\] (3.14)

and

\[
\frac{k_T}{k_s + k_T} = \frac{a'_t (\alpha - 1)^2}{a'_s (\alpha - 1)^2 + a'_t \alpha^2} = \frac{1}{1 + \frac{a'_t}{a'_s} \left(\frac{\alpha - 1}{\alpha}\right)^2}
\] (3.15)

In deriving Eqs. (3.14) and (3.15), we have assumed the same electron and hole mobilities, and \( n \) and \( p \) for both singlet and triplet cases. \( a'_s(a'_t) \) represents singlet (triplet) Bohr radius of CT excitons.

### 3.5 Results and discussions

A study of the diffusion length, diffusion coefficient, fraction of excitons that reach the D-A interface, and recombination of charge carriers into CT excitons have been carried out for both singlet and triplet excitons. We have found that triplet excitons have a lifetime about three orders of magnitude greater than singlet excitons; however, the transfer rate of singlet excitons is about three orders of magnitude larger than that of triplet excitons, which results in a higher diffusion coefficient for singlet excitons. The diffusion length as clearly shown in Eqs. (3.6) and (3.7) are dependent on the product of the lifetime and the transfer rate for singlet and triplet excitons, this product is the dominant term in both expressions.

For calculating the diffusion lengths and diffusion coefficients for singlet and triplet excitons using Eqs. (3.6)-(3.9), we require some material-dependent input parameters. For this, we have selected a few materials used as donors and listed their available input parameters in Table 3.1.
Table 3.1 Input parameters for calculating the diffusion length \( (L_D \text{ calc.}) \) from Eqs. (3.6) and (3.7) and diffusion coefficient \( (D) \) from Eqs. (3.8) and (3.9) for excitons in several donor materials.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>Exciton multiplicity</th>
<th>( \tau_i ) ((i = S \text{ or } T)) (ns)</th>
<th>( R_j ) ((j = S \text{ or } T)) (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>S</td>
<td>3.5</td>
<td>1.9</td>
<td>[64]</td>
</tr>
<tr>
<td>CBP</td>
<td>S</td>
<td>0.7</td>
<td>2.2</td>
<td>[64]</td>
</tr>
<tr>
<td>SubPc</td>
<td>S</td>
<td>( \leq 1 )</td>
<td>1.5</td>
<td>[64]</td>
</tr>
<tr>
<td>PTCDA</td>
<td>S</td>
<td>3.2</td>
<td>1.4</td>
<td>[64]</td>
</tr>
<tr>
<td>DIP (upright)</td>
<td>S</td>
<td>1.8</td>
<td>2.0</td>
<td>[64]</td>
</tr>
<tr>
<td>DIP (flat)</td>
<td>S</td>
<td>1.8</td>
<td>1.7</td>
<td>[64]</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Monomer</td>
<td>800</td>
<td>0.7</td>
<td>[64]</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Dimer</td>
<td>2800</td>
<td>0.7</td>
<td>[64]</td>
</tr>
<tr>
<td>Ir (ppy)(_3)</td>
<td>T</td>
<td>1330</td>
<td>1.1</td>
<td>[61]</td>
</tr>
<tr>
<td>Meo-POV</td>
<td>S</td>
<td>0.055</td>
<td>1.9</td>
<td>[65]</td>
</tr>
<tr>
<td>PDHFV</td>
<td>S</td>
<td>0.05</td>
<td>2.2</td>
<td>[65]</td>
</tr>
<tr>
<td>PTEH</td>
<td>S</td>
<td>0.23</td>
<td>2.4</td>
<td>[65]</td>
</tr>
<tr>
<td>PDHFHPPV</td>
<td>S</td>
<td>0.71</td>
<td>4.3</td>
<td>[65]</td>
</tr>
</tbody>
</table>

By using Eqs. (3.6) - (3.9) and the input parameters given in Table 3.1, the diffusion lengths and diffusion coefficients have been calculated for some of the donor materials; these are listed in Table 3.2. According to Table 3.2, the calculated diffusion lengths in different donors for singlet excitons range from 4.5 to 129.8 nm,
which agree reasonably well with the available experimental values, which range from 5.1 to 21.8 nm. Likewise, the calculated diffusion lengths for triplet excitons range from 1.3 to 30.2 nm and the experimental counterparts from 13.1 to 18.0 nm, which are also in agreement. Therefore, in view of these results, it may be concluded that the diffusion lengths of singlet and triplet excitons in most organic donors are comparable.

The relation between the diffusion length and the fraction of excitons that reach the D-A interface is given by [66]:

\[
\frac{L_{d\text{ex}}}{d} \frac{1 - \exp(-2d/L_{d\text{ex}})}{1 + \exp(-2d/L_{d\text{ex}})}
\]

where \(d\) is the distance between the donor and acceptor molecules. By using the diffusion lengths calculated from Eqs. (3.6) and (3.7), we have plotted the fraction of excitons that reach the D-A interface from Eq. (3.16) as a function of \(d\) in Figure 3.2 for some organic semiconductors listed in Table 3.1. According to Figure 3.2, the comparable diffusion lengths allow a fairly good fraction between 0.99 to 0.64 of both singlet and triplet excitons to reach the D-A interface for \(d\) values between 10 and 15 nm. A typical exciton diffusion length in bulk heterojunction (BHJ) solar cells is in the 10 – 15 nm range [30]; however, in BHJ for which the donor and acceptor materials are mixed to form an interpenetrating nanoscale network of D-A blend, we will expect the interface to be at a distance less than the diffusion length. Thus, at a distance of \(d = 5\) nm, an appreciable fraction (> 0.93) of excitons can make it to the interface in most organic molecules, as shown in Figure 3.2. However, in PTCDA, just 0.71 of excitons are able to reach the interface at the same 5 nm distance.
The formation of CT excitons may mediate the exciton dissociation and charge separation due to the excess energy released in the process. However, in the event that a CT exciton does not dissociate, it may recombine due to the Coulomb interaction between e-h in the exciton.

**Figure 3.2** Plot of fraction of the singlet (S) and triplet (T) excitons reaching the D-A interface as a function of the distance \(d\) calculated from Eq. (3.10) for some selected organic semiconductors given in Table 3.1.

The formation of CT excitons may mediate the exciton dissociation and charge separation due to the excess energy released in the process. However, in the event that a CT exciton does not dissociate, it may recombine due to the Coulomb interaction between e-h in the exciton.
Table 3.2 Calculated diffusion length ($L_D$ calc.) from Eqs. (3.6) and (3.7), diffusion coefficient ($D$) from Eqs. (3.8) and (3.9) and measured diffusion length ($L_D$ meas.) of excitons in some organic semiconductors. Calculated values at $R_w = 0.5$ nm.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>Exciton multiplicity</th>
<th>Calc. $D$ (cm$^2$/s) $\times 10^{-4}$</th>
<th>$L_D$ calc. (nm)</th>
<th>$L_D$ meas. (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>S</td>
<td>3.6</td>
<td>11.2</td>
<td>5.1</td>
<td>[64]</td>
</tr>
<tr>
<td>CBP</td>
<td>S</td>
<td>43.2</td>
<td>17.4</td>
<td>16.8</td>
<td>[64]</td>
</tr>
<tr>
<td>SubPc</td>
<td>S</td>
<td>$\geq 3.0$</td>
<td>$\leq 5.5$</td>
<td>8.0</td>
<td>[64]</td>
</tr>
<tr>
<td>PTCDA</td>
<td>S</td>
<td>0.6</td>
<td>4.5</td>
<td>10.4</td>
<td>[64]</td>
</tr>
<tr>
<td>DIP (upright)</td>
<td>S</td>
<td>9.5</td>
<td>13.1</td>
<td>16.5</td>
<td>[64]</td>
</tr>
<tr>
<td>Dip (flat)</td>
<td>S</td>
<td>2.6</td>
<td>8.0</td>
<td>21.8</td>
<td>[64]</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Monomer</td>
<td>0.000021</td>
<td>1.3</td>
<td>18.0</td>
<td>[64]</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Dimer</td>
<td>0.000006</td>
<td>1.3</td>
<td>13.1</td>
<td>[64]</td>
</tr>
<tr>
<td>Meo-POV</td>
<td>S</td>
<td>228.1</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDHFV</td>
<td>S</td>
<td>604.7</td>
<td>17.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTEH</td>
<td>S</td>
<td>221.6</td>
<td>22.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir (ppy)$_3$</td>
<td>T</td>
<td>0.069</td>
<td>30.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDHFHPPV</td>
<td>S</td>
<td>2374.2</td>
<td>129.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is therefore critical to know the energy of the CT exciton formed. For instance, on the one hand, if the CT exciton energy is above the energy of the donor triplet exciton state, the CT exciton may go back to the donor triplet exciton state through intersystem crossing without being dissociated. On the other hand, if the CT exciton state energy is lower than the donor triplet exciton state then the CT exciton
cannot be transferred back to the donor and it may dissociate [55].

A CT exciton state can be generated in three ways: 1) A singlet exciton from the donor can become a singlet CT exciton, 2) a triplet exciton excited in the donor can become a triplet CT exciton, and 3) a singlet exciton in the donor may go through an intersystem crossing to the donor triplet exciton state before going to the CT state. Thus, if a triplet CT exciton is formed and its energy is lower than that of the triplet donor exciton state, it cannot go back to the donor and may dissociate eventually into e-h pair. This is evident from observing a high photovoltaic performance in platinumacetylide polymer, which exclusively generated triplet excitons due to the introduction of heavy metal atom Pt, which induces strong spin-orbit interaction and thus rapid singlet to triplet intersystem crossing \((k_{isc} > 10^{11} s^{-1})\) with possible absorption to triplet excitons, resulting into triplet CT excitons at an energy sufficiently lower than the triplet state of the donor polymer to favour charge separation after excitation [40, 62].

A free e-h pair does not have a distinct singlet or triplet spin character [59]; however, prior to dissociation, a CT exciton will still be spin correlated to the singlet or triplet state. In Eqs. (3.12) and (3.13) we have derived spin-dependant recombination rate constants from which we can calculate how, prior to charge separation of dissociated exciton, the charges can still be drawn back to their original excitonic state and possibly decay to the ground state. The exciton Bohr radii found in most conjugated polymers are similar in magnitude, especially, for rigid-rod polymers. For singlet excitons, the calculated Bohr radius is 0.40 nm for ladder-type poly-\(p\)-phenylene oligomers and the experimental value is 0.72 nm, as reported for methyl-substituted ladder-type poly(\(para\)-phenylene) polymers [67, 68]. The triplet
exciton Bohr radii are not known in these materials. As the dielectric constant of most organic solids is about the same, it is expected that the Bohr radius of an exciton and that of its corresponding CT state will be similar. The CT exciton Bohr radii for singlet and triplet states have been simulated in solid pentacene to be $a'_s = 0.8\text{ nm}$ and $a'_t = 0.1\text{ nm}$, respectively [69]. Therefore, for calculating the probabilities of recombination from Eqs. (3.14) and (3.15) for different polymers, we have assumed that the CT exciton Bohr radii for singlet exciton as 0.72 nm and for triplet as 0.1 nm, which is the same as for solid pentacene. We have thus found the probability of recombination of singlet [Eq. (3.14)] and triplet excitons [Eq. (3.15)] to be about 65.6 % and 34.4 %, respectively, by using $\alpha = 1.37$ [15]. This suggests that the Langevin-type recombination rate $k_i$ of triplet excitons is much lower in organic semiconductors.

3.6 Conclusions

By using Föster and Dexter transfer rates, we derived a relation for the diffusion length and diffusion coefficient of singlet and triplet excitons, respectively. We showed that excitons in both singlet and triplet states have comparable diffusion lengths, because the longer lifetime of triplet states are compensated for by their lower transfer rates, due to lower diffusion coefficients. These results are consistent with experimental observations [64]. Furthermore, we showed that triplet excitons can be considered to contribute to free charge carriers in OSCs if the CT exciton state is lower in energy than the triplet state of the donor polymer.
Chapter 4 Charge carrier mobility dependent open-circuit voltage in organic and hybrid solar cells

This work has been published in the following paper:


Statement of contribution of each author:

The candidate D. Ompong has carried out all the research activities to obtain the results presented in this chapter under the supervision of J. Singh.
Abstract

A better understanding of the open-circuit voltage ($V_{oc}$) related losses in organic solar cells (OSCs) is desirable in order to assess their photovoltaic performance. We have derived $V_{oc}$ as a function of charge carrier mobilities ($\mu_e$ and $\mu_h$) for organic and hybrid solar cells by optimising the drift-diffusion current density. The $V_{oc}$ thus obtained depends on the energy difference between the highest occupied molecular orbital (HOMO) level and the quasi-Fermi level of holes of the donor material and on the ratio of the electron ($\mu_e$) and hole ($\mu_h$) mobilities in the blend. It is found that the $V_{oc}$ increases with the increase of the mobility ratio $\mu_e/\mu_h$. The most loss in $V_{oc}$ is contributed by the energetics of the donor and acceptor materials.
4.1 Introduction

The development of new materials for photovoltaic applications coupled with device optimisation has led to a dramatic increase in OSCs’ performance in recent years [70]. A major research focus now lies in finding ways for further optimisation of the PCE, guided by a deeper understanding of the fundamental processes that influence the photovoltaic properties of OSCs [71]. The following four processes of OSCs and organic hybrid solar cells (OHSCs) make them remarkably different from their inorganic counterparts: i) photon absorption and exciton generation; ii) diffusion of excitons to the donor-acceptor (D-A) interface; iii) dissociation and charge separation at the interface; and iv) carrier collection by the electrodes [16, 72]. These four processes have to be sufficiently efficient to reduce or eliminate energy losses leading to reduction in the short-circuit current density $J_{sc}$ and open-circuit voltage $V_{oc}$, and hence, reduction in the power conversion efficiency of OSCs and OHSCs.

The current density $J$ in the drift-diffusion model is a function of both the electrical and chemical potential gradients, denoted by $\nabla U$ and $\nabla C$, respectively. In OSCs, $\nabla U$ is negligible because there is no built-in electric field like the one in inorganic solar cells due to the property of p-n junction [73]. Therefore, in OSCs and OHSCs $J$ depends mainly on the gradient of the chemical potential [73], which is a function of $V_{oc}$ as shown below. Thus, $J$ becomes a function of $V_{oc}$ and by optimising $J$ with respect to $V_{oc}$ one can determine the optimal value of $J$ corresponding to $V_{oc}$.

It is established that the $V_{oc}$ of OSCs [74-77] depends on the energy difference between the HOMO of the donor material and LUMO of the acceptor material or the conduction band of the inorganic nanoparticle in the case of OHSCs [78]. In addition, simulation[70, 71] and experimental [79-81] works show that charge transport have
effect on PCE of OSCs and a detailed analysis of bulk heterojunction organic solar cells reveals that low $V_{oc}$ is the main factor limiting this efficiency [75]. This implies that the $V_{oc}$ of an OSC depends on the transport properties of the charge carrier in the material, which has not yet been studied adequately.

In this work, we have derived an analytical expression for $V_{oc}$ by optimising the drift-diffusion current density $J$. The $V_{oc}$ thus obtained depends explicitly on the electron and hole mobilities and donor and acceptor HOMO and LUMO energy levels. In a previous study [70], the effective carrier mobility $\mu_{eff} = \sqrt{\mu_e \mu_h}$ is used to define the external voltage applied across an OSC, however, in our approach the concept of the effective mobility is not used. Instead, it is found that the $V_{oc}$ depends on the ratio of the electron ($\mu_e$) to hole ($\mu_h$) mobility such that if the ratio $\mu_e / \mu_h = p$ increases the $V_{oc}$ also increases.

### 4.2 Derivation of Open-Circuit Voltage ($V_{oc}$)

The open-circuit voltage is given by the energy difference between the electron and hole quasi-Fermi levels as [73]:

$$- qV_{oc} = E_{F,e} - E_{F,h}$$  \hspace{1cm} (4.1)

In OSCs and OHSCs, the open-circuit voltage is also related to the HOMO energy level of the donor ($E_{HOMO}^D$) and the LUMO energy level of the acceptor ($E_{LUMO}^A$) as [82]:

$$- qV_{oc} = E_{HOMO}^D - E_{LUMO}^A - \Delta E_{loss}$$  \hspace{1cm} (4.2)

where $\Delta E_{loss}$ is an empirical value representing energy losses in transporting charge...
carriers to the electrodes. According to the drift-diffusion model, the total current density \( J \) in a semiconductor under bias can be written as the sum of the electron and hole current densities, given by [83]:

\[
J = J_n + J_p = \mu_e n \nabla E_{F,e} + \mu_h p \nabla E_{F,h}
\]  
(4.3)

where \( J_n = \mu_e n \nabla E_{F,e} \) is the electron current density and \( J_p = \mu_h p \nabla E_{F,h} \) is the hole current density. Here \( n(p) \) is the electron (hole) density, \( \mu_e (\mu_h) \) is the electron (hole) mobility, and \( \nabla E_{F,e} (\nabla E_{F,h}) \) is the gradient of the electron (hole) quasi-Fermi level.

The charge-carrier densities \( n \) and \( p \) of electrons and holes inside the active layer are, respectively, given as [84]:

\[
n = N_e \exp[(E_{F,e} - E_{LUMO}^A)/k_B T]
\]  
(4.4)

and

\[
p = N_v \exp[(E_{HOMO}^D - E_{F,h})/k_B T]
\]  
(4.5)

where \( N_e (N_v) \) is the effective density of states for the LUMO (HOMO) of acceptor (donor) material and \( E_{F,e} (E_{F,h}) \) is the energy of the corresponding Fermi levels. By using Eqs. (4.1) - (4.5), the total current density in (4.3) can be written as a function of \( V_{oc} \) as:

\[
J = \mu_e N_e \nabla E_{F,e} \exp\left[(-2qV_{oc} + E_{F,h} - E_{HOMO}^D + \Delta E_{ion})/k_B T\right] \\
+ \mu_h N_v \nabla E_{F,h} \exp\left[(-2qV_{oc} + E_{LUMO}^A - E_{F,e} + \Delta E_{ion})/k_B T\right]
\]  
(4.6)

The total current density \( J \) in equation (4.6) can be optimised with respect to \( V_{oc} \) as

\[
\frac{d(J(V_{oc}))}{dV_{oc}} = 0,
\]

which gives:
\[ \mu_h N_c \nabla E_{F,h} \exp\left[\frac{(E_{LUMO}^A - E_{F,e})}{k_B T}\right] = -\mu_e N_c \nabla E_{F,e} \exp\left[\frac{(E_{F,h} - E_{HOMO}^D)}{k_B T}\right] \] (4.7)

In OSCs, the chemical potential energy gradient \( \nabla C \) drives the electrons and holes in the opposite direction [73], this explains the significance of the minus sign on the right hand side of equation (4.7); the minus sign is dropped from here onwards for convenience.

Multiplying both sides of Eq.(4.7) by \( \exp\left[\frac{(E_{F,h} - E_{HOMO}^D)}{k_B T}\right] \) we get:

\[ \exp\left[(-E_g + qV_{oc})/k_B T\right] = \mu_e N_c \nabla E_{F,e} / \mu_h N_c \nabla E_{F,h} \exp\left[2(E_{F,h} - E_{HOMO}^D)/k_B T\right] \] (4.8)

where \( E_g = |E_{HOMO}^A - E_{LUMO}\) is the effective band gap or the D-A interface energy gap.

Rearranging equation (4.8) we obtain \( V_{oc} \) as:

\[ V_{oc} = \frac{1}{q} \left\{ E_g - 2(E_{F,h} - E_{HOMO}^D) + k_B T \ln \left( \frac{\mu_e N_c \nabla E_{F,e}}{\mu_h N_c \nabla E_{F,h}} \right) \right\} \] (4.9)

Following earlier works [70, 84] we assume \( N_c = N_e \) and \( \nabla E_{F,e} = \nabla E_{F,h} \) which gives Eq.(4.10):

\[ qV_{oc} = E_g - \Delta; \text{ where } \Delta = 2(E_{F,h} - E_{HOMO}^D) - k_B T \ln \left( \frac{\mu_e}{\mu_h} \right) \] (4.10)

Here \( \Delta \) is the energy loss contributed by the energetic (first term) and charge transport (second term).

**4.3 Results**

We have used Eq.(4.10) to calculate \( V_{oc} \) in several D-A materials listed in Table 4.1. The input parameters required for each D-A in the calculations are also listed in Table 4.1. In addition, for calculating \( V_{oc} \) from Eq. (4.10) we need the values of the energy of the donor HOMO (\( E_{HOMO}^D \)) and acceptor LUMO (\( E_{LUMO}^A \)) which are listed in
Table 4.2. It may be noted that following [84], we have used $(E_{F,h} - E_{HOMO}^D) \approx 0.2 \text{ eV}$ in Eq.(4.10) for all D-A materials used in Tables 4.1 and 4.2. By using these input parameters the calculated values of $V_{oc}$ are listed in Table 4.2 along with their experimental values obtained for these materials. According to Table 4.2, the calculated $V_{oc}$ values are in reasonable agreement with those obtained experimentally.

![Figure 4.1](image)

**Figure 4.1** $V_{oc}$, in Eq.(4.10) plotted as a function of electron : hole mobility ratio, 

$$P = \frac{\mu_e}{\mu_h}.$$ 

According to Eq.(4.10) the $V_{oc}$ increases if the ratio $P > 1$, that means, when the electron mobility is higher than the hole mobility as shown in Figure 4.1. In a material with equal mobility of electrons and holes, the contribution of the transport term to the $V_{oc}$ vanishes. The analytical results of the dependence of $V_{oc}$ on the charge carrier mobilities derived in Eq.(4.10) agree with the experimental observation as well.
as with the numerical simulation [85]. In Figures 4.2(a) and (b) we have reproduced the J-V characteristics measured on P3HT:PCBM BHJ OSCs annealed at two different temperatures, 52 °C and 70 °C, respectively [85].

![Figure 4.2](image)

**Figure 4.2** Measured current-voltage characteristics normalised to the short-circuit current (open circles) of two P3HT/PCBM solar cells annealed at 52 °C (a) and 70 °C (b). The solid lines denote simulations using slowest carrier recombination constant $\gamma = \zeta \min(\mu_e, \mu_h)$, while the dashed lines correspond to simulations using average carrier recombination constant $\gamma = \zeta (\mu_e + \mu_h)$. (Reproduced with permission from [85]. Copyright 2006, AIP Publishing LLC.)
The measured mobility in P3HT:PCBM of electrons and holes is found to be 
\[
\mu_e = 2.5 \times 10^{-8} \text{ (m}^2\text{V}^{-1}\text{s}^{-1}), \quad \mu_h = 3.0 \times 10^{-12} \text{ (m}^2\text{V}^{-1}\text{s}^{-1}) \text{ at 52 °C (Figure 4.2a) and}
\]
\[
\mu_e = 1.1 \times 10^{-7} \text{ (m}^2\text{V}^{-1}\text{s}^{-1}), \quad \mu_h = 1.1 \times 10^{-10} \text{ (m}^2\text{V}^{-1}\text{s}^{-1}) \text{ at 70 °C (Figure 4.2b) [85]. Using}
\]
these values, we find that the mobility ratio \( P \) decreases from 8.3x10^{3} to 1.0x10^{3} when one anneals the sample at 52 °C and 70 °C. According to Eq.(4.10), this means that one should get a higher value of \( V_{oc} \) at the annealing temperature of 52 °C than at 70 °C. This result is quite consistent with that shown in Figures 4.2(a) and (b), where the measured and simulated \( V_{oc} \) at 52 °C is about 0.04 V higher than that at 70 °C.

Mobility dependent J-V characteristics have also been simulated by assuming \( \mu_e = \mu_h \) [70]. The \( V_{oc} \) is found to be independent of the charge carrier mobility in the range from 1 to 10^{-6} cm²/Vs. According to Eq.(4.10) also, the mobility dependent term vanishes for \( \mu_e = \mu_h \) and hence \( V_{oc} \) becomes constant which is consistent with this result.

**Table 4.1** Input values for calculating \( V_{oc} \) with donor–acceptor materials forming the active layer, electron mobility \( \mu_e \), hole \( \mu_h \) mobility, and mobility ratio \( P \).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Active Layer</th>
<th>( \mu_e ) (cm²V⁻¹s⁻¹)</th>
<th>( \mu_h ) (cm²V⁻¹s⁻¹)</th>
<th>( P = \mu_e/\mu_h )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSC</td>
<td>PTB7:PCBM</td>
<td>1.0x10⁻³</td>
<td>2.0x10⁻⁴</td>
<td>5.0</td>
<td>[86]</td>
</tr>
<tr>
<td>OSC</td>
<td>PCDTBT:PCBM</td>
<td>2.9x10⁻³</td>
<td>3.0x10⁻⁵</td>
<td>96.7</td>
<td>[87]</td>
</tr>
<tr>
<td>OSC</td>
<td>P3HT:PCBM</td>
<td>x10⁻³</td>
<td>x10⁻⁴</td>
<td>10.0</td>
<td>[88]</td>
</tr>
<tr>
<td>OSC</td>
<td>MDMOPPV:PCBM</td>
<td>x10⁻³</td>
<td>x10⁻⁴</td>
<td>10.0</td>
<td>[88]</td>
</tr>
<tr>
<td>OSC</td>
<td>PBDTBD : Bis-PCBM</td>
<td>9.6x10⁻⁵</td>
<td>1.3x10⁻⁴</td>
<td>0.7</td>
<td>[76]</td>
</tr>
<tr>
<td>OSC</td>
<td>PBDTBD : PCBM</td>
<td>8.8x10⁻⁴</td>
<td>1.4x10⁻⁳</td>
<td>0.6</td>
<td>[76]</td>
</tr>
<tr>
<td>OSC</td>
<td>P3HT: Bis-PCBM</td>
<td>9.6x10⁻⁵</td>
<td>1.0x10⁻⁴</td>
<td>1.0</td>
<td>[76]</td>
</tr>
<tr>
<td>OSC</td>
<td>MEHPPV:PCBM</td>
<td>x10^{-3}</td>
<td>x10^{-6}</td>
<td>1000.0</td>
<td>[89]</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------</td>
<td>----------</td>
<td>----------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>OSC</td>
<td>Si-PCPDTBT:PCBM</td>
<td>2.5x10^{-4}</td>
<td>3.0x10^{-5}</td>
<td>8.3</td>
<td>[90]</td>
</tr>
<tr>
<td>OHSC</td>
<td>MDMOPPV:nc-ZnO</td>
<td>2.8x10^{-3}</td>
<td>5.5x10^{-6}</td>
<td>5.1</td>
<td>[78]</td>
</tr>
<tr>
<td>OHSC</td>
<td>P3HT: Si-NCs</td>
<td>x10^{-3}</td>
<td>x10^{-3}</td>
<td>1.0</td>
<td>[91]</td>
</tr>
</tbody>
</table>

### 4.4 Discussions

According to Eq.(4.10) the open-circuit voltage becomes equal to the effective band gap energy and hence independent of the charge carrier mobilities when the hole quasi-Fermi level is equal to the HOMO level of the donor molecule and the electron and hole mobilities are equal. It is to be noted that the $V_{oc}$ derived in Eq.(4.10), depends on the electron and hole mobilities directly. The material with $\mu_e < \mu_h$ will have greater energy loss ($\Delta$) and hence lower $V_{oc}$ in comparison with materials with $\mu_e > \mu_h$, which will have lesser $\Delta$ and hence higher $V_{oc}$. From this point of view, one may prefer to use materials with $\mu_e > \mu_h$ for obtaining higher $V_{oc}$ in OSCs.

As stated above, in the calculation of $V_{oc}$ from Eq.(4.10), we have assumed a constant value for $(E_{F,h} - E_{HOMO}^D) \approx 0.2$ eV, which is valid only if the charge carrier concentration remains constant and that means the mobilities of charge carriers are not very high or very low. For example, in OSCs based on P3HT:PCBM where a mobility ratio $\mu_e / \mu_h = 10$ is considered [88], it is found that if both charge carrier mobilities at this ratio are high, then this will lead to the efficient extraction of charge carriers which reduces the charge carrier concentration. This reduction in carrier concentration is expected to draw the hole quasi-Fermi level away from the HOMO...
level of the donor material, which according to Eq.(4.10) will reduce the $V_{oc}$. This will eventually reduce the PCE as found in [88]. Likewise, at low charge carrier mobilities at the same ratio, the recombination will be enhanced which will reduce the short-circuit current density [71, 88], leading to reduction in PCE. In this view, the derived $V_{oc}$ in Eq.(4.10) may be regarded to be valid only at moderate electron and hole mobilities leading to high PCE.

**Table 4.2** Donor- Acceptor materials, Donor HOMO level $E_{HOMO}^D$, Acceptor LUMO level $E_{LUMO}^A$, Effective band gap $E_g = |E_{HOMO}^D - E_{LUMO}^A|$, transport loss term $k_BT\ln(\mu_e/\mu_h)$, $V_{oc}^{calc}$ calculated from Eq.(4.10), and experimental open-circuit voltage $V_{oc}^{exp}$.

<table>
<thead>
<tr>
<th>Donor material</th>
<th>$E_{HOMO}^D$ (eV)</th>
<th>Acceptor material</th>
<th>$E_{LUMO}^A$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$k_BT\ln(\mu_e/\mu_h)$ (eV)</th>
<th>$V_{oc}^{calc}$ (V)</th>
<th>$V_{oc}^{exp}$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7</td>
<td>5.15</td>
<td>PCBM</td>
<td>4.06</td>
<td>1.09</td>
<td>0.04</td>
<td>0.73</td>
<td>0.75</td>
<td>[86]</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>5.50</td>
<td>PCBM</td>
<td>4.30 [92]</td>
<td>1.20</td>
<td>0.12</td>
<td>0.92</td>
<td>0.85</td>
<td>[87]</td>
</tr>
<tr>
<td>P3HT</td>
<td>5.10</td>
<td>PCBM</td>
<td>4.06</td>
<td>1.04</td>
<td>0.06</td>
<td>0.69</td>
<td>0.63</td>
<td>[77]</td>
</tr>
<tr>
<td>MDMOPPV</td>
<td>5.36</td>
<td>PCBM</td>
<td>4.06</td>
<td>1.30</td>
<td>0.06</td>
<td>0.96</td>
<td>0.83</td>
<td>[77]</td>
</tr>
<tr>
<td>PBDTBDD</td>
<td>5.23</td>
<td>Bis-PCBM</td>
<td>3.80</td>
<td>1.43</td>
<td>-0.01</td>
<td>0.97</td>
<td>1.00</td>
<td>[76]</td>
</tr>
<tr>
<td>PBDTBDD</td>
<td>5.23</td>
<td>PCBM</td>
<td>3.94</td>
<td>1.29</td>
<td>-0.01</td>
<td>0.88</td>
<td>0.86</td>
<td>[76]</td>
</tr>
<tr>
<td>P3HT</td>
<td>5.10</td>
<td>Bis-PCBM</td>
<td>3.80</td>
<td>1.30</td>
<td>0.00</td>
<td>0.89</td>
<td>0.74</td>
<td>[76]</td>
</tr>
<tr>
<td>MEHPPV</td>
<td>5.20</td>
<td>PCBM</td>
<td>3.95</td>
<td>1.00</td>
<td>0.18</td>
<td>0.88</td>
<td>0.74</td>
<td>[79]</td>
</tr>
<tr>
<td>Si-PCPDTBT</td>
<td>4.86</td>
<td>PCBM</td>
<td>3.88</td>
<td>0.98</td>
<td>0.05</td>
<td>0.63</td>
<td>0.59</td>
<td>[90]</td>
</tr>
</tbody>
</table>
For highlighting the role of the charge carrier mobility, it may be desirable to consider the two D-A combination materials MDMOPPV:PCBM and P3HT:Bis-PCBM in Table 4.2. These two combinations have the same effective gap of 1.30 eV but the second term of $\Delta$ in Eq.(4.10) is 0.06 eV for the first combination and zero for the second (see Table 4.2). As a result, the value of $\Delta$ is less in the first combination than in the second, producing higher $V_{oc}$ (0.96 eV) in MDMOPPV:PCBM in comparison with that of 0.89 eV in P3HT:Bis-PCBM. It may be interesting to note that, using $(E_{F,h} - E_{HOMO}^D) \approx 0.2$ eV in Eq.(4.10), we get, $\Delta = 0.4 - k_B T \ln(\mu_e/\mu_h)$ which shows that the loss of 0.4 eV due to the energy difference is much bigger than the second term due to the charge transport, whose calculated values are listed in column 6 of Table 4.2.

### 4.5 Conclusions

We have derived a mobility dependant expression for $V_{oc}$ of OSCs and OHSCs. We have shown that if the difference between the electron and hole mobilities is small, the $V_{oc}$ derived here does not depend on the charge carrier mobilities significantly. According to our model, the $V_{oc}$ of a D-A material depends on two terms; the first depends on the energetics and the second on the electron and hole
mobility ratio. This may be expected to be useful in predicting the PCE of OSCs and OHSCs prior to their fabrications from a combination of D-A materials.
Chapter 5 Optimisation of Photocurrent in Bulk Heterojunction Organic Solar Cells using Optical Admittance Analysis Method

This work has been submitted to the Journal of Materials Science: Materials in Electronics for publication.

Statement of contribution of each author:

D. Ompong performed literature review, aspects of methodology and results and discussion. M. Narayan and J. Singh assisted in methodology and results and guided and edited the manuscript.
Abstract

The optical admittance analysis method allows one to calculate the optical properties of any multilayer structure, such as thin film solar cells, which consist of a few thin layers. The optimised thicknesses of the active individual layers in organic thin film solar cells are obtained using optical admittance analysis method (OAAM). We have used OAAM to simulate the optical properties of two bulk heterojunction (BHJ) organic solar cells (OSCs) of structures: (1) ITO/PEDOT:PSS /P3HT:PCBM/LiF/Al and (2) ITO/ZnO /PTB7:PCBM /LiF/Ag. The short-circuit current density ($J_{sc}$) is simulated and is found to be maximum at the thicknesses of 75 nm and 115 nm in P3HT:PCBM and PTB7:PCBM blend layers, respectively, which agree very well with the experimental values. The optimal thickness of the Al cathode is also simulated and found to be 40 nm. By optimising the thickness of the two BHJ OSCs structures, one can increase the short-circuit current density of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al BHJ OSC by 4.8% and that of ITO/ZnO /PTB7:PCBM /LiF /Ag by 13.3% using our optimal designs.
5.1 Introduction

The interest in OSCs for the last two decades has spurred extensive research effort around the globe to understand and improve the performance of these cells [8, 93]. The bulk heterojunction (BHJ) OSCs in which the organic donor and acceptor (D-A) blend creates nanoscale interconnected neat and mixed phases have produced high power conversion efficiency (PCE) and hence are currently the preferred device structure for further investigations [94-96].

In BHJ OSCs a thinner active layer thickness is desirable for efficient charge extraction, reduced charge carrier recombination, and minimum material cost, but then this occurs at the expense of reduced light absorption which increases with increase in layer thickness. Although the extinction coefficients of organic semiconductors can be more than a magnitude higher than that of inorganic semiconductors such as silicon, the low charge carrier mobilities in organic solids present a transport limitation in OSCs [97, 98]. In other words, due to the low charge carrier mobilities in organic semiconductors, the optimal active layer thickness is always a compromise between the photon absorption and charge carrier collection. For this reason light trapping schemes are very important in designing efficient organic and hybrid-organic solar cells [99, 100]. However, OSCs have thin active layers comparable to the coherence length of the incident light so their optical properties are substantially influenced by interference effects that contribute to the electromagnetic field modulation inside the device, such that absorption due to interference effects can sometimes dominate over that due to increased optical path length where diffraction grating is used [24, 25]. Since most of the solar energy is concentrated in the visible and near-infrared (IR) regions, OSCs designed to
efficiently harvest solar energy must have a large overlap between its absorption spectra and the solar spectrum. Efficient absorption in the whole solar spectrum should be the first design rule if the total efficiency of the solar cells is to improve [8]. Recent achievements in highly efficient thin film single-junction polymer solar cells are mainly based on advances in light manipulation schemes capable of enhancing photon absorption and thus exciton generation in the solar cells [101].

The traditional light trapping schemes, where one applies additional anti-reflection coating or texturing the surface of a thick conventional solar cell to redirect and trap light by total internal reflection (TIR), have limited applications in OSCs. These structures are relatively too large to employ on OSCs [98], of thicknesses in the 20-200 nm range [25]. It may also be noted that in such thin OSCs, less than 80 percent of the overall incident light is ultimately used in generating photocurrent [101]. As the thickness of an OSC is comparable to the wavelength of the incident light, and metal electrodes create highly reflecting interface thus coherent optics and wave effects which exploit the optical interference effects to aid absorption play a significant role in determining the optical properties of OSCs [25, 98].

In this work, we optimise the layer thicknesses of OSCs using optical admittance analysis method (OAAM) for optimal absorption. In particular, we have considered two BHJ OSCs of structures: (1) ITO(180 nm)/PEDOT:PSS (45 nm)/P3HT:PCBM (1:1)(d nm)/LiF (1 nm)/Al (100 nm) and (2) ITO/ZnO(100 nm)/PTB7:PCBM (1:1.5)(d nm)/LiF (15 nm)/Ag (100 nm). MATLAB environment is used for writing the computer simulation code. The optical properties of the OSCs are considered in the solar spectral wavelength range 300 to 900 nm in this modelling, optical isotropy of the D-A blend, and normal incidents of light are assumed.
throughout this work. The short-circuit current density \( J_{sc} \) is calculated at the standard AM 1.5 [102]. The thickness dependence of the \( J_{sc} \) thus calculated is compared with experimental data. The interference effects on \( J_{sc} \) at various interfaces of the layered structure are also studied.

The development of this simulation code was born because at the start of my PhD study I planned to use a commercial simulation software to do the optical modelling of the BHJ OSCs and hybrid solar cells. I later found that the price of the commercial software I had in mind is very expensive. As a result, I decided to use MATLAB to write computer code for the simulation. This resulted in huge consumption of time that would have been used in the simulation activities had I used the commercial software and made it necessary for me to apply for six month extension, as well as, changing the original thesis submission date.

5.2 Theory for the modelling

It is well established that in the propagation of an electromagnetic (EM) wave, the electric \( \vec{E} \) and magnetic \( \vec{H} \) field components, and unit vector \( \vec{s} \) in the direction of propagation are mutually perpendicular to each other and can be expressed as [103, 104]:

\[
\vec{H} = y(\vec{s} \times \vec{E})
\]  

(5.1)

where \( y \) is the admittance of the medium. For the propagation of an EM wave in a structure shown schematically in Figure 5.1(a), the tangential components of the electric and magnetic fields at a boundary are assumed to be continuous across the boundary because there is no mechanism that will change their values. The
magnitudes of the tangential electric and magnetic components at two successive boundaries will defer in phase by a factor due to the optical path difference. Thus the fields between two interfaces are always related by a phase difference. Consider an organic solar cell that has \( m \) layers deposited on a substrate as the \( m+1 \) layer of the whole structure. The thin film layers of the solar cell as shown in Fig. 1(a) are reduced to a single layer with interfaces (a) and (b) (Figure 5.1(b)), by optical admittance analysis method. The effective optical admittance \( (y_{\text{eff}}) \) of this multilayer structure can be written as [104]:

\[
y_{\text{eff}} = \frac{C}{B} \tag{5.2}
\]

where \( B \) and \( C \) are obtained from the characteristic matrix equation [103]:

\[
\begin{bmatrix}
B \\
C
\end{bmatrix} = \prod_{j=1}^{m} \begin{bmatrix}
\cos \delta_j & i \sin \delta_j / y_j \\
i y_j \sin \delta_j & \cos \delta_j
\end{bmatrix} \begin{bmatrix} 1 \\ y_{m+1} \end{bmatrix} \tag{5.3}
\]

where \( y_j \) and \( y_{m+1} \) are the optical admittance of the \( j \)th layer and substrate, respectively, and \( \delta_j \) is the phase difference given by:

\[
\delta_j = \frac{2\pi d_j}{\lambda} N_j \cos \theta \tag{5.4}
\]

Here \( d_j \) is the thickness of the \( j \)th layer, \( N_j = n_j + ik_j \) is the corresponding complex refractive index as a function of the wavelength \( \lambda \), of the incident light, \( n_j \) is the refractive index, \( k_j \) is the extinction coefficient, and \( \theta \) is the angle of refraction on the top interface of the \( j \)th layer. The optical admittance of the substrate is given as:

\[
y_{m+1} = N_s y^o \tag{5.5}
\]
where $N_s$ is the complex refractive index of the substrate and $y^o = \sqrt{\varepsilon_0}$ Siemens is admittance of vacuum. Using $y_{\text{eff}}$ in Eq. (5.2) one can calculate the total reflectance from the whole structure as:

$$R(\lambda) = \left| \frac{y_{\text{air}} - y_{\text{eff}}}{y_{\text{air}} + y_{\text{eff}}} \right|^2$$

(5.6)

where $y_{\text{air}}$ is the optical admittance of air. For a non-absorbing dielectric assembly, the transmittance is $T(\lambda) = [1 - R(\lambda)]$ but for an assembly containing both absorbing
and non-absorbing layer, subsidiary calculations involving the ratio of the output to
the input irradiances are necessary, this gives the total transmittance in the case of
absorption as [103]:

\[ T(\lambda) = [1 - R(\lambda)] \prod_{j=1}^{m} \psi_j \] \tag{5.7} 

where \( \psi_j \) is the ratio of the time average numerical magnitude of the Poynting’s
vector at the \( j \)th and the \((j+1)\)th boundaries [104, 105] given by:

\[ \psi_j = \frac{\text{Re}(y_{j+1})}{\text{Re}(y_j) \cos \delta_j + y_{j+1} \sin \delta_j} \] \tag{5.8} 

where \( \text{Re}(y_j) \) and \( \text{Re}(y_{j+1}) \) represent the real part of the effective admittance for \( j \)th
and the \((j+1)\)th layers, respectively. Thus, the total absorbance of the multilayer
system can be obtained as:

\[ A(\lambda) = 1 - T(\lambda) - R(\lambda) \] \tag{5.9} 

However, in most cases we are not interested in the total absorbance of the whole
structure, like the solar cell, we require only the absorbance in a particular layer which
generates photocurrent. For calculating the absorbance in the \( l \)th layer Eq. (5.10) is
used as [103, 104]:

\[ A_l(\lambda) = [1 - R(\lambda)][1 - \psi_{l}(\lambda)] \prod_{j=1}^{l-1} \psi_j \] \tag{5.10} 

short-circuit current density \( (J_{sc}) \) is obtained as a function of the layer thickness by
integrating the product of the absorbance in Eq. (5.10) and the photon flux at AM1.5
over 300–900 nm spectral range [106] as:

\[ J_{sc} = e \int_{\lambda} A_l(\lambda) \Phi(\lambda) d\lambda \] \tag{5.11} 

73
here \( \Phi(\lambda) \) is the spectral density of the photon irradiance, \( A_i \) is the active layer absorbance which is a dimensionless wavelength dependent number between zero and one. \( J_{sc} \) in Eq. (5.11) can be optimised with respect to the layer thickness.

### 5.3 Results

We have used OAAM thus developed here for studying the following two BHJ OSCs of: 1) poly(3-hexylthiophene):1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C (P3TH:PCBM) and 2) poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexy) carbonyl] thieno [3,4-b] thiophenediyl]]:1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C (PTB7:PCBM) blends. The complex refractive index of the material and the thickness of each layer are needed in the modelling. The sources of the complex refractive indices taken from the library of SETFOS software are; Lithium Floride (LiF), and Silver (Ag) [107], indium tin oxide (ITO), and aluminium (Al) [108], P3TH:PCBM blend [109]. The optical constants for poly[3,4-(ethylenedioxy) thiophene]: poly(styrene sulfonate) (PEDOT:PSS), and PTB7:PCBM are from [110].

The amount of light absorbed in the active layer of a solar cell depends mainly on the values of the material, the optical path length of light inside the layer, and interference effects, if any. Also, an efficient absorbing layer should have an absorption spectrum that overlaps reasonably well with the solar spectrum in the visible and near infrared regions [8]. The absorption coefficient \( \alpha_{ab} \) of P3TH:PCBM (blue solid line) and PTB7:PCBM (blue dash line) blends and photon flux of AM 1.5 solar spectrum (green solid line) are plotted in Figure 5.1 as a function of radiation wavelength. The absorption coefficients are calculated from
$\alpha_{ab} = \frac{4\pi k}{\lambda}$. This Figure indicates that unlike P3TH:PCBM, the PTB7:PCBM system has a wide overlap with the solar spectrum between 400 to 720 nm.

![Absorption coefficients of P3TH:PCBM (blue solid line) and PTB7:PCBM (blue dash line) blends overlaid with the photon flux of AM 1.5 solar spectrum (green solid line) shown on the right axis.](image_url)

**Figure 5.2** Absorption coefficients of P3TH:PCBM (blue solid line) and PTB7:PCBM (blue dash line) blends overlaid with the photon flux of AM 1.5 solar spectrum (green solid line) shown on the right axis.

The calculated absorbance using Eq. (5.10) for the active layers P3TH:PCBM and PTB7:PCBM, each of 75 nm thick, is shown in Figure 5.3 as a function of the wavelength. Absorption in the other layers of the assembly is not considered as it does not contribute to the photocurrent.
The characteristic matrix Eq. (5.3) in OAAM takes into account multiple reflections within the layers [104] and subsequent interference effects [111] and hence the results obtained are expected to be more accurate than those obtained from the traditional Beer-Lambert law. Using Eq. (5.11), we have plotted $J_{sc}$ as a function of the active layer thickness for P3TH:PCBM blend as shown in Figure 5.4 and in Figure 5.5 for PTB7:PCBM blend. From Figures 5.4 and 5.5, the optimum active layer thicknesses required for producing maximum photocurrent in the blends can be extracted.

Figure 5.3 Absorbance of P3TH:PCBM (red solid line) and PTB7:PCBM (blue dash line) blends versus wavelength of light.
Figure 5.4 $J_{sc}$ of P3HT:PCBM blend as a function of blend thickness modelled using OAAM with Al cathode (blue circles), Ag cathode (red squares), and experimental data (black diamonds) extracted from Monestier et al. [109].

Figure 5.5 $J_{sc}$ of PTB7:PCBM blend as a function of blend thickness modelled using OAAM with Al cathode (blue circles), Ag cathode (red squares), and experimental data (black diamonds) extracted from Zheng et al. [112].
For the blends P3TH:PCBM (Figure 5.4) and PTB7:PCBM (Figure 5.5), the optimal thicknesses are obtained as 75 nm and 115 nm, respectively. The calculated $J_{sc}$ variation with active layer thickness is shown in Table 5.1, alongside the experimental $J_{sc}$.

Table 5.1 comparison between theoretical and experimental $J_{sc}$ for the two BHJ OSCs.

<table>
<thead>
<tr>
<th></th>
<th>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</th>
<th>ITO/ZnO /PTB7:PCBM/LiF/Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>d/nm</td>
<td>Theoretical $J_{sc}$</td>
<td>Experimental $J_{sc}$</td>
</tr>
<tr>
<td>55</td>
<td>8.65</td>
<td>8.61</td>
</tr>
<tr>
<td>70</td>
<td>10.14</td>
<td>9.36</td>
</tr>
<tr>
<td>75</td>
<td>10.39</td>
<td>9.91</td>
</tr>
<tr>
<td>82</td>
<td>10.53</td>
<td>9.67</td>
</tr>
<tr>
<td>110</td>
<td>10.16</td>
<td>9.13</td>
</tr>
<tr>
<td>120</td>
<td>9.99</td>
<td>8.93</td>
</tr>
<tr>
<td>160</td>
<td>10.58</td>
<td>9.21</td>
</tr>
<tr>
<td>215</td>
<td>11.77</td>
<td>10.41</td>
</tr>
</tbody>
</table>
The oscillatory behaviour of the $J_{sc}$ as a function of thickness is indicative of interference effect. Such effect is expected in a layered device with a thicker metal cathode like Al, because the metal acts as a mirror for the unabsorbed light in the active layer and reflects it back into the active layer for re-absorption [98]. Depending on the phase difference, the incident and reflected light in the active layer interfere to produce interference patterns as shown in Figure 5.7. Constructive interference patterns in an OSC result in high optical densities at an approximate distance of $(2x+1)\lambda / 4n_j$ from the metal cathode resulting in high photocurrent in the $J_{sc}$ versus

Figure 5.6 (a) $J_{sc}$ of P3HT:PCBM blend as a function of blend thickness with varying thickness of the aluminium metal cathode modelled using OAAM.
thickness curve [11, 24].

Here $x$ is an integer representing the order of interference between the incident light and the unabsorbed light reflected back into the active layer. This is how the interference effects lead to the oscillatory behaviour in the $J_{sc}$ versus thickness curve.

For studying the influence of thickness of the cathode on the absorption, we have plotted $J_{sc}$ as a function of the thickness of the active layer at five different thicknesses, 2, 10, 40, 70 and 100 nm of Al cathode as shown in Figures 5.6 (a) and (b) for P3TH:PCBM and PTB7:PCBM blends, respectively.
It can be clearly seen in Figures 5.6 (a) and (b) that the interference effect becomes pronounced as the thickness of the Al electrode is increased. When the Al thickness is only 2 nm in the simulation, the oscillations in the curves disappear in both OSCs, this can be attributed to the fact that, 2nm is not thick enough to create the needed interference and re-absorption in the active layer. That is, not enough light is reflected back into the active layer after the initial pass.

**Figure 5.7** Constructive interference of incident light wave (blue), reflected light wave (red) which have the same frequency and are in phase to produce wave of higher amplitude.
5.4 Discussions

We have applied optical admittance analysis method (OAAM) for simulating the short-circuit current density in BHJ OSCs. In particular, we have considered two BHJ OSCs of structures: (1) ITO(180 nm)/PEDOT:PSS (45 nm)/P3HT:PCBM (1:1)(d nm)/LiF (1 nm)/Al (100 nm) [109] and ITO/ZnO (100 nm)/PTB7:PCBM (1:1.5)(d nm)/LiF (15 nm)/Ag (100 nm) [112] so that we can compare the calculated results with the experimental ones. It should however be noted that in our simulation in Figure 5.5, we have used ITO and LiF in place of ITO/ZnO and MoO3 used in [112]. In Figure 5.2, we can see that PTB7:PCBM has a wider overlap between its absorption coefficient and the solar spectrum in the 400 to 720 nm wavelength range compared to P3HT:PCBM which has overlap only in the 560 to 650 nm range. This agrees with the broad absorption of PTB7:PCBM into the visible region, as produced in Figure 5.3. As result, the former blend produces a higher $J_{sc}$ than the latter one as discussed below.

It may also be noted that both blends do not have their absorption coefficients overlapping with the solar spectrum between 300 to 400 nm in Figure 5.2, thus one may expect only a small contribution to the absorbance in this range from both blends. However, according to Figure 5.3, we find a significant absorbance in both blends in this spectral range. This absorbance may be attributed to the gradual changes in the refractive index in this range. It is known that graded optical constants can have better anti-reflection properties [33, 113].

According to Figure 5.4, the $J_{sc}$ is found to be maximum at two thicknesses; about 75 nm and 220 nm in the P3HT:PCBM blend, which means that there are two possible thicknesses at which one can expect to produce the optimal $J_{sc}$ in this OSC.
However, it may be important to note that the influence of charge carrier recombination is not considered in this simulation. It is well established that both the absorption as well as recombination increase with the thickness [114] and hence a thickness of 220 nm may be considered to be too thick to get the minimal recombination and hence maximum $J_{sc}$. Therefore, one may expect a thickness of 75 nm to be the optimal for this BHJ OSC. It is interesting to note that experimentally also a higher $J_{sc}$ is observed at a thickness of 220 nm but the increase is not proportional with the thickness. This may be attributed to the higher recombination and therefore, if one chooses the thickness of 220 nm then this will require relatively a large amount of material without getting much gain in the photocurrent.

Likewise, the plot of $J_{sc}$ in Figure 5.5 for PTB7:PCBM shows that the optimal thickness is about 115 nm. This value agrees reasonably well with the 110 nm reported experimentally in [112]. The thicker active layer of PTB7:PCBM blend needed for maximum photocurrent could be due to the ordered packing of PTB7 which allows charge transport over longer distances [112]. For this OSC also one may discard the higher optimal thickness of more than 200 nm due to the reason stated above.

It may be noted that in both Figures 5.4 and 5.5, $J_{sc}$ has been simulated using Ag as cathode as well, which gives slightly higher $J_{sc}$ than using Al without any change in optimal thickness of the active layer. It may also be desirable here to address the issue of the optimal thickness of the cathode using Figures 5.6 (a) and (b) for the two OSCs considered here. Accordingly, the $J_{sc}$ in both OSCs does not change by increasing the thickness of Al cathode beyond 40 nm, which may be considered to
be the optimal thickness of the cathode to get the optimal performance.

5.5 Conclusions

We have applied OAAM to simulate the optimal thicknesses of the active organic layer and Al cathode layer in P3HT:PCBM and PTB7:PCBM BHJ OSCs. The optimal thicknesses thus obtained are 75 nm and 115 nm for P3HT:PCBM and PTB7:PCBM active layers, respectively, which agree well with observed ones. Our analysis reveals that PTB7:PCBM will require thicker active layer material compared to P3HT:PCBM for higher $J_{sc}$. The optimal thickness of Al cathode from the simulation is found to be 40 nm. It is expected that the present results may provide pre-fabrication information for the choice of the thicknesses of the active layer and Al cathode in these OSCs to achieve optimal photovoltaic performance.
Chapter 6 Thesis synthesis and future work

6.1 Summary of chapters

Although organic solar cells have many attractive features, still many challenges have to be overcome before their commercialisation. In particular, there are challenges in clearer understanding of the device physics, high-throughput roll-to-roll processing over large areas on flexible substrates, improvements in the power conversion efficiency, and also improvements in the stability of the organic materials under operational temperatures. Thus, to tackle these challenges effectively, a thorough understanding of the physical, optical, and electrical processes taking place in organic solar cells is essential. However, the organic photovoltaic is still a relatively new field compared to its inorganic counterpart, and some of the processes in the organic solar cells are either hotly debated or not clearly understood, hence, there is a need for further research.

The study in this thesis focuses on enhancing photovoltaic performance of thin film BHJ OSCs. This thesis advances the field of organic solar cells by studying the physics of the processes involved in the operation principle of BHJ OSCs such as light absorption and photocurrent generation, mechanism of intersystem crossing of excitons, diffusion and probability of recombination of excitons at the donor acceptor interface, and charge carrier transport have been presented in chapters 2-5, as described below. Design optimisation of two BHJ OSCs structures is successfully performed by using optical admittance analysis method and optimal thicknesses have been obtained in chapter 5.

In chapter 2, the mechanism of intersystem crossing of excitons from singlet to
triplet state after photo-excitation is studied. This is because the selection rules for the
electronic dipole transitions allow generation of only singlet excitons by exciting an
electron from the singlet ground state during photo-excitation. In organic solids, the
triplet exciton state usually lies below the singlet exciton state and their vibronic states
overlap in energy. Thus, when a singlet exciton is excited by absorption of photons
into higher vibronic energy level, which is iso-energetic with the vibronic level of the
triplet state, the presence of a strong exciton-spin-orbit interaction flips the spin of the
excited electron to triplet and the exciton crosses to the triplet state. Although the
process of intersystem is an old topic, to the best of the candidate’s knowledge, no rate
of the intersystem crossing has yet been derived. Also, no transition operator
responsible for intersystem crossing is found in the literature.

In this chapter, following the above mechanism, the rate of intersystem
crossing is derived by using the first order perturbation theory, where a new exciton-
spin-orbit-vibrational interaction operator derived by the candidate is used as a
perturbation operator to flip the spin of the singlet exciton to triplet exciton. The
newly derived interaction operator is given as:

$$\hat{H}_I \approx \frac{12\hbar^2 g k e^2}{\mu_c e^2 r_s^4} \sum_{\nu,\sigma_\nu,\sigma_v} (q_{\nu v} - q_{\nu v o}) a_{\nu} (\sigma_\nu) d_{\nu} (\sigma_v) \delta_{\sigma_\nu,\sigma_v} (b_{\nu v}^* + b_{\nu v})$$  \hspace{1cm} (6.1)

Using Fermi’s golden rule then the rate of intersystem crossing is obtained as:

$$k_{isc} = \frac{3072\pi^2 e^6 k^2 Z^2 e^4 \hbar^3}{\mu_i^2 e^4 a_i^6 (\hbar\omega_e)^3} (\Delta E)^2$$  \hspace{1cm} (6.2)

where symbols have their usual meanings described in chapter 2. The rate derived in
Eq. (6.2) depends on excitonic Bohr radius, molecular vibrational energy, the atomic
number of the heaviest atom and the exchange energy between the singlet and triplet
excited states. According to the rate in Eq. (6.2), it is the exciton-spin-orbit interaction operator that flips the spin of the singlet exciton to triplet state, which is then transferred to the triplet energy state. The singlet exciton state is usually at a higher energy $\Delta E$ from the triplet exciton state in organic solids. Using Eq. (6.2), the rates of intersystem crossing have been calculated for some OSC materials and compared to experimental results. The study in chapter 2 is expected to help in designing OSCs with enhanced triplet exciton concentration.

After an exciton is formed in the donor or acceptor organic material, it must get to the donor-acceptor interface by diffusion. The diffusion process and probability of recombination of free charges into singlet or triplet excitonic state are outlined in chapter 3. The exciton transfer mechanisms that govern the diffusion of singlet and triplet excitons to the donor-acceptor interface are the Förster and Dexter transfer mechanisms. The diffusion lengths of singlet (S) and triplet (T) excitons are, respectively, obtained as:

$$L_D(S) = \frac{R_f}{\sqrt[3]{\tau_s k_f}} \frac{\sqrt{6}}{\sqrt{3}}$$

(6.3)

and

$$L_D(T) = \sqrt{\frac{\tau_f k_d}{6}} \left[ R_d - \frac{L}{2} \ln(\tau_f k_d) \right]$$

(6.4)

and the corresponding diffusion coefficients are obtained as:

$$D(S) = \frac{R_f^2}{6} \left( \frac{k_f^2}{\tau_s} \right)$$

(6.5)

and

$$D(T) = \frac{k_d}{6} \left( R_d - \frac{L}{2} \ln(\tau_f k_d) \right)^2$$

(6.6)
We found that triplet excitons tend to have longer lifetime, about three orders of magnitude greater than the lifetime of singlet excitons; however, the transfer rate of singlet excitons is also about three orders of magnitude larger than that of triplet excitons, which results in a higher diffusion coefficient for singlet excitons. Therefore singlet and triplet excitons have comparable diffusion lengths, because of the product of lifetime and transfer rate in Eq. (6.3) and (6.4). The comparable diffusion length of both singlet and triplet excitons is supported by experimental evidences.

After diffusion to the donor-acceptor interface, the exciton may dissociate into free charge carriers by first forming a CT exciton. A singlet CT exciton can decay to the ground state or dissociate into free charge carriers; the latter can occur for both single and triplet excitons. Once dissociated, some fraction of the charge carriers may return to form CT excitons again. Therefore, long-lived CT excitons can act as a precursor for free charge carriers. By using the Langevin recombination theory, we derived the probability of recombination of free charges into the singlet and triplet CT states, respectively as:

\[
\begin{align*}
\frac{k_S}{k_S + k_T} &= \frac{a'_T \alpha^2}{a'_T \alpha^2 + a'_S (\alpha - 1)^2} = \frac{1}{1 + \frac{a'_T}{a'_S} \left(\frac{\alpha - 1}{\alpha}\right)^2} \\
\frac{k_T}{k_S + k_T} &= \frac{a'_S (\alpha - 1)^2}{a'_S (\alpha - 1)^2 + a'_T \alpha^2} = \frac{1}{1 + \frac{a'_S}{a'_T} \left(\frac{\alpha - 1}{\alpha}\right)^2}
\end{align*}
\]

(6.7) (6.8)

where symbols have their usual meanings as described in chapter 3. We have found that in some organic polymers the probabilities of recombination of free charge carriers back into the singlet and triplet states are approximately 65.6% and 34.4 %, respectively. In chapter 3, it is concluded that the generation of triplet excitons may be more advantageous in organic solar cells than singlet excitons.
In chapter 4, by deriving an analytical expression for charge carrier mobility dependent open-circuit voltage in organic and hybrid solar cells, we have studied how mobility of free charge carriers influences the open-circuit voltage. The open circuit voltage thus derived is obtained as:

$$V_{oc} = \frac{1}{q} \left( E_g - 2(E_{F,h} - E_{HOMO}^D) + k_B T \ln\left( \frac{\mu_e}{\mu_h} \right) \right)$$

(6.9)

where symbols have their usual meanings as defined in chapter 4. According to Eq.(6.9), if the ratio of electron to hole mobility is higher, then this will lead to higher $V_{oc}$. However, if the electron and hole mobilities are higher leading to the efficient extraction of charge carriers and hence reducing the charge carrier concentration. This reduction in carrier concentration is expected to draw the hole quasi-Fermi level away from the HOMO level of the donor material, which according to Eq.(6.9) will reduce the $V_{oc}$. The reduced $V_{oc}$ will eventually reduce the PCE. Likewise, at low electron and hole mobilities, the recombination will increase which will reduce the short-circuit current density $J_{sc}$. The reduced $J_{sc}$ will also reduce the PCE. Also, it was found that if the difference between the electron and hole mobilities is small, the $V_{oc}$ derived here in Eq. (6.9) does not depend on the charge carrier mobilities significantly.

The optical properties of two BHJ OSCs are investigated using computer simulation code based on optical admittance analysis method (OAAM), as described in chapter 5. OAAM is more accurate than the optical properties obtained from the traditional Beer-Lambert law, since it takes into account multiple reflections between two interfaces. The thickness of each active layer is optimised for maximum photon absorption. We have used OAAM to simulate the optical properties of two BHJ
organic solar cells (OSCs) of structures: (1) ITO/PEDOT:PSS /P3HT:PCBM/LiF/Al and (2) ITO/ZnO /PTB7:PCBM /LiF/Ag. By maximising the absorbance, short-circuit current density ($J_{sc}$) is simulated and is found to be maximum at the thicknesses of 75 nm and 115 nm in P3HT:PCBM and PTB7:PCBM blend layers, respectively.

By optimising the thickness of the solar cells, one can increase the short-circuit current density of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al BHJ OSC by 4.8% and that of ITO/ZnO /PTB7:PCBM /LiF/Ag by 13.3% using our optimal designs. Thus, an increase of more than 2 and 6% in power conversion efficiency can be achieved in ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al and ITO/ZnO/PTB7:PCBM /LiF/Ag OSCs, respectively. It is expected that the present results may provide prefabrication design for the thickness of the active layer and Al cathode in these OSCs to achieve optimal photovoltaic performance.

6.2 Future work

As described below, several challenges exist for the continuation of the work in this thesis to further deepen the understanding of the device physics and the development of organic solar cells towards commercialisation.

1. This work can also be extended to hybrid OSCs. The candidate planned to carry out optimisation of hybrid solar cells too, however, due to the lack of complex refractive index of the organic-inorganic blend in hybrid solar cells, it could not be done. Effective medium approximations for evaluating the complex refractive index were found to be of very limited use. Any future work can focus on developing effective medium approximations that will be useful for calculating the complex
refractive index of organic-inorganic blends.

2. The analytical expression for open-circuit voltage derived in chapter 4 can be extended to charge carrier mobility dependent PCE instead of just the $V_{oc}$ and further study on recombination of Frenkel excitons, CT excitons, and free charge carriers in organic solar cells is needed. How these different types of recombination affect the $J_{sc}$, $V_{oc}$, and fill factor need to be investigated in more detail.

3. While understanding the device physics in order to improve the low PCE is one major challenge, the stability and degradation of organic components of OSCs are the other major challenges. Although some advances have been made with regards to the stability, such that 95% PCE is retained after 1 year of outdoor operation in the encapsulation, more still needs to be done if OSC are to be used in commercial products.

6.3 Conclusions

This chapter brings together the processes involved in the operation of BHJ OSCs discussed in this thesis, as well as the optimisation carried out on two BHJ OSCs. The thesis started with the derivation of rate of intersystem crossing of excitons, diffusion length and diffusion coefficient of excitons, probability of free charges carriers recombining at the donor acceptor interface, and an analytical expression for charge carrier mobility dependent open-circuit voltage in organic and hybrid solar cells. These processes are shown to be directly relevant to the performance OSCs. After these theoretical derivations, the optimisation of two BHJ OSCs structures is successfully performed by using optical admittance analysis.
method. Future work on device physics and development of organic solar cells towards commercialisation has also been highlighted.
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Appendix A  Derivation of spin orbit operator

We want to write the spin orbit operator (A1) in terms of electron (hole) raising and lowering operators. The starting equation is

\[ s \cdot l = \frac{j^2 - l^2 - s^2}{2} \]  
(A1)

we write the components of the dot product, which gives

\[ J^2 = l^2 + s^2 + 2s \cdot l = l^2 + s^2 + 2(l_z s_x + l_y s_y + l_z s_z) \]  
(A2)

We then define the components of the dot product in (A2) in terms of orbital angular momentum raising (lowering) operator as \( L_+ = l_x + il_y \) (\( L_- = l_x - il_y \)) and spin angular momentum raising (lowering) operator as \( S_+ = s_x + is_y \) (\( S_- = s_x - is_y \)), respectively and we obtain

\[ J^2 = l^2 + s^2 + 2\left[ \left( \frac{L_+ + L_-}{2} \right) \left( \frac{S_+ + S_-}{2} \right) + \left( \frac{L_+ - L_-}{2i} \right) \left( \frac{S_+ - S_-}{2i} \right) + l_z s_z \right] \]  
(A3)

expanding the terms in the parenthesis of (A3) and simplifying the resulting expression gives

\[ = 1^2 + s^2 + 2\left[ \left( \frac{L_+ S_+ + L_- S_- + L_+ S_- + L_- S_+}{4} \right) - \left( \frac{L_+ S_- - L_- S_+ - L_+ S_+ + L_- S_-}{4} \right) + l_z s_z \right] \]

\[ = 1^2 + s^2 + \frac{1}{2} \left[ (L_+ S_- + L_- S_+ + L_+ S_- + L_- S_+) + 2l_z s_z \right] \]

\[ = 1^2 + s^2 + \left[ L_+ S_- + L_- S_+ + 2l_z s_z \right] \]

\[ J^2 - l^2 - s^2 = L_+ S_- + L_- S_+ + 2l_z s_z \Rightarrow \frac{J^2 - l^2 - s^2}{2} = \frac{L_+ S_-}{2} + \frac{L_- S_+}{2} + l_z s_z = s \cdot l \]

\[ s \cdot l = l_z s_z + \frac{L_+ S_-}{2} + \frac{L_- S_+}{2} \]  
(A4)

where \( S_+ \) increases the spin in the z direction from \( \frac{\hbar}{2} \) to \( \frac{\hbar}{2} \), and \( S_- \) lowers the z component
of the spin from $\frac{1}{2}$ to $-\frac{1}{2}$. Thus $S_+$ and $S_-$ allow us to jump from one spin state to another.

**Spin flip by operator $s \cdot l$**

\[
(s_e \cdot l_{en} + s_h \cdot l_{hn}) (a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) + a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) =
\]

\[
(s_e \cdot l_{en}) a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) + (s_h \cdot l_{hn}) a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) +
\]

\[
(s_e \cdot l_{en}) a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) + (s_h \cdot l_{hn}) a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h)
\]

(A5)

Using Eq. (A4) for the spin-orbit terms, the first two terms in (A5) are evaluated as follows

\[
\left( l_{en} s_{en} + \frac{L_{en} S_{en}}{2} + \frac{L_{en} S_{en^+}}{2} \right) a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) + \left( l_{hn} s_{hn} + \frac{L_{hn} S_{hn}}{2} + \frac{L_{hn} S_{hn^+}}{2} \right) a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h)
\]

The expression above has 6 terms, applying the spin raising and lowering operators, the 3rd and 6th terms go to zero

\[
\frac{\hbar}{2} l_{en} a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) + \frac{\hbar}{2} l_{en} a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) - \frac{\hbar}{2} l_{hn} a_L^\dagger (-\sigma_e) d_H^\dagger (-\sigma_h) - \frac{\hbar}{2} l_{hn} a_L^\dagger (+\sigma_e) d_H^\dagger (+\sigma_h)
\]

Applying the orbital raising and lowering operators, the 2nd and 4th terms also go to zero because the electron cannot be raised outside the LUMO and the hole cannot be raised outside the HOMO. This leaves us with a triplet exciton.

\[
\frac{\hbar}{2} a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) - \frac{\hbar}{2} a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) \Rightarrow \frac{\hbar}{2} \left( a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) - a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) \right)
\]

When the same analogy is used the last two terms

\[
\left( l_{en} s_{en} + \frac{L_{en} S_{en}}{2} + \frac{L_{en} S_{en^+}}{2} \right) a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) + \left( l_{hn} s_{hn} + \frac{L_{hn} S_{hn}}{2} + \frac{L_{hn} S_{hn^+}}{2} \right) a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h)
\]

this will lead to

\[
\frac{\hbar}{2} \left( a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) - a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h) \right)
\]

\[
(s_e \cdot l_{en} + s_h \cdot l_{hn}) (a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) + a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h)) =
\]

\[
\frac{\hbar}{2} a_L^\dagger (+\sigma_e) d_H^\dagger (-\sigma_h) - \frac{\hbar}{2} a_L^\dagger (-\sigma_e) d_H^\dagger (+\sigma_h)
\]

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\[
\frac{h}{2} \left( a^*_L (\sigma_+) d^*_H (-\sigma_h) - a^*_L (-\sigma_+) d^*_H (+\sigma_h) \right)
\]

Here we have assumed \( l_{x^*} \approx l_{h^*} = l_z \) and the following identities have been used.
Appendix B Simulation Code

%% This is a program written using Optical Admittance Analysis Method to calculate the absorbance in a layered structure like a solar cell. It code uses MATLAB environment and it is a script file.

%% The wavelength(nm) range is from 300 nm to 900 nm in steps of 5 nm

%% Input data n,k values and thickness(nm) of a layer

%% Lowest layer ITO. Use n,k values and evaluate layer admittance and matrix

%% This section calculates the optical properties of P3HTPCBM

ITON=complex(ITOn,-ITOk);

dITO=180;
yITO=ITON/377;

CONSTITO=(2*pi*dITO./lambda);

PhaseDifITO=CONSTITO.*ITON;

COSdelITO=cos(PhaseDifITO);

SINdelITO=sin(PhaseDifITO);

TRITO=j.*SINdelITO./yITO;

BLITO=j.*yITO.*SINdelITO;

for h=1:121;
    ITOMatrix(:,:,h)=[COSdelITO(h) TRITO(h);BLITO(h) COSdelITO(h)];
end

%%

HTLN=complex(PEDOTPSSn,-PEDOTPSSk);

dHTL=45;
yHTL=HTLN/377;
CONSTHTL=(2*pi*dHTL./lambda);

PhaseDifHTL=CONSTHTL.*HTLN;

COSdelHTL=cos(PhaseDifHTL);
SINdelHTL=sin(PhaseDifHTL);

TRHTL=j.*SINdelHTL./yHTL;
BLHTL=j.*yHTL.*SINdelHTL;

for h=1:121;

    HTLMatrix(:,:,h)=[COSdelHTL(h) TRHTL(h);BLHTL(h) COSdelHTL(h)];
end

%%

% Evaluate active layer (P3HT:PCBM) layer admittance and matrix

N=complex(P3HTPCBMn,-P3HTPCBMk);
d=75;
yActLayer=N/377;

CONST=(2*pi*d./lambda);

PhaseDif=CONST.*N;

COSdel=cos(PhaseDif);

SINdel=sin(PhaseDif);

TR=j.*SINdel./yActLayer;

BL=j.*yActLayer.*SINdel;

for h=1:121;

    ActLayerMatrix(:,:,h)=[COSdel(h) TR(h);BL(h) COSdel(h)];
end

%%
ETLN=complex(LiFn,-LiFk);

dETL=1;

yETL=ETLN/377;

CONSTETL=(2*pi*dETL./lambda);

PhaseDifETL=CONSTETL.*ETLN;

COSdelETL=cos(PhaseDifETL);

SINdelETL=sin(PhaseDifETL);

TRETL=j.*SINdelETL./yETL;

BLETL=j.*yETL.*SINdelETL;

for h=1:121;
    ETLMatrix(:,:,h)=[COSdelETL(h) TRETL(h);BLETL(h) COSdelETL(h)];
end

%%

% Evaluate cathode layer admittance and matrix

AlN=complex(Aln,-Alk);

dAl=100;

yAl=AlN/377;

CONSTAl=(2*pi*dAl./lambda);

PhaseDifAl=CONSTAl.*AlN;

COSdelAl=cos(PhaseDifAl);

SINdelAl=sin(PhaseDifAl);

TRAl=j.*SINdelAl./yAl;

BLAl=j.*yAl.*SINdelAl;

for h=1:121;
\[
\text{AlMatrix(:,:,h)} = \begin{bmatrix}
\cos(\text{delAl}(h)) & \text{TRAl}(h) \\
\text{BLAl}(h) & \cos(\text{delAl}(h))
\end{bmatrix};
\]

end

%%

% Evaluate substrate(Glass) and air admittance and matrix

\text{SubN} = \text{complex(Subn,Subk)};

\text{ys} = \text{SubN}/377;

dSub = 500;

\text{CONSTSub} = (2\pi * \text{dSub}/\lambda);

\text{PhaseDifSub} = \text{CONSTSub} * \text{SubN};

\text{COSdelSub} = \cos(\text{PhaseDifSub});

\text{SINdelSub} = \sin(\text{PhaseDifSub});

%% Total Reflectance

% 1

\text{for h=1:121};

% \text{TotalMatrix(:,:,h)} = \text{AlMatrix(:,:,h)} * \text{ActLayerMatrix(:,:,h)} * \text{ITOMatrix(:,:,h)};

\text{TotalMatrix(:,:,h)} = \text{ITOMatrix(:,:,h)} * \text{HTLMatrix(:,:,h)} * \text{ActLayerMatrix(:,:,h)} * \text{ETLMatrix(:,:,h)} * \text{AlMatrix(:,:,h)};

%% The determinant of each of these individual 2x2 matrices ought to be 1, including the product of the matrices.

\text{SubMatrix(:,h)} = [1; \text{ys(h)}];

\text{CMatrix} = \text{TotalMatrix(:,:,h)} * \text{SubMatrix};

% \text{CMatrix1} = \text{ActLayerMatrix(:,:,h)} * \text{AlMatrix(:,:,h)} * \text{SubMatrix};

\text{CMatrix1} = \text{ActLayerMatrix(:,:,h)} * \text{ITOMatrix(:,:,h)} * \text{SubMatrix};

% \text{CMatrix2} = \text{AlMatrix(:,:,h)} * \text{SubMatrix};
CMatrix2=ITOMatrix(:,:,h)*SubMatrix;

B=CMatrix(1);
C=CMatrix(2);
B1=CMatrix1(1);
C1=CMatrix1(2);
B2=CMatrix2(1);
C2=CMatrix2(2);
yeff(h,:)=(C/(B));
yeff1(h,:)=(C1/(B1));
yeff2(h,:)=(C2/(B2));
r=abs(((0.00265-yeff)./(0.00265+yeff)));
rsqr=(r.^2);
R=[rsqr];
end

%% % Total Transmittance.

for h=1:121;
    RAIN=real(AlN);
    RETL=real(ETLN);
    RN=real(N);
    RHTL=real(HTLN);
    RITON=real(ITON);
    Y5=1;
    Y4=(Y5.*COSdelAl+j.*AlN.* SINdelAl)./(COSdelAl+(j.*Y5.*SINdelAl)./AlN);
    a4=real(Y4);
end
Y3=(Y4.*COSdelETL+j.*ETLN.*
SINdelETL)./(COSdelETL+(j.*Y4.*SINdelETL)./ETLN);
a3=real(Y3);
Y2=(Y3.*COSdel+j.*N.* SINdel)./(COSdel+(j.*Y3.*SINdel)./N);
a2=real(Y2);
Y1=(Y2.*COSdelHTL+j.*HTLN.*
SINdelHTL)./(COSdelHTL+(j.*Y2.*SINdelHTL)./HTLN);
a1=real(Y1);
Y0=(Y1.*COSdelITO+j.*ITON.*
SINdelITO)./(COSdelITO+(j.*Y1.*SINdelITO)./ITON);
a0=real(Y0);
Psi1Abs1=(abs(COSdelITO+(j.*Y1.*SINdelITO)./ITON)).^2;
Psi1=(a1./(a0.*Psi1Abs1));
Psi1Abs2=(abs(COSdelHTL+(j.*Y2.*SINdelHTL)./HTLN)).^2;
Psi2=(a2./(a1.*Psi1Abs2));
Psi1Abs3=(abs(COSdel+(j.*Y3.*SINdel)./N)).^2;
Psi3=(a3./(a2.*Psi1Abs3));
Psi1Abs4=(abs(COSdelETL+(j.*Y4.*SINdelETL)./ETLN)).^2;
Psi4=(a4./(a3.*Psi1Abs4));
Psi1Abs5=(abs(COSdelAI+(j.*Y5.*SINdelAI)./AlN)).^2;
Psi5=(a5./(a4.*Psi1Abs5));
PsiTotal=Psi1.*Psi2.*Psi3.*Psi4.*Psi5;
end
T=(1-R).*PsiTotal;  
%.*PsiTotal;
%%
% Total Absorbance of the multilayer system
A=1-T-R;
%%
% Active layer Absorbance

ActL=((1-R).*(1-Psi3)).*Psi1.*Psi2;
%%
% This plot calculates the absorbance in the active layer as a function of the wavelength
plot(lambda,ActL,'r')

ITON=complex(ITOn,-ITOk);
dITO=50;
yITO=ITON/377;
CONSTITO=(2*pi*dITO./lambda);
PhaseDifITO=CONSTITO.*ITON;
COSdelITO=cos(PhaseDifITO);
SINdelITO=sin(PhaseDifITO);
TRITO=j.*SINdelITO./yITO;
BLITO=j.*yITO.*SINdelITO;
for h=1:121;
    ITOMatrix(:,:,h)=[COSdelITO(h) TRITO(h);BLITO(h) COSdelITO(h)];
end
%%
% Evaluate active layer (P3HT:PCBM) layer admittance and matrix

N=complex(P3HTPCBMn,-P3HTPCBMk);
alphap3htpcbm=4000000000.*pi.*P3HTPCBMk./lambda;% Absorption coefficient

\[ d = 90; \]

\[ y_{\text{ActLayer}} = N/377; \]

\[ \text{CONST} = (2\pi d/\lambda); \]

\[ \text{PhaseDif} = \text{CONST} \times N; \]

\[ \text{COSdel} = \cos(\text{PhaseDif}); \]

\[ \text{SINdel} = \sin(\text{PhaseDif}); \]

\[ \text{TR} = j \times \text{SINdel}/y_{\text{ActLayer}}; \]

\[ \text{BL} = j \times y_{\text{ActLayer}} \times \text{SINdel}; \]

\[ \text{for } h = 1:121; \]

\[ \text{ActLayerMatrix}(:,:,h) = [\text{COSdel}(h) \ \text{TR}(h); \text{BL}(h) \ \text{COSdel}(h)]; \]

\[ \text{end} \]

%%
% Evaluate cathode layer admittance and matrix

\[ \text{AlN} = \text{complex(Aln},-\text{Alk}); \]

\[ d_{\text{Al}} = 40; \]

\[ y_{\text{Al}} = \text{AlN}/377; \]

\[ \text{CONSTAl} = (2\pi d_{\text{Al}}/\lambda); \]

\[ \text{PhaseDifAl} = \text{CONSTAl} \times \text{AlN}; \]

\[ \text{COSdelAl} = \cos(\text{PhaseDifAl}); \]
SINdelAl=sin(PhaseDifAl);
TRAl=j.*SINdelAl./yAl;
BLAl=j.*yAl.*SINdelAl;
for h=1:121;
    AlMatrix(:,:,h)=[COSdelAl(h) TRAl(h);BLAl(h) COSdelAl(h)];
end

%%
% Evaluate substrate(Glass)and air admittance and matrix
SubN=complex(Subn,Subk);
yN=SubN/377;
dSub=500;
CONSTSub=(2*pi*dSub./lambda);
PhaseDifSub=CONSTSub.*SubN;
COSdelSub=cos(PhaseDifSub);
SINdelSub=sin(PhaseDifSub);

%%  Total R
for h=1:121;
    %TotalMatrix(:,:,h)=AlMatrix(:,:,h)*ActLayerMatrix(:,:,h)*ITOMatrix(:,:,h);
    TotalMatrix(:,:,h)=ITOMatrix(:,:,h)*ActLayerMatrix(:,:,h)*AlMatrix(:,:,h);
    SubMatrix(:,h)=[1;ys(h)];
    CMatrix=TotalMatrix(:,:,h)*SubMatrix;
    %CMatrix1=ActLayerMatrix(:,:,h)*AlMatrix(:,:,h)*SubMatrix;
    CMatrix1=ActLayerMatrix(:,:,h)*ITOMatrix(:,:,h)*SubMatrix;
    %CMatrix2=AlMatrix(:,:,h)*SubMatrix;
CMatrix2=ITOMatrix(:,:,h)*SubMatrix;

B=CMatrix(1);
C=CMatrix(2);
B1=CMatrix1(1);
C1=CMatrix1(2);
B2=CMatrix2(1);
C2=CMatrix2(2);
yeff(h,:)=(C/(B));
yeff1(h,:)=(C1/(B1));
yeff2(h,:)=(C2/(B2));
r=abs((0.00265-yeff)./(0.00265+yeff));
rsqr=(r.^2);
R=[rsqr];

end

%% % Total Transmittance.

for h=1:121;

RAIN=real(AlN);
RN=real(N);
RITON=real(ITON);

Y4=1;
Y3=(COSdelSub+j.*SubN.* SINdelSub)./(COSdelSub+(j.*SINdelSub)./SubN);% What
about starting from the glass instead of ITO

\[
a_3 = \text{real}(Y_3);
Y_2 = \frac{Y_3 \cdot \cos(\Delta \alpha) + j \cdot \text{AlN} \cdot \sin(\Delta \alpha)}{\cos(\Delta \alpha) + \frac{j \cdot Y_3 \cdot \sin(\Delta \alpha)}{\text{AlN}}};
a_2 = \text{real}(Y_2);
Y_1 = \frac{Y_2 \cdot \cos(\Delta \alpha) + j \cdot \text{N} \cdot \sin(\Delta \alpha)}{\cos(\Delta \alpha) + \frac{j \cdot Y_2 \cdot \sin(\Delta \alpha)}{\text{N}}};
a_1 = \text{real}(Y_1);
Y_0 = \frac{Y_1 \cdot \cos(\Delta \text{ITO}) + j \cdot \text{ITON} \cdot \sin(\Delta \text{ITO})}{\cos(\Delta \text{ITO}) + \frac{j \cdot Y_1 \cdot \sin(\Delta \text{ITO})}{\text{ITON}}};
a_0 = \text{real}(Y_0);
\]

\[
\Psi_1 \text{Abs} 1 = |\frac{\cos(\Delta \text{ITO}) + j \cdot Y_1 \cdot \sin(\Delta \text{ITO})}{\text{ITON}}|^2;
\Psi_1 = \frac{a_1}{(a_0 \cdot \Psi_1 \text{Abs} 1)};
\]

\[
\Psi_1 \text{Abs} 2 = |\frac{\cos(\Delta \alpha) + j \cdot Y_2 \cdot \sin(\Delta \alpha)}{\text{N}}|^2;
\Psi_2 = \frac{a_2}{(a_1 \cdot \Psi_1 \text{Abs} 2)};
\]

\[
\Psi_1 \text{Abs} 3 = |\frac{\cos(\Delta \alpha \text{Al}) + j \cdot Y_3 \cdot \sin(\Delta \alpha \text{Al})}{\text{AlN}}|^2;
\Psi_3 = \frac{a_3}{(a_2 \cdot \Psi_1 \text{Abs} 3)};
\]

\[
\Psi_{\text{Total}} = \Psi_1 \cdot \Psi_2 \cdot \Psi_3;
\]

\[
T = (1-R) \cdot \Psi_{\text{Total}}; \quad \% \cdot \Psi_{\text{Total}};
\]
%%
% Total Absorbance of the multilayer system
A=1-T-R;
%%
% Active layer Absorbance
ActL=((1-R).*(1-Psi2)).*Psi1;
%%
% Plots
% plot(lambda,R,'r')
% hold on
% plot(lambda,T,'b')
% hold on
% plot(lambda,ActL,'r')%p3htpcbm
% plot(lambda,attLengthp3htpcbm,'r')
q=1.6e-19;
Wvlength=300:5:900;
Absorbance=ActL;
hc=1.98630e-16;% The nano from wavelength has been factored into it
SpecDensityS=AirMass1.*lambda./(hc);% # of photons count, W/J to give s-1
[H1,H2,H3]=plotyy(lambda,alphap3htpcbm,lambda,SpecDensityS)
set(get(H1(2),'Ylabel'),'String','Number of Photon Counts (m^-2s^-1nm^-1)')
set(H2,'LineStyle','-','color','b')
hold on
% This section calculates the optical properties of PTB7:PCBMk

% Lowest layer ITO. Use n,k values and evaluate layer admittance and matrix

ITON=complex(ITOn,-ITOk);
dITO=50;
yITO=ITON/377;
CONSTITO=(2*pi*dITO./lambda);
PhaseDifITO=CONSTITO.*ITON;
COSdelITO=cos(PhaseDifITO);
SINdelITO=sin(PhaseDifITO);
TRITO=j.*SINdelITO./yITO;
BLITO=j.*yITO.*SINdelITO;

for h=1:121;
    ITOMatrix(:,:,h)=[COSdelITO(h) TRITO(h);BLITO(h) COSdelITO(h)];
end

%%

% Evaluate active layer (PTB7:PCBMk) layer admittance and matrix

N=complex(PTB7PCBMn,-PTB7PCBMk);
alphaptb7pcbm=4000000000.*pi.*PTB7PCBMk./lambda;
d=90;
yActLayer=N/377;
CONST=(2*pi*d./lambda);
PhaseDif=CONST.*N;
COSdel=cos(PhaseDif);
SINdel=sin(PhaseDif);
\[
\text{TR} = j \times \text{SINdel}/y_{\text{ActLayer}}; \\
\text{BL} = j \times y_{\text{ActLayer}} \times \text{SINdel};
\]
for \( h=1:121; \)
\[
\text{ActLayerMatrix}(::,h) = [\text{COSdel}(h) \ \text{TR}(h); \text{BL}(h) \ \text{COSdel}(h)];
\]
end
%
% Evaluate cathode layer admittance and matrix
\[
\text{AlN} = \text{complex}(\text{Aln},-\text{Alk});
\]
dAl=40;
yAl=AlN/377;
\[
\text{CONSTAl} = (2 \pi d_{\text{Al}} / \lambda);
\]
\[
\text{PhaseDifAl} = \text{CONSTAl} \times \text{AlN};
\]
\[
\text{COSdelAl} = \cos(\text{PhaseDifAl});
\]
\[
\text{SINdelAl} = \sin(\text{PhaseDifAl});
\]
\[
\text{TRAl} = j \times \text{SINdelAl}/y_{\text{Al}};
\]
\[
\text{BLAl} = j \times y_{\text{Al}} \times \text{SINdelAl};
\]
for \( h=1:121; \)
\[
\text{AlMatrix}(::,h) = [\text{COSdelAl}(h) \ \text{TRAl}(h); \text{BLAl}(h) \ \text{COSdelAl}(h)];
\]
end
%
% Evaluate substrate(Glass) and air admittance and matrix
\[
\text{SubN} = \text{complex}(\text{Subn},\text{Subk});
\]
ys=SubN/377;
dSub=500;
\text{CONSTSub} = (2\pi \text{dSub}./\lambda);
\text{PhaseDifSub} = \text{CONSTSub}.*\text{SubN};
\text{COSdelSub} = \cos(\text{PhaseDifSub});
\text{SINdelSub} = \sin(\text{PhaseDifSub});

\% \% \text{Total Reflectance}

\text{for \textit{h}=1:121;} \quad \%
\text{TotalMatrix(:,:,h)=AlMatrix(:,:,h)*ActLayerMatrix(:,:,h)*ITOMatrix(:,:,h);} \quad \%
\text{TotalMatrix(:,:,h)=ITOMatrix(:,:,h)*ActLayerMatrix(:,:,h)*AlMatrix(:,:,h);} \quad \%
\text{SubMatrix(:,h)=[1;ys(h)];}
\text{CMatrix=TotalMatrix(:,:,h)*SubMatrix;} \quad \%
\text{CMatrix1=ActLayerMatrix(:,:,h)*AlMatrix(:,:,h)*SubMatrix;} \quad \%
\text{CMatrix1=ActLayerMatrix(:,:,h)*ITOMatrix(:,:,h)*SubMatrix;} \quad \%
\text{CMatrix2=AlMatrix(:,:,h)*SubMatrix;} \quad \%
\text{CMatrix2=ITOMatrix(:,:,h)*SubMatrix;} \quad \%
\text{B=CMatrix(1);} \quad \%
\text{C=CMatrix(2);} \quad \%
\text{B1=CMatrix1(1);} \quad \%
\text{C1=CMatrix1(2);} \quad \%
\text{B2=CMatrix2(1);} \quad \%
\text{C2=CMatrix2(2);} \quad \%
\text{yeff(h,:)=}(\text{C}/(\text{B}));
yeff1(h,:)=(C1/(B1));
yeff2(h,:)=(C2/(B2));

r=abs((0.00265-yeff)./(0.00265+yeff));% Units of yAir and yeff, siemens or free space units/incoherent glass.
rsqr=(r.^2);
R=[rsqr];
end

%%% % Total Transmittance.
for h=1:121;
    RAlN=real(AlN);
    RN=real(N);
    RITON=real(ITON);

    Y4=1;
    Y3=(COSdelSub+j.*SubN.* SINdelSub)./(COSdelSub+(j.*SINdelSub)./SubN);% What about starting from the glass instead of ITO
    a3=real(Y3);
    Y2=(Y3.*COSdelAl+j.*AlN.* SINdelAl)./(COSdelAl+(j.*Y3.*SINdelAl)./AlN);
    a2=real(Y2);
    Y1=(Y2.*COSdel+j.*N.* SINdel)./(COSdel+(j.*Y2.*SINdel)./N);
    a1=real(Y1);
    Y0=(Y1.*COSdelITO+j.*ITON.* SINdelITO)./(COSdelITO+(j.*Y1.*SINdelITO)./ITON);
    a0=real(Y0);
Psi1Abs1=(abs(COSdelITO+(j.*Y1.*SINdelITO)./ITON)).^2;
Psi1=(a1./(a0.*Psi1Abs1));

Psi1Abs2=(abs(COSdel+(j.*Y2.*SINdel)./N)).^2;
Psi2=(a2./(a1.*Psi1Abs2));

Psi1Abs3=(abs(COSdelAl+(j.*Y3.*SINdelAl)./AlN)).^2;
Psi3=(a3./(a2.*Psi1Abs3));

PsiTotal=Psi1.*Psi2.*Psi3;
end

T=(1-R).*PsiTotal;  %.*PsiTotal;
%%
% Total Absorbance of the multilayer system
A=1-T-R;
%%
% Active layer Absorbance
ActL=((1-R).*(1-Psi2)).*Psi1;

% Plots
[H4,H5,H6]=plotyy(lambda,alphaptb7pcbm,lambda,SpecDensityS)

set(get(H4(2),'Ylabel'),'String','Number of Photon Counts (m^-2s^-1nm^-1)')

set(H5,'LineStyle','--','color','b')
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