Nanoscale engineering of thin film morphology for efficient organic photovoltaic cells

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Russell J. Holmes, Advisor

July 2012
Acknowledgements

This dissertation has been the result of endless hours of hard work and enormous persistence. However, as with any major endeavor, the credit goes more to the people who helped me in the process than me. The leader of this pack was my advisor, Professor Holmes, whose continued encouragement and guidance, as well as incredible patience with me, made this dissertation possible. He not only challenged me to solve hard problems, but also helped me resolve many of them whenever I was not able to make progress at any point of my work. In short, Professor Holmes is the chief architect of the researcher that I have become today.

I had the privilege of collaborating with some incredible scientists and students over the course of this dissertation. It would not be an understatement to say that Dr. Greg Haugstad’s RBS characterization of graded thin films in Chapter 3 is the basic foundation of my work on graded heterojunctions. The RBS characterization verified for us that we were working with gradients in thin films. Immense gratitude is due to Professor Andre Mkhoyan and Aloysius Gunawan for their characterization of organic thin films using TEM in Chapter 4, without which one of the most interesting results of my work would have been unexplained.

No Ph.D. student can develop into an effective researcher as an island, a metaphor that applies a hundred percent in my case. I would never have been able to make progress and face difficult questions on my work, had it not been for the constant discussions and critiques from Holmes group members Wade, Grant, Kai, Salil, Nick, Matt, Tyler, Yunlong, Meng, Nathan and Yi. The group’s frequent Friday lunch outings and the non-
scientific conversations were a real reprieve from the sometimes routine nature of research. I am also grateful to the entire Frisbie group for their help and support. I wish all these incredible individuals the very best for their careers and lives.

Finally, the last few years I spent working on this dissertation completely reaffirmed to me that almost nothing can surpass the strength of the bonds of friendship and family. My friends at UMN and in India deserve the most credit for the fun I had during this time, as well as for their persistent support and encouragement. I consider myself really blessed to have an amazing family that always encouraged me to excel at whatever I was doing. I was constantly amazed at the level of interest and intrigue they showed about the technical details of my work and everything around it, despite them not having any expertise in materials science. The toughest of these questions always came from my brother Gaurav, also a Ph.D. graduate from UMN (Computer Science department), who never hesitated in criticizing my methodologies and plans for future work and career, and thus, often made me think outside the box. Last but not the least, I would like to acknowledge my fiancé, Ashutosh, whose love and encouragement over the years has made this dissertation a reality.
Dedication

This dissertation is dedicated to my parents for instilling in me the importance of hard work and innovation, and always believing in me.
Abstract

Organic photovoltaic cells (OPVs) have received significant industrial and academic interest in the last decade as a promising source of inexpensive renewable energy. However, further improvements in device performance and improved lifetimes are required for the commercialization of OPVs. This work is primarily focused on developing a novel device architecture to improve device performance and characterizing structure-property-performance relationships for OPVs.

The excitonic nature of organic semiconductors necessitates the use of an electron donor-acceptor (D-A) heterojunction for efficient exciton dissociation and the generation of photocurrent. In many organic semiconductors, the optical absorption length is much larger than the exciton diffusion length. This trade-off between absorption and exciton diffusion is often overcome by increasing the area of the dissociating D-A interface using engineered film morphologies. This thesis presents an approach to maximize cell efficiency using a continuously graded D-A heterojunction. The graded heterojunction allows for an increase in the D-A interface area for an enhanced exciton diffusion efficiency, while also preserving the charge collection efficiency, leading to a significant improvement in device performance relative to that of optimized planar and uniformly mixed OPVs. In addition, this work correlates the optimized D-A composition gradient to the underlying film morphology and charge transport properties of uniform D-A mixtures. Subsequently, a new characterization technique to calculate the charge collection efficiency of OPVs is discussed. This technique is used to demonstrate the enhanced charge collection efficiency in graded heterojunctions relative to uniformly
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Chapter 1-Introduction

1.1 Background

The finite supply of fossil fuels, the environmental hazards related to CO₂ emission and the increase in the price of natural gas and oil have led to interest in the study and application of alternative sources of energy. Renewable sources of energy including hydroelectric, wind, geothermal, biomass and solar energy, are promising alternatives to conventional fossil fuels due to their inexhaustible nature. Currently, only 7% of the energy requirements of the United States are met from renewable sources of which solar energy contributes approximately 1%. The widespread use of wind and solar energy is limited due to their high cost. Therefore, significant research is essential for the economical implementation of these promising technologies.

The conversion of solar radiation into electric power represents an important renewable energy option that can be a sustainable, plentiful and clean source of energy. Conversion of sunlight into electricity is achieved using a photovoltaic (PV) cell. Modern PVs have numerous attributes which make them a commercially attractive renewable energy technology. For example, PVs are a modular technology which can be easily installed anywhere with sunlight. In addition, they can be integrated directly into building structures, which helps reduce the stress on electrical transmission and distribution systems. The total electricity demand for the United States could be supplied by solar cell systems covering only a small fraction of the land in a high-sunlight area such as the desert in the south-west part of the country. While this approach would be impractical
due to transmission losses, it demonstrates that given a reduction in cost, PVs could provide a much larger fraction of electricity demands than is currently the case.

At present, the PV market is dominated by cells based on crystalline silicon. Even though these PVs have high laboratory-scale power conversion efficiencies exceeding 25%,² they are not widely used due to their high manufacturing cost.³ A number of thin film PV technologies are currently working towards realizing high efficiency at low manufacturing cost in order to make solar energy commercially viable. These cells are often based on active materials like cadmium telluride (CdTe), copper indium gallium selenide (CIGS) and amorphous silicon. These materials are applied as thin films to a supporting substrate such as glass. Since these technologies do not rely on the use of silicon wafer substrates, they can potentially be manufactured at much lower cost.⁴, ⁵ However, there are limitations on how much the cost of this technology can be lowered.⁶ Many of these raw materials like In are scarcely available.⁷ This limited availability might ultimately increase the cost of this technology. The toxicity of cadmium also raises some concerns for these devices.⁷

Recently, PVs based on molecular organic semiconductors (known as OPVs) have drawn interest due to their compatibility with high throughput and potential for low cost. Organic semiconductors are inherently cheap, can be printed onto flexible plastic and foil substrates and are compatible with roll-to-roll fabrication processes (Figure 1.1).¹, ⁸, ⁹ The use of inexpensive processing techniques could make OPVs competitive with inorganic thin-film technologies on a cost-per-Watt basis. Considering these processing advantages, a device efficiency of ~10% and a module efficiency of ~5% are
regarded as critical market-entry values for OPVs.\textsuperscript{10} With attractive processing advantages, OPV commercialization now requires new approaches for cell design to enhance the overall power conversion efficiency and improve lifetime.

\textbf{1.2 Recent progress in organic photovoltaics}

In OPVs, absorption of a photon excites an electron from the highest occupied molecular orbital (HOMO) energy level to the lowest unoccupied molecular orbital (LUMO) energy level of the organic semiconductor (Figure 1.2a). This electron remains bound to the positively charged hole by the Coulomb force with a binding energy of few eVs.\textsuperscript{11} This bound electron-hole pair is called an exciton. This situation is different from
inorganic PVs in which absorption of light creates a free electron-hole pair that is separated by the built-in electric field of the cell. The exciton dissociates to give free charge carriers which are collected at the respective electrodes generating photocurrent. Device operation will be discussed in detail in Chapter 2.

A series of developments have taken place in the field of OPVs over the last 20 years to improve device performance. The first OPV was based on a single organic layer sandwiched between two metal electrodes of different work functions. The photogenerated excitons were dissociated at one of the contacts based on the work function of the contacts used. The highest efficiency obtained with these devices was less than 1%. A major breakthrough was made in the field when Tang published a planar heterojunction structure with an efficiency of 1%. A bilayer OPV consists of a heterojunction of two active organic layers referred to as the electron donor and acceptor (Figure 1.2b). Device performance in the bilayer architecture is limited by the tradeoff between the absorption and exciton diffusion efficiencies, often referred to as the exciton diffusion bottleneck.

![Energy level alignment in a planar heterojunction OPV cell.](image)

**Figure 1.2** (a) Energy level alignment in a planar heterojunction OPV cell. Donor material has shallower HOMO level and acceptor material has deeper LUMO level. (b) Device structure a planar heterojunction (bilayer) OPV cell.
Multiple approaches have been developed to overcome the exciton bottleneck and realize efficient photoconversion in OPVs. The use of long-lived phosphorescent materials has enabled larger exciton diffusion length ($L_D$) than is typically obtained in fluorescent organic materials.\textsuperscript{15-18} Of particular note is the use of C$_{60}$ as an acceptor, permitting thicker active layers and enhanced device performance.\textsuperscript{15} In addition to the improvement on the materials side, significant advances have also been made in the design of device architectures. These different architectures aim to overcome the short $L_D$ by increasing the donor-acceptor interface area. Different device architectures including mixed,\textsuperscript{19,21} hybrid planar-mixed,\textsuperscript{22,23} nano-crystalline networks,\textsuperscript{24} bulk heterojunctions,\textsuperscript{25,26} and in this work, graded heterojunctions, have been used to improve device efficiency. Highest single cell device efficiencies exceeding 10\% have been fabricated by Mitsubishi recently. Further improvement in material and device design may soon allow OPVs to compete with inorganic PVs.

1.3 Overview of this thesis

The morphology of the active layer has been shown previously to impact device performance significantly. Optimizing the morphology of the active layer allows to simultaneously maximize the efficiency of different processes involved in photoconversion. The main focus of the work in this dissertation is to engineer the morphology of the active layer of OPVs to overcome some of the limitations of organic materials and improve device performance. This dissertation is divided into ten chapters. The current chapter, Chapter 1, provides a brief introduction to the current PV
technology. Chapter 2 discusses the concepts underlying the operation of OPVs. The following four chapters (Chapter 3 to Chapter 6) present details of work towards engineering the morphology of the OPV active layer. Chapter 3 presents a novel device architecture for OPVs based on graded heterojunctions of copper phthalocyanine (CuPc) and C₆₀. Chapter 4 discusses a study on bulk heterojunction OPV cells using boron subphthalocyanine chloride (SubPc) and C₆₀ as the donor and acceptor, respectively. The discussion covers the effect of composition of the active layer on nanoscale film morphology, charge transport properties and device performance. Motivated by the results of Chapter 3 and with the understanding of bulk heterojunctions of SubPc and C₆₀, graded heterojunction OPVs were also fabricated with SubPc and C₆₀. Discussion of results obtained for graded heterojunction OPVs using SubPc and C₆₀ is presented in Chapter 5. As an electron acceptor, C₇₀ is a promising alternative to C₆₀ due to its larger contribution to photocurrent. Chapter 6 examines the performance of SubPc and C₇₀ in uniformly mixed and graded heterojunction OPVs. Chapter 7 discusses an experimental technique developed in this work to estimate the charge collection efficiency of OPVs by using reverse bias external quantum efficiency measurements. Subsequently, Chapter 8 examines the optical, structural and electrical characterization of a novel donor material for use in OPVs with sensitivity extending to the near infrared region of the solar spectrum. A brief summary of the research work conducted in this thesis and a detailed plan of the future work is presented in Chapter 9. Finally, Chapter 10 includes a list of references.
Chapter 2-Review of Organic Photovoltaics

2.1 Introduction

Chapter 1 presented motivation for research in the field of photovoltaics and specific advantages of organic photovoltaics (OPVs) over other existing technologies. This chapter will provide a background to the field of OPVs. It will start with a review of organic semiconductors and physical concepts governing their behavior. Subsequently, a description of device operation of OPVs will be presented, which is also contrasted with their inorganic counterparts. This is followed by a summary of the factors that impact device performance. Recent advances in the development of new device architectures for OPVs are discussed at the end of this chapter.

2.2 Inorganic semiconductor physics

As a result of lattice periodicity and strong interatomic interaction, electrons in crystalline materials are arranged in energy bands, as shown in Figure 2.1. The highest energy-filled band is referred to as the valence band, and the lowest empty band is referred to as the conduction band. These energy bands are separated by a range of energies in which no states exist. This region is referred to as an energy gap or band gap. If one or more energy bands of the crystal are partly filled, electrons can move freely in available empty states when an electric field is applied, leading to a high conductivity. Materials with this type of band structure are referred to as metals. A material behaves as an insulator if the valence band is completely filled and the conduction band is

7
completely empty, leaving no empty states for electron transport under an applied electric field. The large band gap of insulators (> 3eV) does not permit excitation across the energy gap. Materials that behave as insulators at 0 K, but have a small band gap (~1 eV) to permit excitation of electrons from the valence band to the conduction band are known as semiconductors.\textsuperscript{27, 28}

2.3 Organic semiconductor physics

A carbon containing material is referred to as an organic compound. Approximately 90\% of the two million known compounds are organic, owing to the tetravalency of carbon which permits it to form single, double and triple bonds. Out of this large number of organic compounds, only a small fraction of these compounds

![Energy Band Structure](image)

**Figure 2.1**: Energy band structure of an insulator, metal and semiconductor. Shaded areas indicate the states filled with electrons. A semiconductor behaves as an insulator at zero temperature but at a finite temperature, thermal energy is sufficient to excite electrons to a higher energy level. The extreme right figure shows a semiconductor at finite temperature with carriers excited thermally.
consisting of conjugated bonds, alternating single and double bonds, display semiconductor behavior.$^{29}$

The electronic configuration of carbon is $1s^22s^22p^2$. In the conjugated configuration, the 2s and two 2p orbitals combine to form three sp$^2$ hybrid orbitals that are coplanar at an angle of 120° from each other. The bonds between these orbitals are referred to as σ bonds. The $p_x$ and $p_y$ orbitals participate in this hybridization while the $p_z$ orbital is perpendicular to the plane of sp$^2$ hybridization (Figure 2.2a).$^{30}$ The overlapping of neighboring $p_z$ orbitals of adjacent carbon atoms creates a π bond.$^{29}$ The π bond leads to a significant delocalization of the electron density above and below the plane of the σ bond (Figure 2.2b). The overlapping π–orbitals of adjacent carbon atoms provide a

Figure 2.2: (a) The $p_z$ orbitals of benzene are orthogonal to the plane of sp$^2$ hybridization. (b) Bonding of $p_z$ orbitals leads to the delocalization of electron density above and below the plane of σ bond. (c) The formation of σ and π bonding and σ* and π* anti-bonding orbitals from two adjacent sp$^2$ hybridized carbon atoms. The π and π* orbitals are referred to as the HOMO and LUMO levels, respectively. (a) and (b) are adapted from Reference 30.
continuous pathway for electron transport. The electronic and optical properties of these organic semiconductors depend strongly on the properties of the π-electrons. The highest-energy occupied and the lowest-energy unoccupied states correspond to the π and π*-orbitals respectively (Figure 2.2c). These orbitals are also referred to as the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, respectively. The HOMO and LUMO levels can be determined by ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES), respectively.\textsuperscript{31, 32} In the presence of a large number of electrons, the π and π* levels approach the limit of continuous bands, where the energy gap between HOMO and LUMO levels is analogous to the band gap in the case of inorganic semiconductors. The electronic transitions from the filled (π) to the unfilled levels (π*) is responsible for the semiconductor behavior of conjugated organic materials.

Organic semiconductors can be classified into two main categories: small molecules and polymers. Small molecules refer to compounds with a well-defined molecular weight. In general, these molecules are deposited by thermal evaporation allowing for well-controlled layer thickness and the growth of ordered films.\textsuperscript{14} Recently, significant effort has gone into developing solution processed small molecules.\textsuperscript{33, 34} On the contrary, polymers are large molecules, composed of repeating structural units connected by covalent bonds. Polymer based OPVs are solution processed. In spite of the differences related to material and device processing, device physics is similar in both cases. This work is focused on thermally evaporated small molecules.
2.3.1 Exciton generation in organic semiconductors

Electrons from the HOMO level can be excited to the LUMO level by thermal, optical and electrical excitation. Photon absorption in organic semiconductors promotes an electron from the HOMO level to the LUMO level. The residual Coulomb binding attraction between the electron and hole creates bound electron-hole pairs which are referred to as excitons. This behavior is different from their inorganic counterpart where photon absorption at room temperature typically creates free electrons and holes. This difference in behavior arises due to two reasons: (1) lower dielectric constant of organic semiconductors (~1-5) relative to inorganic semiconductors (~12-16) extends the Coulomb potential well around the electron-hole pair over a greater volume, and (2)

![Diagram of exciton types](image)

**Figure 2.3:** (a) Frenkel exciton in which exciton radius is much smaller than lattice constant ($a_L$) (b) Wannier-Mott exciton in which exciton radius is much larger compared to the lattice constant (c) Charge-transfer exciton in which the exciton radius is comparable to the lattice constant.
weaker van der Waals forces in organic semiconductors compared to the stronger covalent forces result in smaller Bohr radius of charge carriers.\textsuperscript{37, 38} The former occurs partly because organic semiconductors consist mainly of elements in the first two rows of the periodic table whose electrons are more tightly bound (less polarizable) than those of inorganic semiconductors, which typically consist of more polarizable elements from the 3rd-5th rows.\textsuperscript{37, 39}

There are three types of excitons encountered in semiconductor materials: Frenkel, Wannier-Mott and charge-transfer excitons (Figure 2.3).\textsuperscript{29} The Frenkel exciton is an electron-hole pair often confined to one molecule. The distance between the electron and its corresponding hole (<5 Å) is smaller than the distance between molecules, with binding energy ranging between 0.4 to 1.4 eV.\textsuperscript{40, 41} This type of exciton is most commonly encountered in amorphous organic materials. Conversely, Wannier-Mott type excitons have a radius that is more than an order of magnitude larger than the intermolecular distance (~ 40 - 100 Å). These excitons have binding energy of a few meV and are most commonly encountered in crystalline, inorganic semiconductor systems. For example, the exciton binding energy of silicon is 14.7 meV.\textsuperscript{27} Since the binding energy of silicon is less than thermal energy (~25 meV), photon absorption in silicon creates free electrons and holes that can move around in the lattice. Charge-transfer excitons are intermediate between the other two types of excitons in terms of magnitude of delocalization of the excitons. In this case, the exciton radius is one or two times the nearest-neighbor intermolecular distance and slightly lower binding energy than Frenkel excitons. These are mostly observed in crystalline organic semiconductors.\textsuperscript{29, 42} Frenkel
excitons are assumed to be the dominant type of excitons in this work due to the amorphous nature of most materials and films examined.

2.3.2 Exciton migration (diffusion) in organic semiconductors

Exciton transport (or diffusion) in the organic bulk can be thought of as successive hops or intermolecular energy transfer events. There are three possible mechanisms for energy transfer, namely, cascade energy transfer, Förster energy transfer and Dexter energy transfer.²⁹, ⁴³

Cascade or trivial energy transfer involves the process of photon reabsorption. In this process, a molecule acts as an emitter and releases energy through a photon, followed by the absorption and subsequent excitation of another molecule that acts as the receiver. For this type of energy transfer to occur there must be some spectral overlap between the emission spectrum of the emitter and the absorption spectrum of the receiver (Figure 2.4).²⁹, ⁴³ The rate of energy transfer depends on the emission efficiency of the donor, the

Figure 2.4: Cascade energy transfer requires overlap between emission spectrum of the donor molecule and absorption spectrum of the acceptor molecule.
acceptor absorption efficiency and the spectral overlap between the emission spectrum of the donor molecule with the absorption spectrum of the acceptor molecule but shows no dependence on molecular separation. This is a long range process, typically more than 10 nm (in real space).\(^{29}\)

Förster or resonant energy transfer also depends on the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor. However, Förster energy transfer is a non-radiative process in which energy transfer is mediated by a virtual photon. In this process, both the donor and acceptor molecules act as dipoles, where the electric field associated with the donor induces an oscillating dipole on the acceptor.\(^{29}\) As shown in Figure 2.5, the initially excited electron (1) and the newly promoted electron (2) remain on their respective molecules. As such, there is no physical exchange of electrons. After the exchange of energy, the donor molecule relaxes to its ground state and the acceptor molecule is excited. The rate of Förster energy transfer falls off with sixth power of distance and typically occurs on the length scale of 1-10 nm, and may occur between molecules that are not adjacent.\(^{29}\)

![Figure 2.5: Förster energy transfer occurs via dipole-dipole interaction between donor and acceptor molecules.](image)

\(^{29}\)
Dexter energy transfer is used to describe energy transfer for excitons with electric dipole forbidden transitions. This mechanism of energy transfer involves physical electron exchange as the dominant interaction and hence, occurs over a much shorter molecular separation, and occurs in nearest neighbor interactions (Figure 2.6). Electron exchange requires the overlap of donor and acceptor orbitals. Since the electron densities usually fall off exponentially with distance, the Dexter energy transfer rate also shows the same dependence on distance.

![Electron Exchange Diagram](image)

Figure 2.6: Dexter energy transfer involves a physical exchange of electrons between donor and acceptor species.

### 2.3.3 Charge transport in organic semiconductors

Charge transport in semiconductors is often explained using one of two models: the band model and the hopping model. The band model is applicable where the carrier moves as a delocalized plane wave with a considerably large mean free path. On the contrary, the hopping model is used to explain charge transport when the carrier is highly localized and moves by thermally activated hops from site-to-site (Figure 2.7). Typically, the charge transport mechanism in organic semiconductors lies between these two extremes.
In the band model, intermolecular interaction leads to the formation of energy bands for charge carriers. These bands are delocalized states in which the charge carrier can move from molecule to molecule in a periodic lattice.\textsuperscript{44} Band transport occurs in materials with wide bands. In this case, the mobility ($\mu$) is greater than $1 \text{ cm}^2/\text{Vs}$\textsuperscript{45} and the temperature dependence goes as:\textsuperscript{29}

$$\mu \propto T^{-n}$$

where $n>1$. Organic semiconductors are held together by weak van der Waals interaction which leads to a poor overlap between neighboring molecules. For band transport to occur, the mean free path of charge carrier must be much larger than lattice constant. This

![Figure 2.7: Charge transport mechanisms. (a) Band transport: Charge carrier is delocalized and does not get scattered in a perfect crystal. It gets scattered due to lattice vibrations (phonons) present in a real crystal. Phonons scatter the charge carrier and hence lower its mobility. (b) Hopping transport: This model is used to explain charge carrier mobility in an irregular crystal or if the charge carrier becomes localized on a defect site. In this case lattice vibrations help the charge carrier to move from one site to another.](image-url)
is often not the case in organic semiconductors due to their amorphous or polycrystalline character.

The band model implicitly assumes that the mean free path of the charge carrier is much larger than the lattice constant. However, if the mean free path of charge carriers is comparable to the lattice constant, the hopping model is used to explain charge transport. In this case, a charge carrier resides on one lattice site for a considerable amount of time and then hops to the next site. As such, the carrier has sufficient time to polarize the surrounding lattice which relaxes to a new equilibrium position. Charge carriers reside in potential wells centered at the equilibrium position. The charge carrier and its associated deformation are collectively referred to as a polaron. Charge carriers must overcome an energy barrier to hop from one site to the next. The governing equation for calculating mobility for hopping transport is given by:

\[ \mu \propto \left( \frac{ea^2}{k_BT} \right)^{m} \exp \left(-\frac{E'}{k_BT} \right) \]  

(2.2)

where e is the electronic charge, a is the distance between potential well sites, E’ is the energy barrier, k_B is the Boltzmann’s constant, T is the temperature and m is a constant (typically 0 or 0.5).

At low temperature, the exponential term dominates. Consequently, mobility increases with an increase in temperature. Thus, at very low temperatures, the dominant mechanism for charge transport is hopping transport. At higher temperatures, the power law in temperature dominates, making it difficult to distinguish between band-like and hopping transport. The materials and thin-films explored in this work are typically amorphous, so the charge transport is expected to be dominated by hopping mechanism.
In organic semiconductors, the charge carrier mobility often exhibits a Poole-Frenkel dependence on the applied voltage (or electric field).\textsuperscript{46, 47} This functional dependence is attributed to a random variation in hopping site energies for disordered organic semiconductors, leading to energetic barriers for carrier transport that are overcome with an applied voltage.\textsuperscript{48, 49} In this case, the mobility can be expressed as:

$$\mu(E) = \mu_0 \exp\left[ \gamma \left( E \right)^{1/2} \right]$$  \hspace{1cm} (2.3)

where $\mu_0$ is the zero-field mobility given by Equation 2.2, $E$ is the applied electric field and $\gamma$ is the field activation parameter. A more detailed derivation of Equation 2.3 is presented in Appendix D.

With the basics of exciton generation, exciton migration and charge transport, the operation of OPVs can be explicitly explained. Before we discuss OPVs, a brief overview of the device operation of inorganic photovoltaics (IPVs) is presented.

![Energy-band diagram](image)

Figure 2.8: Plot of energy versus position (Energy-band diagram) of a p-n junction in thermal equilibrium. There is no net current flow at equilibrium.
2.4 Inorganic photovoltaic device operation

The device operation of an IPV cell can be explained in terms of a p-n junction diode. In a p-n junction, the Fermi energy level is constant throughout the entire system at equilibrium (Figure 2.8). When the p-type and n-type semiconductors are brought in contact, majority carriers (electrons) in the n region diffuse to the p region and majority carriers (holes) in the p region diffuse into the n region. Diffusing carriers recombine and the remaining bound charge in the lattice leads to the built-in field (Figure 2.9a). These positive and negative charges induce an electric field in the direction from the positive to the negative charge (Figure 2.9b). The region of net positive and negative charge is referred to as the space charge or depletion region (shown in Figure 2.8). There are two opposing forces acting on electrons and holes. One is the diffusion force due to concentration gradient and the other is due to the induced electric field. At equilibrium, the magnitudes of these forces are equal and the directions are opposite to each other. 

![Diagram of space charge density, electric field, and electric potential through the depletion region.]

Figure 2.9: (a) Space charge density in a uniformly doped p-n junction (b) Electric field in the depletion region of a uniformly doped p-n junction (c) Electric potential through the depletion region.
In the case of equilibrium, a potential barrier is seen by the electrons which prevents them from flowing into the p region. The same potential barrier prevents holes from flowing into the n region. Figure 2.10a illustrates the energy band diagram for the case when a positive bias is applied to the p region with respect to the n region. This case is referred to as the forward bias. The positive voltage lowers the Fermi energy of the p region relative to the n region. The potential barrier seen by either electrons or holes is reduced. Hence, there is a diffusion of electrons from the n region into p region and the holes diffuse into the n region. This flow of electrons and holes produces a net current in the direction from the p region to the n region. Figure 2.10b shows the energy band diagram for the case when a negative bias is applied to the p region with respect to the n region. This is referred to as the reverse bias. Here, the Fermi energy of the n region is lowered relative to the Fermi energy of the p region. The potential barrier seen by either electrons or holes is larger than the equilibrium case. Consequently, there is essentially

Figure 2.10: Plot of energy versus position (Energy-band diagram) of a p-n junction in (a) forward bias (b) reverse bias and (c) under illumination and no applied voltage. Filled circles symbolize electrons and empty circles represent holes. In forward bias in dark, the net current is current is from left to right. Under reverse bias, the net current flows from right to left. Under illumination, the net current flows from right to left. The direction of photocurrent is the same as for a p-n junction under reverse bias.
no charge flow and hence almost no current in reverse bias.\textsuperscript{36,50}

The dark current in an inorganic PV can be modeled using the Shockley equation:

\[ J = J_s \left\{ \exp \left( \frac{e(V - J R_s)}{n k T} \right) - 1 \right\} \] (2.4)

where \( J \) is the current density, \( J_s \) is the reverse-bias saturation current density, \( e \) is the electron charge, \( R_s \) is the series resistance, \( n \) is the ideality factor, \( k \) is the Boltzmann constant, and \( T \) is the temperature. In forward bias (positive voltage), the current density increases exponentially with applied bias. As shown in Figure 2.11, the \( R_s \) governs the value of current density at large voltage whereas the ideality factor determines the slope of the “turn-on” region. An ideality factor of \( n=2 \) indicates that the dark current is dominated by electron-hole recombination whereas \( n=1 \) suggests the dark current is

![Figure 2.11: Dark current density-voltage characteristics in the forward bias for different values of series resistance (\( R_s \)) and ideality factor (\( n \)).](image-url)
primarily from charge carrier diffusion to the opposite electrode.\textsuperscript{50} There is almost no current flow when reverse bias (negative voltage) is applied.

When light is incident on a p-n junction under no applied bias, electron-hole pairs are created. Since, there is a built-in electric field present in the depletion region of the p-n junction, the electron-hole pairs in that region will be swept out due to the electric field. This produces the photocurrent in the direction of reverse bias as shown in Figure 2.10c.\textsuperscript{50}

\section{2.5 Organic photovoltaic device operation}

The most common device architecture for OPVs, known as the planar or bilayer structure, consists of an anode, two optically active semiconductor layers and a cathode (Figure 2.12a). A transparent conducting oxide is commonly used as the anode.\textsuperscript{7} Indium tin oxide (ITO) is the most widely used transparent conducting anode.\textsuperscript{62} However,
materials such as PEDOT,\textsuperscript{53} \(\text{SnO}_2\text{F,}\textsuperscript{54, 55} \) doped ZnO,\textsuperscript{56-58} \) patterned metallic layers\textsuperscript{59-61} and Ag wires\textsuperscript{62} are being explored as alternatives to ITO due to the scarcity of indium in earth’s crust. Typically, Al or Ag are used as cathode in OPVs. The anode and cathode materials are chosen based on the alignment of their work function with the HOMO level of the donor and LUMO level of the acceptor, respectively. The energy alignment between the metal and organic is critical for efficient hole and electron collection.

As mentioned earlier, photo-excitation in organic semiconductors produces an electrically neutral, bound electron-hole pair, referred to as the exciton. The excitonic character of OPVs necessitates the use of a heterojunction comprising two organic materials with offset energy levels for exciton dissociation.\textsuperscript{13} These materials are referred to as the electron donor and electron acceptor. Electron donors have smaller HOMO value relative to vacuum, while electron acceptors have larger LUMO value relative to vacuum (Figure 2.12b).\textsuperscript{63}

![Figure 2.13: Four steps in photoconversion process in an OPV. Blue and purple boxes represent donor and acceptor respectively. Black and white circles denote electrons and holes respectively. (a) Exciton generation on absorption of photon in the donor and acceptor which relaxes to the optical band gap. For simplicity excitons are shown only in the donor layer. (b) Diffusion of photogenerated excitons to the donor acceptor (D-A) interface. (c) Exciton dissociation leading to electron in the acceptor and hole in the donor. (d) Collection of free charges at the respective electrode.](image)
The photoconversion process in OPVs involves four main steps as shown in Figure 2.13. These steps are explained in the following subsections.

2.5.1 Absorption

Photon absorption in OPVs leads to the formation of tightly-bound Frenkel excitons. Organic semiconductors are attractive for use in PV cells due to their high absorption coefficients ($\alpha \sim 10^5 \text{ cm}^{-1}$), permitting the use of thin films (< 100 nm) to achieve high absorption efficiency. Figure 2.13a demonstrates that photon absorption creates an energetic electron-hole pair or polaron pair with energy equal to the electrical bandgap (difference between the HOMO and LUMO of the donor/acceptor). The pair then relaxes to the optical bandgap which is given by:

$$E_{\text{Elec}} = E_{\text{Opt}} + E_B$$

(2.5)

where $E_{\text{Elec}}$ is the electrical band gap, $E_{\text{Opt}}$ is the optical bandgap and $E_B$ is the exciton binding energy.

2.5.2 Exciton diffusion

Creation of excitons in the donor and acceptor is followed by the diffusion of excitons to the donor acceptor (D-A) heterojunction where dissociation of excitons occurs (Figure 2.13b). Exciton diffusion can be explained by one of the three energy transfer processes discussed earlier in Section 2.3.2. One of the main limitations to the performance of OPVs comes from to the trade-off between absorption and exciton diffusion efficiencies. The diffusion length ($L_D$) of organic semiconductors is
typically on the order of 10 nm. However, the absorption length of organic semiconductors is typically ~100 nm. Since exciton dissociation occurs only at the D-A interface, excitons generated farther than \( L_D \) away from the interface may not contribute to photocurrent. As the active layer thickness is decreased to increase the fraction of excitons dissociated, the fraction of light absorbed in the device decreases. These competing effects dictate the optimum organic layer thickness in an OPV.

### 2.5.3 Charge transfer

Once the exciton reaches a heterojunction, the thermodynamic requirement for an exciton to dissociate into holes and electrons is that the D-A HOMO and LUMO offsets are larger than the exciton binding energy. If the energy level alignment of the donor and acceptor is favorable for charge transfer, the dissociation/charge transfer results in an electron polaron in the acceptor material and a hole polaron in the donor material (Figure 2.13c).

Charge transfer efficiency in the semi-classical limit is modeled using the Marcus theory for electron transfer. The rate of electron transfer is given as:

\[
\begin{align*}
    k &= A \exp \left( -\frac{\Delta G^*}{k_B T} \right) \left( \frac{4\pi^3}{h^2 \lambda k_B T} \right)^{1/2} \left( V^*_{\text{RP}} \right)^2 \exp \left( -\frac{\left( \Delta G^0 + \lambda \right)^2}{4\lambda k_B T} \right) \\
\end{align*}
\]

where \( \Delta G^0 \) represents the Gibbs free energy of the reaction, \( V_{\text{RP}} \) is the electronic coupling between reactants and products of the reaction and \( \lambda \) is the reorganization energy.

The Gibbs free energy of the reaction (\( \Delta G^0 \)) is the free energy difference of the products and the reactants involved in the reaction. The entropy contributions to free
energy are neglected because the motion of the molecules is strongly hindered in the solid. Thus, $\Delta G^0$ for exciton dissociation is calculated as:

$$\Delta G^0 = E^{D^+} + E^{A^-} - E^{D^*} - E^A + \Delta E_{\text{Coul}}$$

(2.7)

with

$$\Delta E_{\text{Coul}} = \sum_{D^*} \sum_{A^-} \frac{q_{D^*}q_{A^-}}{4\pi\varepsilon_0\varepsilon_s r_{D^*A^-}} - \sum_{D^+} \sum_{A^+} \frac{q_{D^+}q_A}{4\pi\varepsilon_0\varepsilon_s r_{D^+A}}$$

(2.8)

where $E^{D^*}$ and $E^{D^+}$ represent the total energy of the isolated donor in the equilibrium geometries of the lowest excited state and of the cationic state, respectively. $E^A$ and $E^{A^-}$ represent the total energy of the isolated acceptor in the equilibrium geometries of the ground state and of the anionic state, respectively. The terms $q_D$ and $q_A$ represent the atomic charges on the donor and acceptor molecules in their relevant state respectively; $r_{DA}$ is the separation between the donor and acceptor and $\varepsilon_s$ is the dielectric constant of

Figure 2.14: Potential energy curves as a function of generalized coordinates for the ground state (DA), lowest intramolecular donor excited state (D$^+\text{A}$) and the lowest charge-transfer state (D$^+\text{A}^-$). $\Delta G^0$ and $\lambda$ correspond to the free energy change in the charge transfer process and reorganization energy respectively. Adapted from Reference 65.
the medium. The summation is over all the atoms of the two individual donor and acceptor molecules.\textsuperscript{70}

Reorganization energy ($\lambda$) involves two contributions: (i) the internal part $\lambda_i$, which describes the geometry of the donor and acceptor molecules upon charge transfer and (ii) the external part $\lambda_e$, which is related to the change in electronic and nuclear polarizations of the surrounding medium. Since, $\Delta G^0$ is negative and $\lambda$ is positive, the charge transfer rate is maximum when $|\Delta G^0| = \lambda$. This rate is lower than the maximum value, when $|\Delta G^0| < \lambda$ (referred to as the normal region) and when, $|\Delta G^0| > \lambda$ (referred to as the inverted region). The relative magnitudes of $\Delta G^0$ and $\lambda$ depend on the nature of the excited states. Therefore, these excited states play a significant role in the dynamics of charge generation.

The rate of exciton dissociation (charge transfer) can be evaluated by substituting all the parameter values discussed above in Equation 2.6. The rate of charge transfer is found to lie between $10^{10}$-$10^{15}$ s\textsuperscript{-1}, whereas the rate of recombination lies between $10^1$-$10^5$ s\textsuperscript{-1}. Since the rate of charge transfer is much greater than the rate of competing recombination process, the efficiency of this process is close to 100\%.\textsuperscript{70-72}

2.5.4 Charge collection

The excitons are separated into free charge carriers at the D-A heterojunction. The flux of these charge carriers away from the heterojunction is governed by the gradient of electrochemical potential, which is the sum of electrical ($U$) and chemical potential ($\mu$) energy gradients.\textsuperscript{37, 38, 64, 73} These contributions are generally referred to as the drift and
diffusion component of current, respectively. The general one dimensional current density of electrons $J_n(x)$ is given by:

$$J_n(x) = n(x)\mu_n \{\nabla U(x) + \nabla \mu(x)\}$$  \hspace{1cm} (2.9)

where $n(x)$ is the concentration of electrons and $\mu_n$ is the electron mobility. Equation 2.9 shows that the electron concentration and electron mobility influence the magnitude of the electron flux and $\{\nabla U(x) + \nabla \mu(x)\}$ decides the direction of electron flux.

Figure 2.15a shows the carrier generation rate as a function of position in a planar OPV device. Almost all the carriers are generated in a region near the interface leading to a high concentration gradient of electrons and holes in opposite directions. This makes diffusion ($\nabla \mu$) the dominant force deciding the flux of the charge carriers. For

![Figure 2.15: Charge generation rate vs distance in (a) organic and (b) inorganic photovoltaic cells. In (a) electrons and holes are produced in the acceptor and donor layers respectively via interfacial exciton dissociation. Photo-induced chemical potential gradient ($\nabla \mu_{\text{hv}}$) drives electrons and holes in opposite direction. In (b) electrons and holes are generated everywhere. $\nabla \mu_{\text{hv}}$ drives both charge carriers in the same direction.](image)
photoconversion to be efficient, drift ($\nabla U$) should assist current flow in the same direction as diffusion. However, efficient OPVs can be made based completely on the diffusion driving force ($\nabla U \approx 0$). This is a major distinction in device operation from IPVs. In the case of IPVs, charge carriers have the same spatial distribution (Figure 2.15b). As a result, diffusion drives both the free charge carriers in the same direction. Therefore, the only driving force for current generation in the case of IPVs is drift. An important implication of this difference in operating mechanism is that the open circuit voltage ($V_{OC}$) of IPVs is constrained by the built-in voltage ($\varphi_{bi}$). However, in the case of OPVs, diffusion generally complements the effects of $\varphi_{bi}$ and hence, a larger $V_{OC}$ is achievable. After being transported through the active layer, the holes and electrons are collected at the anode and cathode, respectively generating photocurrent.

### 2.5.5 Recombination

Different mechanisms for electron-hole recombination in an OPV leads to loss of photogenerated charge carriers. An exciton can recombine via radiative (photon emission) or non-radiative (thermal, vibronic) decay mechanisms. In addition, charge carriers can recombine by two possible mechanisms: (i) back electron transfer (geminate recombination) and (ii) recombination with free charge carriers or charge traps (non-geminate recombination) as shown in Figure 2.16. The trade-off between rates of recombination and charge collection determines the performance of OPVs.
The electrical characterization of OPVs involves measuring the current-voltage characteristics under dark and illuminated conditions (Figure 2.17a). Under illumination, the standard reporting conditions use the Air Mass 1.5 Global (or AM 1.5G) solar irradiance spectrum at 25°C with a total irradiance of 1000 W/m² (or 1 Sun) as shown in Figure 2.17b.

Figure 2.17a demonstrates a typical current-voltage (I-V) curve of an OPV under operation. The net current under illumination in OPVs is the sum of the dark current and the photocurrent. Dark current is the current produced in the device when there is no illumination. It reflects the diode characteristics of the device. The charge carriers injected from the electrodes into the organic layers can either recombine or diffuse to the opposite electrode, generating dark current. On the other hand, the photocurrent derives from interfacial exciton dissociation. The chemical potential gradient drives the
photogenerated carriers towards their respective electrodes.\textsuperscript{38, 64, 73} The direction of the photocurrent is the same as reverse bias dark current. While the photocurrent is generally treated as independent of voltage, it is likely more accurate to model the photocurrent as a function of voltage ($V < V_{OC}$).\textsuperscript{12, 75, 76}

![Figure 2.17](image)

Figure 2.17: (a) Typical current density vs. voltage curves of a photovoltaic in the dark and under illumination. The various device parameters are also shown. $V_{OC}$ and $J_{SC}$ represent the open-circuit voltage and the short-circuit current density. $J_{max}$ and $V_{max}$ are the current density and voltage corresponding to the maximum power output. (b) Standard AM 1.5G solar irradiance spectrum.

### 2.6.1 External quantum efficiency ($\eta_{EQE}$)

Devices are tested under monochromatic illumination to measure the external quantum efficiency ($\eta_{EQE}$). The $\eta_{EQE}$ is defined as the ratio of charge carriers collected at the electrodes to the number of photons incident at each wavelength. Since the photoconversion process can be separated into four different steps, as discussed earlier, the $\eta_{EQE}$ can be expressed as the product of the efficiency of these four steps.\textsuperscript{12}
\[ \eta_{\text{EQE}}(\lambda) = \eta_{\lambda}\eta_{\text{Diff}}\eta_{\text{CC}}\eta_{\text{CT}} = \left( \frac{hc}{q\lambda} \right) \left( \frac{J_\lambda}{P_\lambda} \right) \]  

(2.10)

where \( J_\lambda \) is the photocurrent density at wavelength \( \lambda \), \( P_\lambda \) is the power density per nm, \( h \) is the Planck’s constant, \( c \) is the speed of light and \( q \) is the charge of an electron. The short-circuit current density \( (J_{\text{SC}}) \) can be obtained by integrating the \( \eta_{\text{EQE}} \) across the solar spectrum:

\[ J_{\text{SC}} = \left( \frac{q}{hc} \right) \int [\lambda \times P_\lambda \times \eta_{\text{EQE}}(\lambda)]d\lambda \]  

(2.11)

In order to decouple the effect of absorption of the organic layer from the performance of the layers, an additional parameter is defined as the internal quantum efficiency \( (\eta_{\text{IQE}}) \):

\[ \eta_{\text{IQE}} = \frac{\eta_{\text{EQE}}}{\eta_A} = \eta_{\text{Diff}}\eta_{\text{CC}}\eta_{\text{CT}} \]  

(2.12)

The \( \eta_{\text{IQE}} \) depends on the film morphology and device architecture. Hence, it is an important figure of merit when comparing the performance of different device designs.

### 2.6.2 Short-circuit current density \( (J_{\text{SC}}) \)

The \( J_{\text{SC}} \) depends on the absorption spectra (or absorption coefficients) of the active organic materials, the exciton diffusion/dissociation efficiency and the charge collection efficiency. The absorption efficiency depends on thickness of the active layer, which is governed by the absorption length \( (L_A) \) of the material. Donor-acceptor interface area governs the exciton dissociation efficiency. The film morphology affects the charge mobility in the active layer and hence, the charge collection efficiency. In order to
optimize $J_{SC}$, enhanced spectral overlap must be accomplished while preserving exciton diffusion/dissociation and charge collection efficiencies.

2.6.3 Open-circuit voltage ($V_{OC}$)

The $V_{OC}$ is an important parameter for characterizing device performance, and has recently become the subject of much investigation. The $V_{OC}$ of a planar OPV typically lies in the range of 0.5 V to 1 V, whereas the absorbed photons have energy more than 2.5 eV. Hence, the efficiency of OPVs could be improved by 2-5 times if $qV_{OC}$ is approximately equal to the energy of the absorbed photon. In spite of this, the origin of $V_{OC}$ in OPVs is not clearly understood. In IPVs, the $V_{OC}$ is limited to the built-in voltage of the device. However, this is not applicable for OPVs and studies have shown that $V_{OC} > V_{bi}$ in OPVs. In OPVs, it has been suggested that $V_{OC}$ depends on the difference of the HOMO level of the donor and LUMO level of the acceptor, referred to as the interface gap, $I_g$. The effect of $I_g$ on $V_{OC}$ can be explained thermodynamically as well as in terms of the dark current. Larger $I_g$ results in larger absorbed photon energy and consequently, larger energy that can be extracted from the cell ($= qV_{OC}$). Large value of $I_g$ also restricts charge injection into the active organic layers, lowering the dark current. This lower dark current leads to a larger $V_{OC}$. In addition, the $V_{OC}$ has also been shown to depend on other fabrication considerations, such as morphology of the active layer, insertion of buffer layers at the electrodes, as well as the electrode work function.
2.6.4 Fill factor (FF)

The FF is defined as the ratio of the maximum power obtainable from the cell to the maximum potential power. As shown in Figure 2.16a, the FF is calculated as:

$$ FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} $$  \hspace{1cm} (2.13)

Fill factor is a figure of merit indicating how close the I-V characteristics under illumination are to an ideal rectangular shape.\textsuperscript{81} It is affected by the choice of electrodes, interfaces (organic/organic and metal/organic), morphology and thickness of the active layer.\textsuperscript{95, 96} Studies have shown FF to decrease with an increase in the series resistance of the device.\textsuperscript{80} Thus, FF can be maximized by minimizing the series resistance of the cell which can be accomplished by minimizing the contact resistance and optimizing the morphology of the active layer to minimize the bulk resistance.

2.6.5 Power conversion efficiency (\(\eta_P\))

The \(\eta_P\) is the ratio of the maximum electrical power obtained from a PV cell to the total incident optical power. It is calculated as:

$$ \eta_P = \left( \frac{FF \times J_{SC} \times V_{OC}}{P_{inc}} \right) \times 100(\%) $$  \hspace{1cm} (2.14)

where \(P_{inc}\) is the total optical power density incident on the cell. This efficiency is the most important parameter for characterizing the absolute device performance of a PV cell. Some of the most commonly used device architectures and their record efficiencies are discussed below.
2.7 Device architectures for organic photovoltaics

Significant advances have been made in the design of OPV device architectures. These different architectures often aim to increase the D-A interface area while permitting the efficient extraction of dissociated charge carriers. These improvements in device architecture coupled with new materials have allowed OPVs to realize $\eta_P > 10\%$.

2.7.1 Single-layer OPVs

The first OPV was based on a single organic layer sandwiched between two metal electrodes of different work functions.\textsuperscript{97-99} The photogenerated excitons were dissociated at one of the contacts based on the work function of the contacts used. These OPVs realized high values of $V_{OC} > 1V$.\textsuperscript{100} However, the photocurrent was very low due to the faster decay rate of photogenerated excitons compared to the dissociation rate and low charge collection efficiency. As a result, the $\eta_{EQE}$ was rather low (~1%) and the highest $\eta_P$ obtained with the single-layer OPVs was less than 1%.\textsuperscript{64, 101}

2.7.2 Planar heterojunction

The design of OPVs was revolutionized by Tang who developed a new device architecture, referred to as the planar heterojunction, by using two organic materials with dissimilar electronic properties (Figure 2.11a).\textsuperscript{13} The heterojunction allows for an easy separation of the photogenerated excitons and thus an improvement of the PV properties. Tang’s cell was fabricated using copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) as donor and acceptor materials.
respectively. This first small molecule organic cell based on a planar heterojunction had a 
$\eta_P \sim 1\%$. The fabrication of planar heterojunction with polymers is more complicated. It 
has been accomplished by using C$_{60}$ as an acceptor,\textsuperscript{66,102} orthogonal solvents for donor
and acceptor\textsuperscript{103} or by crosslinking the donor.\textsuperscript{104} Since its introduction, organic 
heterojunction structures have been adapted in almost all OPVs.

A major improvement in the planar heterojunction was the introduction of an 
exciton blocking layer (EBL) between the electron acceptor and cathode. Bathocuproine 
(BCP) is the most commonly used EBL.\textsuperscript{105-108} However, 4,7-diphenyl-1,10-
phenanthroline (BPhen) and Tris(acetylacetonato)ruthenium(III) are also used as 
EBLs.\textsuperscript{109} These are wide-gap materials with energy offsets to both the HOMO and 
LUMO levels of the acceptor. This layer serves a number of functions, the most 
important of which is to prevent damage to the acceptor layer due to cathode deposition. 
It also prevents quenching of the excitons in the acceptor layer generated near the cathode 
and allows for optimization of the optical interference pattern in the active organic layers. 
Power conversion efficiencies exceeding 3\% have been realized by optimizing the 
blocking layers used in OPVs.\textsuperscript{110}

As mentioned previously, the performance of the planar heterojunction is limited 
by the exciton diffusion bottleneck. Several device architectures have been developed to 
overcome this limitation.
2.7.3 Mixed heterojunction

Organic photovoltaic cells that contain D-A mixtures of both thermally evaporated small molecules are referred to as mixed heterojunctions.\textsuperscript{19, 20, 23, 111-113} The advantage of a mixed heterojunction over the planar heterojunction is that the large D-A interface area increases the probability of exciton dissociation. However, the use of a mixture may also increase the average distance between molecules of a particular species, potentially reducing the charge carrier mobilities relative to homogeneous layers.\textsuperscript{112} Low mobilities lead to low charge collection efficiency ultimately, limiting the performance of this type of device architecture. Laboratory values of $\eta_\text{P}>5\%$ have been reported for TAPC-C$_{70}$ mixed devices.\textsuperscript{114, 115}

A modification of the uniformly mixed OPV is the planar-mixed heterojunction. This device architecture employs a mixed layer of donor and acceptor molecules sandwiched between homogeneous donor and acceptor layers.\textsuperscript{19, 22, 111, 116-119} Using a mixed layer (~10 nm) increases the interfacial area leading to efficient exciton dissociation. However, these devices are limited by the thickness of the mixed layer which limits the overall absorption efficiency of the device. Recently, $\eta_\text{P}>10\%$ has been realized using this device architecture by Mitsubishi.

2.7.4 Bulk heterojunction

Both polymer and small-molecules have been used to create blends of donor and acceptor molecules, called bulk heterojunctions.\textsuperscript{26, 63, 120-126} Two most commonly used methods for fabricating bulk heterojunction OPVs involve phase separation during the
spin-coating of polymers or phase segregation from a D-A mixture induced by high temperature annealing of blend layers. Optimizing the combination of annealing time and annealing temperature allows for domain formation on the length scale of the $L_D$ as well as interconnected pathways for the efficient collection of dissociated charge carriers.\textsuperscript{33, 122, 127} This device design has been successful at achieving $\eta_{\text{EQE}}$ approaching 80% in the absorption range of the device and $\eta_p$ exceeding 8%.\textsuperscript{25} However, the random distribution of materials in bulk heterojunctions can lead to charge trapping in islands impeding the path of charge carriers to respective electrodes. Another drawback of using bulk heterojunction is the fact that predicting the morphology of the active layer can be difficult. Consequently, device fabrication requires significant optimization to realize high efficiency.

Computational studies have shown that ordered bulk heterojunction is the optimal morphology for OPVs.\textsuperscript{128, 129} This structure consists of pillars of donor and acceptor running perpendicular to the electrodes. The diameter and center-to-center distance of the pillars is on the order of $L_D$ leading to efficient exciton dissociation. Continuous donor and acceptor domains allow for efficient charge transport. Several attempts have been made in the past to fabricate this ordered structure.\textsuperscript{103, 123, 130}
<table>
<thead>
<tr>
<th>Device architecture</th>
<th>Schematic</th>
<th>Advantages</th>
<th>Limitations</th>
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</thead>
<tbody>
<tr>
<td>Planar heterojunction (with exciton blocking layer)</td>
<td><img src="image" alt="Schematic" /></td>
<td>High charge collection efficiency</td>
<td>Low exciton diffusion efficiency</td>
</tr>
<tr>
<td>Mixed heterojunction</td>
<td><img src="image" alt="Schematic" /></td>
<td>High exciton diffusion efficiency</td>
<td>Low charge collection efficiency</td>
</tr>
<tr>
<td>Planar-mixed heterojunction</td>
<td><img src="image" alt="Schematic" /></td>
<td>High exciton diffusion and charge collection efficiency</td>
<td>Thickness of mixed layer (&lt;10 nm)</td>
</tr>
<tr>
<td>Bulk heterojunction</td>
<td><img src="image" alt="Schematic" /></td>
<td>High exciton diffusion and charge collection efficiency</td>
<td>Possible charge trapping in islands</td>
</tr>
<tr>
<td>Ordered bulk heterojunction</td>
<td><img src="image" alt="Schematic" /></td>
<td>High exciton diffusion and charge collection efficiency</td>
<td>Difficult device fabrication</td>
</tr>
</tbody>
</table>

Each device design tries to maintain a delicate balance between exciton diffusion and charge collection efficiencies. Chapters 3, 5 and 6 of this thesis present a novel device architecture for OPVs based on continuously graded D-A heterojunction. The graded heterojunction allows the simultaneous optimization of exciton diffusion and charge collection efficiencies by tuning the concentration gradient in the active layer.
Chapter 3-Organoic photovoltaic cells based on continuously graded donor-acceptor heterojunctions of copper phthalocyanine and C$_{60}$

3.1 Introduction

As mentioned in Chapter 2, multiple approaches have been adopted to overcome the exciton diffusion bottleneck and realize efficient photoconversion in organic photovoltaic cells (OPVs). Refinements in both device design and materials selection have led to significant improvements in device performance. In particular, previous work has emphasized the importance of optimizing film morphology for realizing high power conversion efficiency (η$_P$). This Chapter presents a novel approach to engineer the morphology of the active layer through the use of continuously graded film compositions. The highly tunable gradient permits fine control over device performance, enabling improvements in efficiency.

The use of a uniformly mixed donor-acceptor (D-A) heterojunction is attractive as it permits efficient exciton diffusion by extending the dissociating interface throughout the film. However, the charge carrier mobility is typically reduced in these structures, especially in mixtures of small molecules, potentially leading to a lower charge collection efficiency. A promising alternative to the use of uniform mixtures are graded D-A heterojunctions. The initial work on graded heterojunctions in OPVs focused on the use of thin, uniformly mixed layers of varying D-A composition to simulate a gradient. In these initial investigations, there was no discussion of
gradient performance as a function of the D-A composition ratio or active layer thickness. In addition, no evidence was presented that confirms an enhancement in the charge collection efficiency relative to a uniformly mixed architecture. In order to conclusively demonstrate the merits of the graded architecture, this work utilizes a continuous, D-A concentration gradient throughout the active layer. The graded heterojunction has a larger D-A interface area than a planar heterojunction, and for an optimized composition profile, maintains a high charge collection efficiency relative to a uniform mixture. In addition, the graded heterojunction is expected to have a larger absorption efficiency than a uniform mixture of the same thickness containing the same amount of material because the red (blue) absorber donor (acceptor) material is farther away (closer) from the cathode where the interference maximum for long (short) wavelengths exists. Consequently, the graded architecture allows for significant optimization and tuning of the exciton diffusion and charge collection efficiencies through modifications of the composition profile.

3.2 Gradients of interest

Organic photovoltaic cells were fabricated on glass substrates pre-coated with a 150-nm-thick anode layer of indium-tin-oxide (ITO) having a sheet resistance of 15 Ω/□. Substrates were cleaned following the procedure described in Appendix C. In this Chapter, OPVs based on copper phthalocyanine (CuPc) and C₆₀ as the electron donating and electron accepting materials, respectively will be discussed. The organic layers in the planar and uniformly mixed heterojunctions were grown at a total rate of 0.2 nm/s. In
order to construct films with graded composition profiles, donor and acceptor deposition rates were ramped linearly with time and monitored using two quartz crystal monitors. The concentration gradients explored in this chapter are shown in Figure 3.1. The gradients of Figures 3.1a and 3.1b are henceforth referred to as “zero endpoint” (ZEP) gradients. The gradient displayed in Figure 3.1a contains overall 50 wt.% C$_{60}$, while in Figure 3.1b the gradient comprises overall 67 wt.% C$_{60}$. The ZEP (50 wt.% C$_{60}$) gradient in Figure 3.1a was constructed by varying the growth rates (R) of CuPc and C$_{60}$.

![Graphs showing composition profiles](image)

**Figure 3.1:** Composition profile in (a) a zero endpoint (ZEP) (50 wt.% C$_{60}$) gradient, (b) a ZEP (67 wt.% C$_{60}$) gradient, (c) a non-zero endpoint (NZEP) gradient, and (d) a C$_{60}$-favorable gradient. The zero of thickness is referenced at the anode/organic interface.
according to $R_{\text{CuPc}}=0.2$ nm/s$\rightarrow$0 nm/s and $R_{\text{C60}}=0$ nm/s$\rightarrow$0.2 nm/s, respectively. The gradient of Figure 3.1b was constructed by varying the growth rates according to $R_{\text{CuPc}}=0.1$ nm/s$\rightarrow$0 nm/s and $R_{\text{C60}}=0$ nm/s$\rightarrow$0.2 nm/s, respectively. The non-zero endpoint (NZEP) gradient of Figure 3.1c was constructed by varying the growth rates according to $R_{\text{CuPc}}=0.075$ nm/s$\rightarrow$0.025 nm/s and $R_{\text{C60}}=0.05$ nm/s$\rightarrow$0.15 nm/s, respectively. The NZEP gradient also comprises overall 67 wt.% C$_{60}$. A modified version of the NZEP gradient is the “C$_{60}$-favorable” gradient shown in Figure 3.1d, which maintains a composition of $\geq$50 wt.% C$_{60}$ throughout the gradient. The C$_{60}$-favorable gradient was constructed by varying the growth rates according to $R_{\text{CuPc}}=0.1$ nm/s$\rightarrow$0.033 nm/s and $R_{\text{C60}}=0.1$ nm/s$\rightarrow$0.167 nm/s, respectively. For the aforementioned gradients, the composition endpoints are kept fixed when varying the active layer thickness. This permits a constant injection barrier to be maintained at the electrode-

Figure 3.2: (a) Schematic of a sample. Circles of different colors represent atoms with different atomic numbers. $Z_{\text{blue}} > Z_{\text{green}} > Z_{\text{red}}$ where $Z$ is the atomic number of the atom. (b) Expected RBS spectra for the sample. The energy of the backscattered ions is spaced according to the atomic number of the target atom. The composition profile of the atoms is also reflected in the RBS spectra.
organic interfaces. A 10-nm-thick layer of bathocuproine (BCP) was grown on top of the active layers in all of the OPV architectures to serve as an exciton blocking layer. The organic multilayer is capped with an Al cathode which is deposited through a shadow mask defining devices 1 mm in diameter.

3.3 Characterization of the gradient

Given the use of a dry, evaporative deposition process used for fabricating graded heterojunctions, negligible molecular motion is expected to occur in these films. As such, the composition gradient present in the layer is expected to be identical to the gradient deposited. In order to confirm the existence of gradient in the active layer, the graded layer was characterized through Rutherford Backscattering (RBS). This technique involves measuring the number and energy of ions backscattered after colliding with atoms in a sample at which the beam is targeted. The elemental concentration as a function of depth can be determined based on this measurement. The high sensitivity of RBS to heavy atoms allows us to carefully track Cu atoms through the depth of the sample. Negligible beam damage is observed during this characterization.

In this technique, the incident ion beam loses energy as it penetrates through the depth of the sample. As a result, the ion which backscatters from an atom at some depth in a sample will have lower energy than a particle which backscatters from the same atom on the sample surface. The amount of energy lost on penetration depends on several factors such as the ions used, the energy of the incident ions, the atoms in the sample as well as the concentration of the atoms along the depth of the sample. This dependence of
energy loss on atoms present in the sample and its composition enables depth profiling of
the sample as shown in Figure 3.2.

In order to probe the depth profile of graded heterojunctions, a 70-nm-thick $C_{60}$-
favorable gradient was grown on a Si substrate. Alpha particles with energy of 2 MeV
were used to measure the RBS spectrum of the gradient displayed in Figure 3.3a. The
experimentally measured RBS spectrum is shown in Figure 3.3b. Figure 3.3c shows the
Cu signal in the RBS spectrum. The increasing composition of CuPc (or Cu) along the
deepth of the gradient is reflected in the measured RBS spectrum. The RBS spectrum of
the gradient was simulated using QUARK. For this purpose, the gradient was assumed to
be a multi-step mixture (Figure 3.3a). The simulated RBS spectrum shows a good
agreement with the experimentally measured spectrum confirming the existence of the
desired gradient along the depth of the layer.

![Graphs showing depth profiling results](image)

**Figure 3.3:** (a) Solid lines show the gradient grown and dashed lines are an
approximation used to simulate the RBS spectrum. (b) Experimentally measured and
simulated RBS spectra for the gradient shown in (a). The feature centered around 1500
eV corresponds to Cu whereas the signal around 500 eV corresponds to C and N. (c) Cu
signal in the RBS spectrum. RBS spectrum shows CuPc (or Cu) concentration increases
with depth as expected.
3.4 Dark current density characteristics

The dark current-voltage characteristics of an OPV can provide useful information about the electrical characteristics of the device. As such, the dark current-voltage characteristics for graded heterojunction OPVs were compared to those of conventional planar and mixed architectures (Figure 3.4). Thicknesses of the active layer used for this comparison are mentioned in Table 3.1. As discussed in Chapter 2, the dark current in an OPV is often modeled using the Shockley equation.\textsuperscript{36, 76, 135-138}

![Diagram showing dark current density-voltage characteristics for different OPV architectures](image)

Figure 3.4: Dark current density-voltage characteristics for a variety of optimized CuPc:C\textsubscript{60} OPV architectures. (a) Planar and uniformly mixed (50 wt.% C\textsubscript{60}) heterojunction OPVs. (b) Graded heterojunction OPVs with active layers consisting of either a zero endpoint (ZEP) (50 wt.% C\textsubscript{60}), ZEP (67 wt.% C\textsubscript{60}), non-zero endpoint (NZEP), or C\textsubscript{60}-favorable gradient. The active layer thickness for each device is shown in Table 1.
where $J$ is the current density, $J_s$ is the reverse-bias saturation current density, $e$ is the electron charge, $R_s$ is the series resistance, $n$ is the ideality factor, $k$ is the Boltzmann constant, and $T$ is the temperature.

The dark current density-voltage characteristics were fit using Equation 3.1, and the fit parameters are shown in Table 3.1. The ideality factor is reduced from $(1.95\pm0.02)$ for a planar heterojunction to $(1.40\pm0.02)$ for a mixed heterojunction OPV. For a ZEP (50 wt.% C$_{60}$) graded OPV, the ideality factor decreases with increasing thickness, with a value of $(1.67\pm0.01)$ realized at an optimum active layer thickness of 71 nm. As discussed in Chapter 2, these values indicate that the dark current in the planar architecture is dominated by electron-hole recombination. In the more disordered graded and mixed heterojunction OPVs, the reduced ideality factor suggests an additional contribution to the dark current from charge carrier diffusion to the opposite electrode. Lower $J_s$ values are obtained for mixed and graded OPVs compared to a planar heterojunction OPV due to a reduction in the charge carrier mobilities as a result of molecular intermixing. The $J_s$ value is also observed to decrease from $(1.9\pm0.4)x10^{-7}$ A/cm$^2$ to $(6.0\pm1.3)x10^{-9}$ A/cm$^2$ as the thickness increases from 29 nm to 71 nm, suggesting that the charge collection efficiency could be reduced for thick active layers. Similar trends in $J_s$ are also observed for the other graded and mixed heterojunction OPVs studied in this work. Comparable $R_s$ values are obtained for the various device architectures suggesting that for these thicknesses, $R_s$ may be determined by the energetic barrier at the anode-organic interface.
Table 3.1: Dark current characteristics for various device architectures

<table>
<thead>
<tr>
<th>Structure</th>
<th>Thickness (nm)</th>
<th>n</th>
<th>( J_s ) (A/cm²)</th>
<th>( R_s ) (Ωcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar (20 nm CuPc/40 nm C\textsubscript{60})</td>
<td>60</td>
<td>1.95</td>
<td>5.0x10^{-7}</td>
<td>1.02</td>
</tr>
<tr>
<td>Mixed (50 wt.% C\textsubscript{60})</td>
<td>59</td>
<td>1.56</td>
<td>2.0x10^{-8}</td>
<td>0.96</td>
</tr>
<tr>
<td>ZEP (50 wt.% C\textsubscript{60})</td>
<td>29</td>
<td>1.87</td>
<td>1.9x10^{-7}</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.70</td>
<td>3.0x10^{-8}</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>1.67</td>
<td>6.0x10^{-9}</td>
<td>1.52</td>
</tr>
<tr>
<td>ZEP (67 wt.% C\textsubscript{60})</td>
<td>60</td>
<td>1.47</td>
<td>4.8x10^{-9}</td>
<td>0.57</td>
</tr>
<tr>
<td>NZEP</td>
<td>69</td>
<td>1.51</td>
<td>6.8x10^{-9}</td>
<td>0.93</td>
</tr>
<tr>
<td>C\textsubscript{60}-favorable</td>
<td>73</td>
<td>1.54</td>
<td>8.8x10^{-9}</td>
<td>1.24</td>
</tr>
</tbody>
</table>

3.5 Impact of gradient on device performance

In order to examine the effect of concentration gradient on device performance, OPVs containing ZEP (50 wt.% C\textsubscript{60}), ZEP (67 wt.% C\textsubscript{60}) and NZEP graded heterojunctions were fabricated with varying active layer thickness. Thickness is an important design parameter in OPVs because it determines the optimum balance between light absorption and charge collection. Figure 3.5 shows operating parameters for these devices under simulated AM1.5G solar illumination at 100 mW/cm\textsuperscript{2}. The fill factor (FF) for all three gradients decreases with increasing thickness (Figure 3.5a), reflecting a reduction in the charge collection efficiency, which is further supported by the observed reduction in \( J_s \). The FF increases significantly in moving from ZEP (50 wt.% C\textsubscript{60}) to ZEP (67 wt.% C\textsubscript{60}). The increase in the FF upon increasing the C\textsubscript{60} composition indicates that the charge collection is initially limited by electron transport.\textsuperscript{140} This observation is further supported by the increase in FF observed for the NZEP gradient which contains 67 wt.% C\textsubscript{60}. The short-circuit current density (\( J_{SC} \)) initially increases with thickness for all three gradients as a result of increasing optical absorption (Figure 3.5b).\textsuperscript{24} The \( J_{SC} \)
values are lower for the ZEP architectures relative to the NZEP architecture. The low $J_{SC}$ values observed for the ZEP architectures result from a low exciton diffusion efficiency at the edges of the gradient. The exciton diffusion efficiency is improved by adjusting the ZEP gradient to the NZEP architecture, increasing the D-A interface area near the anode/gradient and gradient/BCP interfaces. The improvement in the exciton diffusion efficiency for the NZEP gradient results in an increase in the $J_{SC}$ relative to the ZEP gradients. The open-circuit voltage ($V_{OC}$) does not depend strongly on gradient type (Figure 3.5c). The $V_{OC}$ in general increases with thickness as a result of increased

![Graphs showing the variation of FF, JSC, VOC, and ηP with active layer thickness for different architectures.](image)

Figure 3.5: The (a) fill factor (FF), (b) short-circuit current density ($J_{SC}$), (c) open-circuit voltage ($V_{OC}$), and (d) power conversion efficiency ($\eta_p$) for devices containing zero endpoint (ZEP) (50 wt.% C$_{60}$), ZEP (67 wt.% C$_{60}$), and non-zero endpoint (NZEP) graded composition profiles under simulated AM1.5G illumination at 100 mW/cm$^2$ as a function of active layer thickness.
photocurrent and reduced dark current with increasing active layer thickness. The large $J_{SC}$ and FF values obtained for the NZEP gradient led to the highest power conversion efficiency ($\eta_P$) of $(2.0\pm0.1)\%$ being observed for this gradient (Figure 3.5d).

The relative absorption and the external quantum efficiency ($\eta_{EQE}$) spectra of these different types of graded OPVs were compared. The active layer thicknesses for the optimum ZEP (50 wt.% C$_{60}$), ZEP (67 wt.% C$_{60}$) and NZEP graded OPVs are 67 nm, 72 nm and 69 nm, respectively. The relative absorption efficiency for each OPV was estimated by measuring normal incidence device transmissivity and reflectivity (R) at an angle of $15^\circ$ from normal. Since transmissivity through the opaque metal cathode is

![Graph](image_url)

Figure 3.6: (a) Relative absorption efficiency (100-Reflectivity)% and (b) external quantum efficiency ($\eta_{EQE}$) spectra for graded heterojunction OPVs with active layers consisting of either a zero endpoint (ZEP) (50 wt.% C$_{60}$) (67 nm), a ZEP (67 wt.% C$_{60}$) (72 nm), or a non-zero endpoint (NZEP) gradient (69 nm).
approximately $10^{-4}$, the relative absorption efficiency can be approximated as $100-R\,\%$. It is important to note that while useful for comparisons of the relative absorption efficiency, this technique is not suitable for the calculation of the absolute absorption efficiency as it also includes absorption in the anode and cathode layers.\textsuperscript{142} In all cases, the photoresponse occurring at wavelengths $\lambda \geq 525$ nm originates from absorption in CuPc (Figure 3.6). The response observed at shorter wavelengths corresponds mainly to absorption in C\textsubscript{60}. The ZEP (50 wt.% C\textsubscript{60}) gradient contains more CuPc than ZEP (67 wt.% C\textsubscript{60}) and NZEP gradient which is reflected in the absorption data. Even though the absorption efficiency of CuPc in the ZEP (67 wt.% C\textsubscript{60}) gradient is lower than the ZEP (50 wt.% C\textsubscript{60}) gradient, they both show a comparable response from CuPc in the $\eta_{\text{EQE}}$. This suggests an increase in the internal quantum efficiency of excitons created on CuPc in moving from a ZEP (50 wt.% C\textsubscript{60}) to a ZEP (67 wt.% C\textsubscript{60}) gradient. The use of NZEP gradient increases the exciton diffusion efficiency and hence, realizes even larger $\eta_{\text{EQE}}$ than the corresponding ZEP (67 wt.% C\textsubscript{60}) gradient. However, the NZEP architecture shows a low C\textsubscript{60} response. The low $\eta_{\text{EQE}}$ observed for C\textsubscript{60} in the NZEP graded device suggests that the internal quantum efficiency for C\textsubscript{60} is not optimized in this gradient.

3.6 Further gradient optimization

As mentioned previously, charge collection in CuPc:C\textsubscript{60} gradients is limited by electron transport. Further improvements in device performance were realized by addressing this specific deficiency. Previous work examining the carrier mobility in uniform mixtures of CuPc and C\textsubscript{60} has shown that the electron mobility in C\textsubscript{60} decreases
if it comprises less than 50 wt.% of the mixture. As such, the NZEP gradient was modified to ensure that the C$_{60}$ component of the gradient remains ≥50 wt.% throughout the film. The composition profile of this C$_{60}$-favorable gradient is shown in Figure 3.1d.

Figure 3.7: The (a) short-circuit current density ($J_{SC}$), (b) fill factor (FF), (c) open-circuit voltage ($V_{OC}$), and (d) power conversion efficiency ($\eta_p$) for devices containing a mixed heterojunction with either 50 wt.% C$_{60}$ or 67 wt.% C$_{60}$, and a C$_{60}$-favorable graded heterojunction under simulated AM1.5G illumination at 100 mW/cm$^2$ as a function of active layer thickness.

Previous studies have shown that optimum performance in mixed heterojunctions based on CuPc:C$_{60}$ is realized at a composition of ~50 wt.% C$_{60}$. Uniformly mixed OPVs containing 50 wt.% C$_{60}$ and 67 wt.% C$_{60}$ were fabricated to compare with the performance of the optimized C$_{60}$-favorable gradient. The OPV parameters for these different architectures as a function of active layer thickness under simulated AM1.5G
solar illumination at 100 mW/cm$^2$ are displayed in Figure 3.7. At an optimum layer thickness of 71 nm, the highest $J_{SC}$ is realized with the C$_{60}$-favorable gradient while the $J_{SC}$ values for mixed devices comprising 67 wt.% C$_{60}$ were lowest (Figure 3.7a). The C$_{60}$-favorable gradient shows the largest $J_{SC}$ implying that this gradient has optimized exciton diffusion and charge collection efficiencies relative to both uniformly mixed architectures. While the FF for mixed heterojunction OPVs containing 50 wt.% C$_{60}$ decreases steeply with increasing active layer thickness, the FFs for the mixed OPVs comprising 67 wt.% C$_{60}$ and C$_{60}$-favorable graded heterojunction OPVs show a much weaker dependence on active layer thickness (Figure 3.7b). The large FF observed for the C$_{60}$-favorable gradient relative to the mixed heterojunction containing 67 wt.% C$_{60}$ confirms that the FF is impacted favorably by the graded composition of the active layer. In addition, the large FF observed at high thickness for the C$_{60}$-favorable gradient relative to the mixed heterojunction containing 50 wt.% C$_{60}$ suggests that the charge transport is significantly improved in graded OPVs with thick active layers. The $V_{OC}$ increases with thickness, as noted previously (Figure 3.7c). These parameters lead to an $\eta_P$ of (2.1±0.1)% for the C$_{60}$-favorable gradient at a thickness of 71 nm and (1.8±0.1)% for the mixed (50 wt.% C$_{60}$) heterojunction at a thickness of 73 nm (Figure 3.7d). The improvement in $\eta_P$ at small thicknesses originates from an increase in the $J_{SC}$, and the improvement at large thicknesses is a result of increased FF.

3.7 Comparison with conventional architectures

In order to highlight the merits of the graded architecture, the performance of
optimized C\textsubscript{60}-favorable graded OPV was compared with optimized planar and mixed (50 wt.% C\textsubscript{60}) heterojunction OPVs. The operating parameters for the optimized OPVs are presented in Figure 3.8 as a function of illumination intensity. The responsivity for all three device architectures decreases with illumination intensity due to a reduction in the charge collection efficiency (Figure 3.8a). The peak responsivity for the C\textsubscript{60}-favorable gradient is (117±6) mA/W at low illumination intensity and decreases to (95±5) mA/W at 100 mW/cm\textsuperscript{2}. The V\textsubscript{OC} increases linearly with the logarithm of illumination intensity for all three devices (Figure 3.8b). The slope of V\textsubscript{OC} versus illumination intensity varies

![Graphs](image)

**Figure 3.8:** The (a) responsivity, (b) open-circuit voltage (V\textsubscript{OC}), (c) fill factor (FF) and (d) power conversion efficiency (\(\eta\textsubscript{P}\)) for CuPc:C\textsubscript{60} OPVs with planar (20 nm CuPc/40 nm C\textsubscript{60}), mixed (50 wt.% C\textsubscript{60}) (73 nm), or C\textsubscript{60}-favorable graded (71 nm) architectures as a function of illumination intensity.
depending on the device architecture, reflecting a difference in the ideality factor.\textsuperscript{113} The disordered graded and mixed heterojunctions have lower fill factors relative to the planar heterojunction due to a reduction in the charge collection efficiency (Figure 3.8c). However, the reduction in FF is more than offset by an increase in responsivity for the C\textsubscript{60}-favorable gradient, resulting in the highest $\eta_P$ being observed for this architecture (Figure 3.8d). Overall, a peak $\eta_P$ of (2.5±0.1)\% is obtained for the C\textsubscript{60}-favorable architecture at 13.5 mW/cm\textsuperscript{2}, falling to (2.1±0.1)\% at 100 mW/cm\textsuperscript{2}, compared to (1.8±0.1)\% for a uniformly mixed device, and (1.4±0.1)\% for a planar device. The operating parameters obtained for planar and uniformly mixed OPVs are consistent with those published elsewhere for comparable active materials and device architectures.\textsuperscript{19, 24, 144-146}

Figure 3.9 compares the spectral response of optimized planar, mixed (50 wt.\% C\textsubscript{60}), and C\textsubscript{60}-favorable graded OPVs. The use of graded and mixed heterojunctions leads to a significant enhancement in the response from CuPc relative to a planar device due to the short exciton diffusion length in this material.\textsuperscript{12} An increase in the $\eta_{EQE}$ is realized by using the C\textsubscript{60}-favorable gradient, which relative to the NZEP gradient has optimized exciton diffusion and charge collection efficiencies for both active materials. Compared to a uniformly mixed OPV, the C\textsubscript{60}-favorable gradient shows a ~15% increase in the CuPc response at $\lambda$~620 nm. Since C\textsubscript{60}-favorable gradient contains less CuPc, this improvement implies that the C\textsubscript{60}-favorable architecture has a larger internal quantum efficiency for excitons generated on CuPc than the uniformly mixed OPV. Given the high diffusion efficiency characteristic of a mixture, this result also indicates that the charge collection efficiency is larger in the C\textsubscript{60}-favorable gradient than in a uniform mixture.
3.8 Conclusions

The impact of various continuously graded D-A heterojunctions on the performance of OPVs was examined in this Chapter. The existence of a gradient in the active layer is confirmed through RBS. The ZEP gradients at optimum active layer thickness show a higher \( \eta_P \) than optimized planar heterojunction. However, these are less efficient than mixed heterojunctions due to lower overall exciton diffusion efficiency in this architecture. This was overcome by modifying the endpoints of the gradient to non-zero acceptor (donor) concentration adjacent to ITO (BCP). An increase in the exciton diffusion efficiency combined with high charge collection efficiency allows the NZEP and \( C_{60} \)-favorable gradients to realize a higher \( \eta_P \) than the optimized mixed
heterojunctions. In spite of the same amount of CuPc and C_{60} present in the C_{60}-favorable gradient and mixed (67 wt.% C_{60}) OPVs, the gradient has a significantly higher device performance. This shows that the performance of OPVs is determined by the spatial distribution of donor and acceptor molecules in the active layer and not merely the overall D:A composition.

This work shows conclusively that the large D-A interface area in a gradient increases the exciton diffusion efficiency relative to a planar heterojunction. In addition, the graded heterojunction improves charge transport relative to a uniformly mixed OPV. This is reflected in the higher $\eta_{\text{EQE}}$ response for CuPc from the C_{60}-favorable gradient and ~20% higher FF for C_{60}-favorable gradient at large thicknesses than that of a uniformly mixed (50 wt.% C_{60}) heterojunction. The use of gradients is a general technique and can be applied to any D-A system. Ultimately, the true potential of this approach to OPV design is the ability to tune the exciton diffusion and charge collection efficiencies based on the choice of D-A concentration gradient in order to maximize overall efficiency.
Chapter 4-Efficient organic photovoltaic cells based on nanocrystalline mixtures of boron subphthalocyanine chloride and C$_{60}$

4.1 Introduction

A key limitation for realizing high efficiency in OPVs based on CuPc:C$_{60}$ discussed in Chapter 3 is the low open-circuit voltage ($V_{OC}$) attainable with this donor-acceptor (D-A) pairing. One way to overcome this limitation is to use a donor material such as boron subphthalocyanine chloride (SubPc) with a deeper highest occupied molecular orbital (HOMO) energy level than CuPc.$^{145}$ Recently, the D-A pairing of SubPc and C$_{60}$ has received significant attention due to demonstrations of high $V_{OC}$ and power conversion efficiencies.$^{133, 145, 147, 148}$ However, SubPc has a short exciton diffusion length ($L_D$) (~10.7 nm) which is significantly smaller than the optical absorption length (~100 nm).$^{67, 68}$ The short $L_D$ can limit the fraction of photogenerated carriers that reach the dissociating D-A interface and contribute to photocurrent. One way to overcome this limitation is to use uniform mixtures of SubPc and C$_{60}$ so that the dissociating interface lies within $L_D$ of every photogenerated exciton. This arrangement permits efficient exciton dissociation throughout the active layer.$^{20, 111, 117, 140}$ While an increase in the area of the dissociating interface may enhance the exciton diffusion efficiency, the use of a mixture can also increase the average separation between molecules of a particular species, potentially reducing the charge carrier mobilities.$^{112}$ A reduction in the electron and hole mobilities can hinder charge collection and limit the overall performance of a
uniformly mixed OPV.\textsuperscript{112, 131} Therefore, the exciton diffusion and charge collection efficiencies must be simultaneously optimized in order to realize high efficiency. This Chapter seeks to correlate the structural\textsuperscript{*} and electrical properties of uniformly mixed films of SubPc and C\textsubscript{60}. Film morphology and device performance are observed to vary significantly with the D-A composition of the mixed film. Even more interesting however is the observation of optimum efficiency in OPVs that are very C\textsubscript{60}-rich in composition.

### 4.2 Performance of devices based on SubPc:C\textsubscript{60} mixtures

Organic photovoltaic cells were fabricated on glass substrates pre-coated with a 150-nm-thick anode layer of indium-tin-oxide (ITO) having a sheet resistance of 15 Ω/□. Substrates were cleaned based on the procedure described in Appendix C. The device structures studied in this work are shown in Figure 4.1. The active layer of the optimized planar architecture consists of 13 nm SubPc/35 nm C\textsubscript{60}, while the optimized mixture contains a 64-nm-thick layer of SubPc:C\textsubscript{60} (80 wt.% C\textsubscript{60}). A 10-nm-thick layer of

![Device structure for optimized devices](image)

Figure 4.1: Device structure for optimized (a) planar heterojunction with an MoO\textsubscript{3} interlayer (b) mixed heterojunction and (c) mixed heterojunction with an MoO\textsubscript{3} interlayer.

\textsuperscript{*}TEM characterization and analysis was performed by A. A. Gunawan and Dr. K. A. Mkhoyan

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bathocuproine (BCP) was used in all the OPV cells to prevent exciton quenching at the cathode and block holes that leak through the active layer. An Al cathode was deposited through a shadow mask to define an active area that is 1 mm in diameter. The current density-voltage characteristics for planar and mixed heterojunction OPVs were compared both in the dark and under simulated AM1.5G solar illumination (134 mW/cm²). As shown in Figure 4.2a, the mixed device without a MoO₃ layer has the largest dark current density. This is possibly due to the leakage of electrons across the active layer to ITO. A 10-nm-thick layer of MoO₃ was incorporated next to the ITO anode in all OPV cells. The inclusion of an MoO₃ interlayer between the active layer and ITO reduces electron leakage and hence, the dark current. As a result of lower dark current, the mixed device with a MoO₃ blocking layer has a larger V₉ₒc compared to the device without an interlayer. Under illumination, the mixed OPVs show comparable values of the short-circuit current density (Jₛₜₜ) which is significantly higher than planar cell.

A series of mixed OPVs containing either 50 wt.% C₆₀, 80 wt.% C₆₀ or 90 wt.% C₆₀ were fabricated with varying active layer thickness to determine the optimum composition and thickness. The operating parameters of these mixed OPVs under simulated AM1.5G solar illumination at 100 mW/cm² are displayed as a function of the mixture thickness in Figure 4.3. The fill factor (FF) for all three mixed heterojunction OPVs decreases with increasing active layer thickness possibly due to a reduction in the charge collection efficiency. The C₆₀-rich mixtures show a significantly larger FF compared to OPVs containing 50 wt.% C₆₀. The FF for the 80 wt.% C₆₀ mixture is the
largest over all thicknesses, suggesting improved charge transport relative to other mixtures. The $J_{\text{SC}}$ increases with thickness as a result of increasing optical absorption and decreases at high thicknesses due to a reduction in the charge collection efficiency and a saturation of the absorption efficiency.\textsuperscript{92} The $V_{\text{OC}}$ does not show a strong dependence on the D-A composition ratio or on the active layer thickness. This is due to the use of electron and hole blocking layers of MoO$_3$ and BCP, respectively, which ensure a low dark current over all mixture compositions. The high FF and $J_{\text{SC}}$ of mixed OPVs

![Graph](image)

Figure 4.2: Current density-voltage characteristics in (a) dark and (b) under simulated AM1.5G solar illumination at 134 mW/cm$^2$ for a planar heterojunction OPV (13 nm SubPc/35 nm C$_{60}$) with an MoO$_3$ interlayer and mixed heterojunction OPVs (64 nm 80 wt.% C$_{60}$) both with and without an MoO$_3$ interlayer.
containing 80 wt.% C₆₀ leads to a peak power conversion efficiency (ηₚ) of (3.7±0.1)% at an active layer thickness of 64 nm. Relative to a planar heterojunction, this optimum mixture shows a higher exciton diffusion efficiency due to larger D-A interface area leading to a ~75% increase in the J_{SC} as shown in Table 4.1. In contrast, the planar heterojunction shows a significantly higher FF compared to the mixed OPVs. This is attributed to a reduced charge collection efficiency in the mixed heterojunction under forward bias. Overall, an increase in the exciton diffusion efficiency in an optimized

![Graphs showing photovoltaic operating parameters for mixed SubPc:C₆₀ OPVs.]

Figure 4.3: Photovoltaic operating parameters for mixed SubPc:C₆₀ OPVs containing 50 wt.% C₆₀, 80 wt.% C₆₀, and 90 wt.% C₆₀ at 100 mW/cm² as a function of mixture thickness. (a) Fill factor (FF), (b) short-circuit current density (J_{SC}), (c) open-circuit voltage (V_{OC}), and (d) power conversion efficiency (ηₚ).
mixed heterojunction OPV more than offsets the reduction in charge collection efficiency leading to a ~20% increase in the $\eta_P$ compared to an optimized planar heterojunction OPV.

Table 4.1: Operating device parameters for optimized planar and mixed heterojunction

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta_P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>4.50</td>
<td>1.08</td>
<td>0.62</td>
<td>3.05</td>
</tr>
<tr>
<td>Mixed (50 wt.% C$_{60}$)</td>
<td>4.30</td>
<td>0.95</td>
<td>0.38</td>
<td>1.55</td>
</tr>
<tr>
<td>Mixed (80 wt.% C$_{60}$)</td>
<td>7.90</td>
<td>1.07</td>
<td>0.44</td>
<td>3.70</td>
</tr>
<tr>
<td>Mixed (90 wt.% C$_{60}$)</td>
<td>7.10</td>
<td>1.10</td>
<td>0.44</td>
<td>3.44</td>
</tr>
</tbody>
</table>

The absorption spectra of neat SubPc and C$_{60}$ are expected to change as a function of the mixing composition. Absorption spectra for a variety of films grown on glass substrates were measured using a OLIS Cary-14 spectrophotometer. The normalized absorption spectra for a neat film of SubPc and mixtures of SubPc:C$_{60}$ containing either 50 wt.% C$_{60}$, 80 wt.% C$_{60}$ and 90 wt.% C$_{60}$ are shown in Figure 4.4a. Interestingly, a long wavelength tail extending from 650 to 750 nm is observed in the absorption spectra of the mixed films. A similar feature in the near-infrared has been previously attributed to charge-transfer state absorption in mixtures of zinc phthalocyanine and C$_{60}$.

In order to compare the relative contribution of SubPc and C$_{60}$ to $J_{SC}$ in different device architectures, the external quantum efficiency ($\eta_{EQE}$) of optimized planar and mixed OPVs was measured (Figure 4.4b). The optimum active layer thicknesses for mixtures containing 50 wt.% C$_{60}$, 80 wt.% C$_{60}$ and 90 wt.% C$_{60}$ are 62 nm, 64 nm and 57 nm, respectively. The photoresponse occurring at short wavelengths originates mainly from C$_{60}$ while the response at $\lambda \geq 500$ nm corresponds to absorption in SubPc. The long
L_D of C_60 likely leads to a high exciton diffusion efficiency for excitons created on C_60 for all three compositions.^{12, 17} Improved charge transport combined with an increase in the absorption efficiency of C_60 in moving from 50 wt.% C_60 to 90 wt.% C_60 leads to increased C_60 response in the η_EQE. Even though the absorption efficiency of SubPc in a mixture containing 80 wt.% C_60 is significantly lower than that of a mixture containing 50 wt.% C_60, the mixture containing 80 wt.% C_60 shows the largest response from SubPc in the η_EQE. This reflects an improvement in the charge collection efficiency for mixed films

![Normalized Absorption Spectrum and η_EQE](image)

Figure 4.4: (a) Normalized absorption spectra for neat SubPc and mixtures of SubPc:C_60 as a function of composition. (b) External quantum efficiency (η_EQE) spectra for a planar heterojunction OPV (13 nm SubPc/35 nm C_60) and mixed SubPc:C_60 OPVs with active layers containing (thickness) 50 wt.% C_60 (62 nm), 80 wt.% C_60 (64 nm), or 90 wt.% C_60 (57 nm).
containing 80 wt.% C₆₀, and also suggests that the internal quantum efficiency is maximized for excitons created on SubPc. High SubPc and C₆₀ peaks in the η_{EQE} for mixed cells containing 80 wt.% C₆₀ lead to the highest J_{SC} at this composition. The η_{EQE} of all three mixed OPVs shows the same long wavelength tail observed in Figure 4.4a as a result of charge-transfer state absorption.

4.3 Charge transport in mixtures of SubPc:C₆₀

The peak in J_{SC} and FF in mixed films comprising 80 wt.% C₆₀ suggest optimum charge transport at this composition. Charge transport properties of uniform mixtures depend in part on the mobility of charge carriers in the mixture. In order to determine the trend in charge transport as a function of composition, single carrier devices were examined to extract the electron and hole mobilities. The current density-voltage characteristics for uniformly mixed electron- and hole-only devices were analyzed using a model of space-charge-limited current (SCLC).¹⁵¹⁻¹⁵³ In the absence of traps, the space-charge-limited current density (J) can be written as a function of the applied voltage (V) as:

\[ J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3} \]  

(4.1)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the relative dielectric constant of the organic thin film, \( \mu \) is the charge carrier mobility, and \( d \) is the organic film thickness. In this work, the relative dielectric constant is approximated as \( \varepsilon = 4 \).
As discussed extensively in Chapter 2, the charge carrier mobility often exhibits a Poole-Frenkel dependence on the electric field in organic semiconductors.\(^46, 47\) This functional dependence is attributed to a random variation in hopping site energies for disordered organic semiconductors, leading to energetic barriers for carrier transport that are overcome with an applied voltage.\(^48, 49\) In this case, the mobility can be expressed as:

\[
\mu(E) = \mu_0 \exp\left[\gamma(E)^{1/2}\right]
\]  
(4.2)

where \(\mu_0\) is the zero-field mobility, \(E\) is the electric field and \(\gamma\) is the field activation parameter. Equation 4.1 is combined with equation 4.2 in order to extract both the zero-field mobility and field activation parameter from single-carrier current density-voltage characteristics. Current density-voltage characteristics for electron- and hole-only devices with a variety of mixture compositions were measured for organic film thicknesses of 150 nm, 200 nm and 250 nm. The values of the extracted mobility and field activation parameter are as follows:

- SubPc: C\(_{60}\):
  - Electron transport along the lowest unoccupied molecular orbital (LUMO) energy level of C\(_{60}\).
  - Hole transport along the highest occupied molecular orbital (HOMO) energy level of SubPc.

\begin{align*}
\text{(a) electron transport} & : 3.6 \text{ eV} \\
\text{SubPc: C}_{60} & : 4.5 \text{ eV} \\
\text{ITO} & : 5.6 \text{ eV} \\
\text{(b) hole transport} & : 3.6 \text{ eV} \\
\text{SubPc: C}_{60} & : 4.5 \text{ eV} \\
\text{ITO} & : 5.6 \text{ eV} \\
\text{(c) hole-only device} & : 3.6 \text{ eV} \\
\text{SubPc: C}_{60} & : 4.5 \text{ eV} \\
\text{Au} & : 5.6 \text{ eV}
\end{align*}

Figure 4.5: Molecular orbital energy level diagram for a SubPc:C\(_{60}\) mixture showing (a) electron transport along the lowest unoccupied molecular orbital (LUMO) energy level of C\(_{60}\), (b) hole transport along the highest occupied molecular orbital (HOMO) energy level of SubPc and (c) hole-only device with a 15-nm-thick layer of C\(_{60}\).
parameter for each thickness were found to be within experimental error, confirming that the measured properties reflect the bulk behavior of the film.

4.3.1 Electron transport

Electron-only devices were fabricated to characterize electron transport in the mixture along molecules of C\textsubscript{60}. These devices used an electron-injecting contact
consisting of LiF/Al, and an electron-collecting contact of Al. The molecular orbital energy level diagram for electron-only device is shown in Figure 4.5a. It was observed that the electron current density using a LiF/Al cathode was almost three orders of magnitude larger than that obtained using an Al cathode, consistent with previous work on similar systems. Figure 4.6a shows fits to the electron-only current density-voltage characteristics using Equations 4.1 and 4.2, with the corresponding fit parameters for various mixture compositions shown in Table 4.2. For a neat film of C_{60}, a zero-field
electron mobility of $\mu_0=(3.3\pm0.2)\times10^{-2}$ cm$^2$/Vs is extracted, which is in close agreement with values reported previously.$^{112}$ This high mobility is maintained to a composition of 80 wt.% C$_{60}$ and decreases with a further reduction in the C$_{60}$ composition (Figure 4.7). The distance between C$_{60}$ molecules is likely increased upon dilution with SubPc leading to a reduction in the electron mobility for mixtures containing <80 wt.% C$_{60}$.

4.3.2 Hole transport

Hole transport along molecules of SubPc was characterized using hole-injecting and -collecting electrodes of ITO and Au, respectively (Figure 4.5b). The hole mobilities in neat films of SubPc and C$_{60}$ were separately measured to be $\mu_0=(4.5\pm2.3)\times10^{-8}$ cm$^2$/Vs

![Figure 4.8](image-url)  
Figure 4.8: Current density-voltage characteristics for hole-only devices comprising 80 wt.% C$_{60}$ with and without a 15-nm-thick C$_{60}$ blocking layer. The current density reduces significantly in the presence of a C$_{60}$ blocking layer eliminating the possibility of hole transport along C$_{60}$ molecules.
and \( \mu_0 = (2.8 \pm 1.4) \times 10^{-7} \text{ cm}^2/\text{Vs} \), respectively. The measured value for \( C_{60} \) is in good agreement with those previously reported in the literature.\(^{143}\) Interestingly, the hole mobility extracted for mixtures of SubPc:C\(_{60}\) is observed to increase by two orders of magnitude on increasing the C\(_{60}\) composition from 0 wt.% to 80 wt.%, and decreases with a further increase in the C\(_{60}\) concentration (Figure 4.7). Similar behavior has been previously observed in blends of a conjugated polymer donor and fullerene acceptor.\(^{152,153}\) In polymer blends, this increase is usually attributed to hole transport along the acceptor species or, is the result of improved molecular packing of the donor species upon addition of the fullerene acceptor. In this work, the potential for hole transport along molecules of C\(_{60}\) was ruled out by comparing the current density-voltage characteristics of a hole-only device containing a uniformly mixed film of SubPc:C\(_{60}\) with those of a hole-only device that also contained a 15-nm-thick hole-blocking layer of C\(_{60}\) between the mixed layer and the hole-collecting Au electrode (Figure 4.5c). For devices containing a C\(_{60}\) blocking layer, the current density is reduced substantially, confirming that hole transport in the mixture occurs along molecules of SubPc (Figure 4.8). In addition, hole-only devices were also fabricated with an MoO\(_3\) interlayer between ITO anode and mixed layer. Hole mobility values measured with and without a MoO\(_3\) interlayer were within experimental error, providing further evidence of bulk limited transport in single-carrier devices (Figure 4.7).
Table 4.2: Parameters extracted from mixed SubPc:C₆₀ single carrier devices

<table>
<thead>
<tr>
<th>Composition (% C₆₀)</th>
<th>Electron</th>
<th>Hole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ₀ (cm²/Vs)</td>
<td>γ (cm/V)¹/²</td>
</tr>
<tr>
<td>0 (100% SubPc)</td>
<td>5.2x10⁻¹⁰</td>
<td>1.2x10⁻³</td>
</tr>
<tr>
<td>10</td>
<td>5.7x10⁻¹⁰</td>
<td>5.3x10⁻³</td>
</tr>
<tr>
<td>30</td>
<td>1.9x10⁻⁶</td>
<td>1.0x10⁻³</td>
</tr>
<tr>
<td>50</td>
<td>1.5x10⁻⁶</td>
<td>2.9x10⁻³</td>
</tr>
<tr>
<td>80</td>
<td>1.1x10⁻²</td>
<td>4.2x10⁻³</td>
</tr>
<tr>
<td>90</td>
<td>1.5x10⁻²</td>
<td>4.6x10⁻³</td>
</tr>
<tr>
<td>100</td>
<td>3.3x10⁻²</td>
<td>2.4x10⁻³</td>
</tr>
</tbody>
</table>

4.4 Film morphology in mixtures of SubPc:C₆₀

Since hole transport in mixtures of SubPc:C₆₀ occurs along molecules of SubPc, the increase in hole mobility on diluting SubPc with 80 wt.% C₆₀ suggests some change in nanoscale morphology of mixtures.

4.4.1 Characterization by X-Ray Diffraction

In order to characterize the morphology of neat and mixed layers of C₆₀ and SubPc, X-ray diffraction (XRD) spectra were collected from 100-nm-thick organic films grown on a Si (111) substrate covered with native oxide. The measurements were performed using a microdiffractometer in the θ-2θ geometry using Cu Kα radiation (λ=1.54 Å). Figure 4.9 shows diffraction spectra obtained for neat films of C₆₀ and SubPc, as well as for mixtures of varying composition. For a neat film of C₆₀, peaks are observed at diffraction angles of 2θ=(10.7±0.1)°, (17.6±0.1)° and (20.7±0.1)°. These correspond to crystal lattice d-spacings of (8.3±0.1) Å, (5.0±0.1) Å and (4.3±0.1) Å and the (111), (220) and (311) planes of C₆₀.¹⁴⁶,¹⁵⁴ Diffraction peaks are indexed according to
the face-centered cubic (FCC) structure of C\textsubscript{60} with a lattice spacing of 14.17 Å. In contrast, a neat film of SubPc shows no diffraction peaks indicating that the film is amorphous, as noted in previous reports using similar growth conditions\textsuperscript{147, 155}. The C\textsubscript{60} peaks in XRD are observed to weaken in intensity upon adding SubPc, and are barely resolved in a mixed film containing 90 wt.% C\textsubscript{60}. Mixed films with 50 wt.% C\textsubscript{60} and 80 wt.% C\textsubscript{60} do not show evidence of substantial crystallinity for SubPc or C\textsubscript{60} in XRD.

![X-ray diffraction spectra](image)

**Figure 4.9:** X-ray diffraction spectra for neat films of C\textsubscript{60} and SubPc, as well as for mixtures of SubPc:C\textsubscript{60} with varying composition. Also shown is the X-ray diffraction spectrum for the Si wafer substrate. All spectra are measured in the θ-2θ geometry with Cu K\textsubscript{α} radiation. All organic layers are 100 nm thick. The raw data has been offset for clarity.
4.4.2 Characterization by Transmission Electron Microscopy

While XRD is the most commonly used technique to determine the crystallinity of organic semiconductor thin films, substantial additional insight into the nanoscale morphology can be obtained using transmission electron microscopy (TEM).\textsuperscript{124, 146} A

![High resolution TEM image (top view) for thin films containing (a) neat C\textsubscript{60}, (b) 90 wt.% C\textsubscript{60} (10 wt.% SubPc), (c) 80 wt.% C\textsubscript{60}, and (d) 50 wt.% C\textsubscript{60}. The inset figures show fast-Fourier transforms of the selected region of the corresponding image.]

Figure 4.10: High resolution TEM image (top view) for thin films containing (a) neat C\textsubscript{60}, (b) 90 wt.% C\textsubscript{60} (10 wt.% SubPc), (c) 80 wt.% C\textsubscript{60}, and (d) 50 wt.% C\textsubscript{60}. The inset figures show fast-Fourier transforms of the selected region of the corresponding image.
series of TEM images (top view) for a neat film of C\textsubscript{60}, as well as mixed films containing 90 wt.% C\textsubscript{60}, 80 wt.% C\textsubscript{60} and 50 wt.% C\textsubscript{60} were collected to further characterize the distribution of crystalline and amorphous regions (Figure 4.10). The microscope is an FEI Tecnai G2 F30 (S)TEM at the University of Minnesota, operated at 200 kV.\textsuperscript{156} Rigorous TEM imaging was carried out both on Si (single crystal) substrates and lacey carbon grids (amorphous). Similar morphology was observed in both cases suggesting film morphology is independent of the underlying substrate. All images were filtered to enhance visibility. A neat film of C\textsubscript{60} (Figure 4.10a) exhibits a substantially crystalline network embedded in an otherwise amorphous matrix. The appearance of bright spots in the fast-Fourier transform (FFT) of a 8x8 nm\textsuperscript{2} region of the image (shown as inset figures) further highlights the presence of crystallinity. Upon adding 10 wt.% SubPc to C\textsubscript{60} (Figure 4.10b), the crystallinity of C\textsubscript{60} is reduced, consistent with the XRD results of Figure 4.9. Interestingly, upon adding 20 wt.% SubPc to C\textsubscript{60}, the film shows clear nanocrystalline domains (Figure 4.10c). The FFT intensity maxima observed from the 80

![Figure 4.11: Selected area electron diffraction (SAED) patterns for thin films containing (a) neat C\textsubscript{60}, (b) 90 wt.% C\textsubscript{60} (10 wt.% SubPc) and (b) 80 wt.% C\textsubscript{60} (20 wt.% SubPc).]
wt.% $C_{60}$ mixture are the strongest among all compositions investigated, indicating the presence of a crystalline phase in this mixture. The further addition of SubPc to construct a mixture containing 50 wt.% $C_{60}$ (Figure 4.10d) reduces the crystalline content and the film becomes effectively amorphous. The TEM imaging of a neat film of SubPc exhibited no signatures of crystallinity, consistent with the XRD spectrum of Figure 4.9.

In addition to image analysis via FFT, selected area electron diffraction (SAED) was also performed to determine the molecular structure of the observed nanocrystalline regions. For SAED, beam energy of 300 keV and a region 5 µm in diameter was used.

![Figure 4.12: Experimentally determined d-spacings for the spectra of neat $C_{60}$, 90 wt.% $C_{60}$, 80 wt.% $C_{60}$ and theoretically predicted values based on the crystal structures of SubPc and $C_{60}$.](image-url)
No substantial beam damage was observed during TEM imaging. Quantifying the SAED data provides information regarding the d-spacing which can help to identify which component(s) of the mixture contribute to the crystallinity. Figures 4.11a, b and c show the SAED data obtained from neat C$_{60}$, 90 wt.% C$_{60}$ and 80 wt.% C$_{60}$ films, respectively. The presence of well-defined rings in the diffraction pattern for neat C$_{60}$ implies that the film is polycrystalline, consistent with the XRD data of Figure 4.9. Some of the polycrystalline phase of C$_{60}$ is still retained at 90 wt.% with a reduced azimuthal intensity distribution indicative of smaller grains. In contrast to neat C$_{60}$, the diffraction pattern collected from films containing 80 wt.% C$_{60}$ is characterized by high intensity spots scattered over a wide radial range. Figure 4.12 shows the comparison of d-spacings observed experimentally using SAED for neat C$_{60}$ and mixed (80 wt.% and 90 wt.% C$_{60}$) films with the theoretically predicted d-spacings for SubPc and C$_{60}$. The three rings observed for electron diffraction from neat C$_{60}$ correspond to the (111), (220) and (311) planes (FCC) in agreement with the XRD data of Figure 4.9. The same three planes are also observed in the SAED spectra collected for mixed films containing 90 wt.% C$_{60}$. For mixed films containing 80 wt.% C$_{60}$, reflections corresponding to a d-spacing of 4.7 Å are observed that cannot be attributed to crystalline C$_{60}$. This d-spacing correlates well with the (220) plane of orthorhombic SubPc.$^{155,157}$ This analysis suggests the presence of nanocrystalline domains of SubPc in addition to C$_{60}$ crystallinity in the mixed film containing 80 wt.% C$_{60}$. Given that the SAED measurement integrates over a circular area with a diameter of 5 µm, these results may suggest that the structure observed in Figure 4.10c consists of nanocrystalline domains of SubPc in a partially crystalline
matrix of C\textsubscript{60}. While the mechanism for the growth of crystalline SubPc in films containing 80 wt.% C\textsubscript{60} requires further investigation, this phenomenon may be the result of crystal nucleation at the C\textsubscript{60} surface. Interestingly, the observation of SubPc crystallinity requires a critical balance between SubPc and C\textsubscript{60}, and is only observed at 80 wt.% C\textsubscript{60}.

4.5 Impact of morphology on charge transport

Neat films of SubPc are amorphous and characterized by a low hole mobility. The construction of a uniformly mixed film containing 20 wt.% SubPc and 80 wt.% C\textsubscript{60} leads to the formation of nanocrystalline domains of SubPc which likely exist through the depth of the mixture forming pathways for hole transport. The increase in SubPc crystallinity shown in Figure 4.10c correlates well with the observed increase in hole mobility for mixtures of SubPc:C\textsubscript{60} upon the addition of C\textsubscript{60}, peaking at a composition of 80 wt.% C\textsubscript{60}. No significant SubPc crystallinity is observed in mixed films containing 90 wt.% C\textsubscript{60}, leading to a reduction in the hole mobility upon further addition of C\textsubscript{60}.

The presence of crystalline C\textsubscript{60} in neat film and in mixtures of 90 wt.% C\textsubscript{60} and 80 wt.% C\textsubscript{60} likely permits a uniformly high electron mobility over this range of composition (Figure 4.7). This crystallinity is lost with a further reduction in the C\textsubscript{60} composition, suggesting that mixtures with <80 wt.% C\textsubscript{60} comprise essentially amorphous mixtures of SubPc and C\textsubscript{60}. Correspondingly, the electron mobility is also noted to decrease significantly at these compositions. As such, a high C\textsubscript{60} composition in the SubPc:C\textsubscript{60} mixture leads to both high electron and hole mobilities and hence, effective charge
transport in an OPV. This leads to a high FF and \( J_{SC} \) for OPV cells based on \( C_{60}\)-rich mixtures (Figure 4.2).

4.6 Conclusions

This Chapter has investigated the connection between device performance, charge transport and film morphology of mixtures of SubPc:C\(_{60}\). Here, we show that a uniform mixture of SubPc:C\(_{60}\) containing 80 wt.% \( C_{60}\) shows optimum device performance. Both hole and electron mobilities are simultaneously optimized at 80 wt.% \( C_{60}\) leading to optimum charge transport and hence, device performance at this composition. This behavior is in stark contrast to mixtures of the archetypical small molecule D-A system of CuPc:C\(_{60}\), where optimum device performance is realized in mixtures containing ~50 wt.% \( C_{60}\) as discussed in Chapter 3.\(^{113, 158}\) In CuPc:C\(_{60}\) mixtures, the hole mobility decreases with increasing \( C_{60}\) composition, while the electron mobility is noted to increase.\(^{112}\) As a result, the optimum composition is ~50 wt.% \( C_{60}\), where both the electron and hole mobility are simultaneously maximized. The difference between the CuPc:C\(_{60}\) and SubPc:C\(_{60}\) systems arises from a difference in donor crystallinity. While neat films of SubPc are amorphous, SubPc forms nanocrystalline domains in mixed film when \( C_{60}\) comprises 80 wt.% of the mixture, leading to an increase in the hole mobility. On the contrary, neat CuPc is polycrystalline, and the addition of 25 wt.% \( C_{60}\) results in an amorphous mixture.\(^{112}\) This loss of crystallinity leads to a reduction in the hole mobility of CuPc:C\(_{60}\) mixtures with increasing \( C_{60}\) composition.\(^{112}\)
For SubPc:C\textsubscript{60} OPVs containing an optimized mixture, a maximum power conversion efficiency of $\eta_P = (3.7\pm0.1)\%$ is realized compared to $\eta_P = (3.0\pm0.1)\%$ obtained for a planar heterojunction cell at 100 mW/cm\textsuperscript{2} under simulated AM1.5G solar illumination. Here, the formation of nanocrystalline domains of SubPc in C\textsubscript{60}-rich mixtures makes it possible to realize high exciton diffusion efficiency combined with a high charge collection efficiency. Indeed, it is interesting that SubPc can be crystallized solely by varying the overall D-A film composition, without the need for any thermal treatments. An improved understanding of the crystallization behavior of SubPc:C\textsubscript{60} may ultimately permit additional improvements in device performance for this system.
Chapter 5-Graded donor-acceptor heterojunctions for efficient organic photovoltaic cells

5.1 Introduction

Chapter 4 presented an extensive study on the optimization of uniformly mixed OPVs based on SubPc and C_{60} as the electron donating and accepting materials, respectively. However, as discussed in Chapter 3, further enhancement in power conversion efficiency ($\eta_P$) can be realized through the use of graded heterojunctions. A careful optimization of the graded heterojunction permits the realization of a network of donor and acceptor materials for optimized exciton and charge carrier transport, leading to a significant improvement in device performance relative to that of optimized planar and uniformly mixed OPVs. This Chapter presents a systematic optimization of SubPc:C_{60} gradients for high efficiency OPVs.

The gradients containing SubPc and C_{60} as the active materials were optimized differently from gradients using CuPc and C_{60}. As discussed previously, both hole and electron mobilities fall off with dilution in uniform mixtures of CuPc and C_{60}.^{112, 131} As such, the optimum performance is realized in uniform mixtures containing ~50 wt.% C_{60} when both hole and electron mobilities are balanced. In contrast, in uniform mixtures of SubPc:C_{60}, hole mobility increases by almost two orders of magnitude on diluting pure SubPc with 80 wt.% C_{60}.^{96} This peak in hole mobility is accompanied by high electron mobility at this composition. Consequently, optimum performance in uniform mixtures of
SubPc:C$_{60}$ is realized at a composition of 80 wt.% C$_{60}$. As such, the graded heterojunction OPVs explored in this work were all C$_{60}$-rich.

5.2 Gradients of interest

Concentration gradients explored in this work are shown in Figure 5.1. The gradients of Figures 5.1a, 5.1b and 5.1c are referred to as “zero endpoint” (ZEP) gradients, and are characterized by overall 75 wt.% C$_{60}$, 80 wt.% C$_{60}$ and 85 wt.% C$_{60}$, respectively. Figure 5.1: Composition profiles in (a) a zero endpoint (ZEP) 75 wt.% C$_{60}$ gradient, (b) a ZEP 80 wt.% C$_{60}$ gradient, (c) a ZEP 85 wt.% C$_{60}$ gradient, and (d) a non-zero endpoint (NZEP) 80 wt.% C$_{60}$ gradient. The zero of thickness is referenced at the anode/organic interface.
respectively. All of the ZEP gradients were constructed by varying the growth rate (R) of SubPc according to $R_{\text{SubPc}} = 0.1 \text{ nm/s} \rightarrow 0 \text{ nm/s}$. The growth rate of $C_{60}$ was varied as $0 \text{ nm/s} \rightarrow 0.x \text{ nm/s}$, where $x = 3, 4$ or 5 for ZEP 75 wt.% $C_{60}$, 80 wt.% $C_{60}$ and 85 wt.% $C_{60}$ gradients, respectively. Figure 5.1d shows a “non-zero endpoint” (NZEP) gradient that is characterized by overall 80 wt.% $C_{60}$. The NZEP (80 wt.% $C_{60}$) gradient permits an increase in the D-A interface area at the edges of the gradient. The NZEP (80 wt.% $C_{60}$) gradient was constructed by varying the growth rates according to $R_{\text{SubPc}} = 0.5 \text{ nm/s} \rightarrow 0.3 \text{ nm/s}$ and $R_{C_{60}} = 0.5 \text{ nm/s} \rightarrow 2.7 \text{ nm/s}$. The optimized planar device used for comparison consisted of a 13-nm-thick layer of SubPc and a 35-nm-thick layer of $C_{60}$ and the optimized mixed heterojunction contains 80 wt.% $C_{60}$ at a thickness of 64 nm. A 10-nm-thick layer of molybdenum oxide (MoO$_3$) was included adjacent to the ITO anode in the planar, mixed and NZEP graded OPVs in order to reduce the dark current. All OPVs constructed for this study contained a 10-nm-thick exciton and hole blocking layer of bathocuproine (BCP).$^{15,106}$

5.3 Impact of gradient on device performance

Figure 5.2 shows the dark current density-voltage characteristics of various gradients. A non-zero composition for both the donor and acceptor materials across the active layer can provide a pathway for hole and electron leakage, leading to an increased dark current and reduced open-circuit voltage ($V_{OC}$). The layer of BCP serves to block holes that leak through the gradient, in addition to preventing exciton quenching at the cathode.$^{109}$ In order to reduce electron leakage and maintain a low dark current, a 10-nm-
thick layer of MoO₃ was inserted at the anode/ NZEP gradient interface.¹⁵⁹, ¹⁶⁰ The electron blocking layer of MoO₃ is not required in ZEP structures since the zero acceptor and donor composition at the anode/active layer and active layer/BCP interfaces prevents the formation of a pathway for significant charge carrier leakage. Comparable dark current in all the ZEP gradients and NZEP gradient with an MoO₃ interlayer suggests minimum charge carrier leakage to the opposite electrode on the insertion of MoO₃ interlayer (Figure 5.2).

The OPV operating parameters for devices with ZEP (75 wt.% C₆₀), ZEP (80 wt.% C₆₀) and ZEP (85 wt.% C₆₀) graded heterojunction OPVs and (b) NZEP (80 wt.% C₆₀) graded heterojunction OPV with and without MoO₃ interlayer.

Figure 5.2: Current density -voltage characteristic in dark for SubPc:C₆₀ OPVs with (a) ZEP (75 wt.% C₆₀), ZEP (80 wt.% C₆₀) and ZEP (85 wt.% C₆₀) graded heterojunction OPVs and (b) NZEP (80 wt.% C₆₀) graded heterojunction OPV with and without MoO₃ interlayer.
wt.% C$_{60}$), ZEP (85 wt.% C$_{60}$) and NZEP (80 wt.% C$_{60}$) graded heterojunctions as a function of active layer thickness under simulated AM1.5G solar illumination at 100 mW/cm$^2$ are displayed in Figure 5.3. As mentioned in Chapter 3, thickness is an important parameter for device optimization in OPVs since it determines the balance between absorption and charge collection efficiencies. Initially, the short-circuit density ($J_{SC}$) is observed to increase with active layer thickness for all gradients due to increasing optical absorption (Figure 5.3a). At larger thicknesses, the $J_{SC}$ rolls-off due to a reduction in the charge collection efficiency and saturation in absorption efficiency.$^{24}$ The peak $J_{SC}$

Figure 5.3: Photovoltaic operating parameters for devices containing zero endpoint (ZEP) (75 wt.% C$_{60}$), ZEP (80 wt.% C$_{60}$), ZEP (85 wt.% C$_{60}$), and non-zero endpoint (NZEP) (80 wt.% C$_{60}$) graded composition profiles at 100 mW/cm$^2$ as a function of active layer thickness. (a) Short-circuit current density ($J_{SC}$), (b) open-circuit voltage ($V_{OC}$), (c) fill factor (FF), and (d) power conversion efficiency ($\eta_P$).
values for the ZEP (75 wt.% C\textsubscript{60}) and ZEP (80 wt.% C\textsubscript{60}) structures are comparable at \( \sim 7 \) mA/cm\(^2\). The \( V_{\text{OC}} \) does not vary significantly with composition for ZEP graded heterojunctions, and is nearly constant with active layer thickness (Figure 5.3b). The fill factor (FF) decreases with thickness for all three ZEP graded heterojunctions due to a reduction in the charge collection efficiency with increasing thickness.\(^{95}\) The FF for the ZEP (75 wt.% C\textsubscript{60}) graded heterojunction is lower than the ZEP (80 wt.% C\textsubscript{60}) and ZEP (85 wt.% C\textsubscript{60}) graded heterojunctions. This trend reflects the dependence of the electron and hole mobilities of SubPc and C\textsubscript{60} upon dilution in a mixture discussed in Chapter 4. The hole mobility of a SubPc:C\textsubscript{60} mixture was observed to increase on increasing the C\textsubscript{60} composition from 0 wt.% to 80 wt.%. Concomitantly, the electron mobility is reduced if C\textsubscript{60} comprises <80 wt.% of the mixture. Consequently, in the case of SubPc:C\textsubscript{60}, a high

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Figure 5.4: Comparison of (a) hole and (b) electron mobilities between ZEP (80 wt.% C\textsubscript{60}) and NZEP (80 wt.% C\textsubscript{60}) gradients. The gradient is assumed to comprise thin slabs of uniform mixtures.
C_{60} composition in the active layer ensures high electron and hole mobilities and effective charge transport. Here, the ZEP (75 wt.% C_{60}) graded heterojunction has a lower C_{60} composition across the active layer than the ZEP (80 wt.% C_{60}) and ZEP (85 wt.% C_{60}) structures, leading to reduced charge carrier mobilities and a lower FF. These parameters lead to a peak efficiency of (3.2±0.1)% for the ZEP (75 wt.% C_{60}) and ZEP (85 wt.% C_{60}) graded heterojunctions, and (3.5±0.1)% for the ZEP (80 wt.% C_{60}) graded heterojunction (Figure 5.3d).

The highest performing ZEP (80 wt.% C_{60}) graded heterojunction was modified to incorporate a non-zero concentration of C_{60} and SubPc at both the anode/active layer and active layer/BCP interfaces. Increasing the D-A interface area near the edges of the active layer increases the exciton diffusion efficiency. Modifying the gradient profile also

![Graph showing EQE spectra for different compositions](image)

**Figure 5.5:** External quantum efficiency (\(\eta_{\text{EQE}}\)) spectra for graded heterojunction OPVs with active layers consisting of either a zero endpoint (ZEP) (75 wt.% C_{60}) gradient (67 nm), a ZEP (80 wt.% C_{60}) gradient (63 nm), a ZEP (85 wt.% C_{60}) gradient (69 nm), or a non-zero endpoint (NZEP) (80 wt.% C_{60}) (60 nm) gradient.
favorably affects the charge transport properties of the active layer. The charge carrier mobility across the gradient can be plotted if the gradient is considered as a series of thin slabs of uniform mixtures with varying composition. In this way, the mobility data obtained for uniform mixtures of SubPc:C$_{60}$ presented in Chapter 4 can be used to qualitatively explain charge transport in gradients. The hole and electron mobilities across the ZEP (80 wt.% C$_{60}$) and NZEP (80 wt.% C$_{60}$) gradients are shown in Figure 5.4. The NZEP (80 wt.% C$_{60}$) gradient has higher hole and electron mobilities across the gradient suggesting higher charge collection efficiency in the NZEP (80 wt.% C$_{60}$) gradient relative to the ZEP (80 wt.% C$_{60}$) gradient. Increase in both exciton diffusion and charge collection efficiencies leads to a ~15% increase in the peak value of $J_{SC}$ of the NZEP graded heterojunction (Figure 5.3a). Figure 5.3c shows that the FF of the NZEP (80 wt.% C$_{60}$) graded heterojunction is larger than that of the ZEP (80 wt.% C$_{60}$) graded heterojunction, and exhibits a much weaker dependence on gradient thickness up to an active layer thickness of 100 nm. This is in stark contrast to the behavior of the ZEP graded heterojunctions, where the FF is noted to decrease with increasing active layer thickness. This result may suggest some degree of connectivity in the donor and acceptor phases across the NZEP graded active layer. For the NZEP (80 wt.% C$_{60}$) graded heterojunction, a peak power conversion efficiency ($\eta_P$) of (4.5±0.1)% is realized at an active layer thickness of 60 nm (Figure 5.3d).

Figure 5.5 shows the external quantum efficiency ($\eta_{EQE}$) of optimized OPVs based on ZEP (75 wt.% C$_{60}$), ZEP (80 wt.% C$_{60}$), ZEP (85 wt.% C$_{60}$) and NZEP (80 wt.% C$_{60}$) graded heterojunctions. The photoresponse occurring at wavelengths $\lambda \leq 500$ nm
originates mainly from $C_{60}$ while the response at longer wavelengths corresponds to absorption in SubPc. The active layer thicknesses for the optimized ZEP (75 wt.% $C_{60}$), ZEP (80 wt.% $C_{60}$) and ZEP (85 wt.% $C_{60}$) graded heterojunction OPVs are 67 nm, 63 nm and 69 nm, respectively. Since the optimum active layer thickness of each ZEP gradient is comparable, the amount of $C_{60}$ increases and concomitantly, the amount of SubPc decreases in going from a ZEP (75 wt.% $C_{60}$) to ZEP (85 wt.% $C_{60}$) graded heterojunction. The expected reduction in the diffusion efficiency for excitons in $C_{60}$ on increasing the $C_{60}$ concentration leads to its smaller response in the ZEP (85 wt.% $C_{60}$) gradient. Interestingly, the peak $\eta_{EQE}$ value for SubPc remains constant across all the ZEP gradients explored in this work. This suggests that the reduction in the optical absorption of SubPc in going from 75 wt.% $C_{60}$ to 85 wt.% $C_{60}$ is exactly balanced by an increase in

Figure 5.6: Current density (J)-voltage characteristic under simulated AM1.5G solar illumination at 134 mW/cm$^2$ for SubPc:$C_{60}$ OPVs with planar (13 nm SubPc/35 nm $C_{60}$), mixed (80 wt.% $C_{60}$) (64 nm), or NZEP (80 wt.% $C_{60}$) graded (60 nm) architectures.

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the product of exciton diffusion and charge collection efficiencies. Enhancement in the exciton diffusion and charge collection efficiencies on modifying the ZEP (80 wt.% C\textsubscript{60}) to NZEP (80 wt.% C\textsubscript{60}) gradient leads to the highest SubPc and C\textsubscript{60} response for this particular gradient.

**5.4 Comparison with conventional structures**

The performance of optimized NZEP (80 wt.% C\textsubscript{60}) graded heterojunction was compared with optimized planar and mixed (80 wt.% C\textsubscript{60}) OPVs. Figure 5.6 shows

![Graphs showing various parameters against intensity](image)

Figure 5.7: (a) Responsivity, (b) open-circuit voltage (V\textsubscript{oc}), (c) fill factor (FF) and (d) power conversion efficiency (η\textsubscript{p}) as a function of illumination intensity for SubPc:C\textsubscript{60} OPVs with planar (13 nm SubPc/35 nm C\textsubscript{60}), mixed (80 wt.% C\textsubscript{60}) (64 nm), or NZEP (80 wt.% C\textsubscript{60}) graded (60 nm) architectures. All the devices included a MoO\textsubscript{3} blocking layer.
current density-voltage characteristics for optimized OPVs based on planar, mixed (80 wt.% C₆₀), and NZEP (80 wt.% C₆₀) architectures under simulated AM1.5G solar illumination at 134 mW/cm². The OPV operating parameters for these optimized devices are displayed as a function of illumination intensity in Figure 5.7. The improvement in responsivity of the graded heterojunction relative to the planar heterojunction is ascribed primarily due to an increase in the exciton diffusion efficiency (Figure 5.7a). However, the enhancement in performance compared to a mixed heterojunction originates from improved charge transport across the graded active layer and slightly enhanced absorption efficiency. The neat donor and acceptor layers in the planar heterojunction ensure efficient charge transport, resulting in a high FF for this device architecture (Figure 5.7b). The lower charge collection efficiency in the more disordered mixed and graded cells results in a lower FF for these devices. The $V_{OC}$ realized with all three device architectures are comparable (Figure 5.7c). Of note is the fact that in the absence of MoO₃, the $V_{OC}$ of the mixed and graded architectures is ~0.8V. The inclusion of a layer of MoO₃ in the mixed (80 wt.% C₆₀) and NZEP (80 wt.% C₆₀) graded OPVs reduces the dark current (Figure 5.2b) significantly and increases the $V_{OC}$. Overall, $\eta_p=(4.5\pm0.1)\%$ is obtained for the NZEP (80 wt.% C₆₀) graded heterojunction at 100 mW/cm², compared to $\eta_p=(4.0\pm0.1)\%$ for an optimized mixture, and $\eta_p=(3.4\pm0.1)\%$ for a planar architecture (Figure 5.7d). The operating parameters obtained for the planar OPV cell are consistent with those published elsewhere for the same device architecture. The OPV operating parameters reported for optimized planar and mixed OPVs are slightly higher than those reported in Chapter 4 because of higher purity of materials used in this Chapter.

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Figure 5.8 compares the spectral response of optimized planar, mixed (80 wt.% C\textsubscript{60}) and NZEP (80 wt.% C\textsubscript{60}) graded heterojunction cells. As discussed previously, the observed increase in the response from both SubPc and C\textsubscript{60} on comparing a planar OPV to the NZEP (80 wt.% C\textsubscript{60}) gradient proves that any reduction in the charge collection efficiency is overwhelmingly offset by increases in the absorption and exciton diffusion efficiencies. The NZEP (80 wt.% C\textsubscript{60}) gradient also exhibits enhanced response for SubPc and C\textsubscript{60} compared to a uniformly mixed (80 wt.% C\textsubscript{60}) cell. The mixed heterojunction is characterized by high exciton diffusion efficiency and hence, the enhancement in the response from both SubPc and C\textsubscript{60} relative to a mixed OPV suggests that the graded cell has enhanced absorption and charge collection efficiencies in addition to a high exciton diffusion efficiency. The \(\eta_{\text{EQE}}\) of all graded and mixed heterojunctions

![Graph showing spectral response comparison](image)

Figure 5.8: Comparison of \(\eta_{\text{EQE}}\) for optimized SubPc:C\textsubscript{60} OPVs with planar (13 nm SubPc/35 nm C\textsubscript{60}), mixed (80 wt.% C\textsubscript{60}) (64 nm), or NZEP (80 wt.% C\textsubscript{60}) graded (60 nm) architectures. All the devices included a MoO\textsubscript{3} blocking layer.
shows a long wavelength tail extending from 650 to 750 nm which is attributed to charge-transfer state absorption in mixtures and gradients.\textsuperscript{150}

### 5.5 Conclusions

Based on this study, we conclude that graded heterojunctions are an attractive approach to enhance the efficiency of small molecule OPVs. The performance of OPVs depends strongly on the choice of donor-acceptor (D-A) gradient. The NZEP graded OPVs are significantly more efficient than the corresponding ZEP graded OPVs due to enhancements in both exciton diffusion and charge collection efficiencies. The NZEP graded OPVs show significant improvement in the value of $J_{SC}$ relative to a planar heterojunction OPV. This is attributed to an increase in the D-A interface area which significantly enhances the exciton diffusion efficiency. Simultaneously, the optimum gradient improves charge carrier transport as well as absorption compared to a uniformly mixed heterojunction leading to an enhancement in $J_{SC}$. This results in an increase in $\eta_P$ of ~35\% and ~15\% relative to optimized planar and uniformly mixed heterojunction OPVs under simulated AM1.5G solar illumination at 100 mW/cm$^2$, respectively. To date, the peak efficiency of (4.5±0.1)% is the highest reported for this materials system.\textsuperscript{161} This high performance is made possible by the ability of the graded heterojunction to allow for the simultaneous optimization of the exciton diffusion and charge collection efficiencies, representing a highly tunable device architecture for small molecule OPVs.
Chapter 6-Efficient, bulk heterojunction organic photovoltaic cells based on boron subphthalocyanine chloride-C$_{70}$

6.1 Introduction

Previous studies in this thesis have relied on the use of C$_{60}$ as an acceptor primarily due to its high electron mobility and large exciton diffusion length. However, its small extinction coefficient and poor absorption overlap with the solar spectrum limits its contribution to device photocurrent. These limitations have prompted the growing use of C$_{70}$ as an electron accepting material in bulk heterojunction OPVs due to its red-shifted absorption edge and increased extinction coefficient, permitting a larger contribution to

Figure 6.1: Comparison of optical constants of C$_{60}$ and C$_{70}$. Solid lines depict the extinction coefficient and dashes lines represent the refractive index. Variable angle spectroscopic ellipsometry was used to measure the optical constants.
the overall photocurrent (Figure 6.1). Table 6.1 presents a comparison of a few properties of C₆₀ and C₇₀. To date, the electron donor-acceptor (D-A) pairing of boron subphthalocyanine chloride (SubPc) and C₇₀ has not been examined. As mentioned in previous chapters, SubPc is a promising electron donor material due to its large extinction coefficient in the visible and deep highest occupied molecular orbital (HOMO) energy level. In this chapter, we examine the performance of this D-A pairing in planar, uniformly mixed and graded heterojunction OPVs.

**Table 6.1: Comparison of properties of C₆₀ and C₇₀**

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Electron Mobility (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆₀</td>
<td>6.3 (UPS)¹⁶³</td>
<td>3.9 (IPES)¹⁶²</td>
<td>3.3x10⁻² (SCLC) (This work)</td>
</tr>
<tr>
<td>C₇₀</td>
<td>6.2 (UPS)¹⁶³</td>
<td>3.9 (IPES)¹⁶²</td>
<td>1.3x10⁻³ (OFET)¹⁶²</td>
</tr>
</tbody>
</table>

**6.2 Device performance of uniformly mixed heterojunctions**

Organic photovoltaic cells were fabricated on glass substrates pre-coated with a 150-nm-thick anode layer of indium-tin-oxide (ITO) having a sheet resistance of 15 Ω/□. Substrates were cleaned using the procedure described in the Appendix C. The organic
active layers in planar and mixed devices were deposited at room temperature with a total rate of 0.2 nm/s. A 7-nm-thick layer of MoO$_3$ was incorporated between ITO and the active layer in all the OPVs to reduce the dark current.$^{92, 149}$ A 10-nm-thick exciton-blocking layer of bathocuproine (BCP) was grown on top of the active layers in all OPV architectures.$^{109}$ All devices were capped with a 65-nm-thick Al cathode through a shadow mask having 1 mm diameter openings.

Organic photovoltaic cells based on uniform mixtures of SubPc:C$_{70}$ were fabricated with varying active layer composition to determine the optimum mixing ratio. Figure 6.2 shows the operating parameters for uniformly mixed SubPc:C$_{70}$ OPVs under

![Figure 6.2](image)

Figure 6.2: (a) Short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), (b) fill factor (FF) and power conversion efficiency ($\eta_P$) under simulated AM1.5G solar illumination at 100 mW/cm$^2$ for uniformly mixed OPVs as a function of the active layer composition.
simulated AM 1.5G solar illumination at 100 mW/cm² as a function of the active layer composition. The short-circuit current density ($J_{SC}$) value is peaked at a composition of 80 wt.% C$_{70}$ with a value of (11.2±0.6) mA/cm². The open-circuit voltage ($V_{OC}$) realized with all of the mixed OPVs is greater than 0.9 V. The fill factor (FF) is maximized in mixed OPVs containing ≥50 wt.% C$_{70}$. Similar trends in FF with composition in uniform mixtures of SubPc:C$_{60}$ were discussed in Chapter 4. The peak in $J_{SC}$ leads to a peak in $\eta_{P}$ with a value of (4.7±0.2)% at a composition of 80 wt.% C$_{70}$.

Figure 6.3: Optimized composition profile for a gradient containing overall 80 wt.% C$_{70}$. The zero of thickness is referenced to the MoO$_3$/organic interface.

6.3 Further optimization using graded heterojunctions

In order to further increase device efficiency, devices containing a continuously graded D-A heterojunction were also constructed. Previous chapters on graded heterojunctions have shown that the graded heterojunction has a larger exciton diffusion
efficiency relative to a planar heterojunction due to the large D-A interface area. In addition, the graded heterojunction can realize larger charge collection and optical absorption efficiencies compared to a uniformly mixed heterojunction. As such, tuning the concentration gradient in the active layer allows for the simultaneous optimization of the exciton diffusion and charge collection efficiencies. Based on the compositional dependence of device performance for uniformly mixed SubPc:C\textsubscript{70} OPVs, graded heterojunction devices containing an overall composition of 80 wt.% C\textsubscript{70} were fabricated and optimized. The optimum concentration gradient is shown in Figure 6.3. The optimized gradient was constructed by varying the growth rates according to $R_{\text{SubPc}} = 0.06 \text{ nm/s} \rightarrow 0.04 \text{ nm/s}$ and $R_{C70} = 0.04 \text{ nm/s} \rightarrow 0.36 \text{ nm/s}$, respectively. The performance of optimized planar, uniformly mixed and graded heterojunctions OPVs was compared.

Figure 6.4: Current density-voltage characteristics under simulated AM1.5G solar illumination at 134 mW/cm\textsuperscript{2} for optimized SubPc:C\textsubscript{70} OPVs with a planar (11 nm SubPc/35 nm C\textsubscript{70}), a uniformly mixed 80 wt.% C\textsubscript{70} (52 nm), or a 80 wt.% C\textsubscript{70} graded (54 nm) heterojunction.
Figure 6.4 compares the current density-voltage characteristics of the optimized OPVs under simulated AM 1.5G illumination at 134 mW/cm$^2$. The optimized planar heterojunction OPV consisted of an 11-nm-thick layer of SubPc and a 35-nm-thick layer of C$_{70}$.

Figure 6.5 compares the OPV operating parameters of optimized planar, uniformly mixed and graded heterojunction OPVs as a function of illumination intensity. The responsivity is defined as the ratio of $J_{SC}$ and illumination intensity. The planar heterojunction cell has the lowest responsivity and $\eta_P$ at all illumination intensities. The

![Graphs showing various OPV parameters as a function of intensity](image)

Figure 6.5: (a) Responsivity, (b) fill factor (FF), (c) open-circuit voltage ($V_{OC}$) and (d) power conversion efficiency ($\eta_P$) as a function of illumination intensity for optimized SubPc:C$_{70}$ OPVs with a planar (11 nm SubPc/35 nm C$_{70}$), a uniformly mixed 80 wt.% C$_{70}$ (52 nm), or a 80 wt.% C$_{70}$ graded (54 nm) heterojunction.
largest responsivity is realized with the graded heterojunction. The $V_{OC}$ realized with all the device architectures is comparable, at a value of ~1 V. The $V_{OC}$ realized with OPVs based on the D-A pairing of SubPc and C$_{70}$ is equal to the $V_{OC}$ of corresponding SubPc:C$_{60}$ OPVs since the lowest unoccupied molecular orbital (LUMO) energy levels of C$_{60}$ and C$_{70}$ are both measured at 3.9 eV. The pure SubPc and C$_{70}$ layers in the planar heterojunction minimize recombination losses leading to a high FF for this device architecture. On the contrary, mixed and graded architectures likely have a lower FF due in part to a larger recombination rate. The significant increase in responsivity for the graded heterojunction relative to a planar heterojunction more than offsets the reduction in FF, leading to the highest $\eta_p = (5.4\pm0.2)\%$ under simulated AM1.5G illumination at 100 mW/cm$^2$. With further optimization of film morphology, additional enhancements in FF may be possible, leading to even higher efficiency. This efficiency is significantly higher than $\eta_p = (4.5\pm0.1)\%$ realized with optimized graded heterojunction cells containing SubPc and C$_{60}$. This enhancement comes as a result of a significant increase in the responsivity. As discussed previously, the larger and red-shifted extinction coefficient of C$_{70}$ compared to C$_{60}$ leads to a larger photocurrent contribution from C$_{70}$.

Figure 6.6 compares the $\eta_{EQE}$ of optimized planar, uniformly mixed and graded heterojunction OPVs. The response occurring at wavelengths $\lambda \leq 500$ nm originates mainly from C$_{70}$ while the response at longer wavelengths corresponds to absorption in both SubPc and C$_{70}$. Despite having a high charge collection efficiency, the planar heterojunction OPV has the lowest $\eta_{EQE}$ across all wavelengths, likely due to the low exciton diffusion efficiency for SubPc and C$_{70}$. Both mixed and graded
heterojunction OPVs have a large exciton diffusion efficiency owing to the large D-A interface area in these architectures. Compared to a uniformly mixed heterojunction, the graded heterojunction shows a ~15% increase in $\eta_{\text{EQE}}$ across all wavelengths. Since these structures have comparable exciton diffusion efficiencies, the enhancement in $\eta_{\text{EQE}}$ is attributed to enhancement in charge collection and optical absorption efficiencies in the graded heterojunction.\textsuperscript{167} A more detailed discussion on the comparison of $\eta_{\text{EQE}}$ of optimized mixed and graded OPVs is presented in Chapter 7.

![Comparison of external quantum efficiency ($\eta_{\text{EQE}}$) for optimized SubPc:C\textsubscript{70} OPVs with a planar (11 nm SubPc/35 nm C\textsubscript{70}), a uniformly mixed 80 wt.% C\textsubscript{70} (52 nm), or a 80 wt.% C\textsubscript{70} graded (54 nm) heterojunction.](image)

Figure 6.6: Comparison of external quantum efficiency ($\eta_{\text{EQE}}$) for optimized SubPc:C\textsubscript{70} OPVs with a planar (11 nm SubPc/35 nm C\textsubscript{70}), a uniformly mixed 80 wt.% C\textsubscript{70} (52 nm), or a 80 wt.% C\textsubscript{70} graded (54 nm) heterojunction.
6.4 Conclusions

In summary, this Chapter explored the compositional dependence of device performance for bulk heterojunction OPVs based on the D-A pairing of SubPc:C\textsubscript{70}. A peak power conversion efficiency of $\eta_P = (4.7 \pm 0.2)\%$ is realized in uniformly mixed OPVs containing 80 wt.% C\textsubscript{70} which is ~25% higher than optimized planar heterojunction. This improvement originates from increased D-A interface area leading to a larger exciton diffusion efficiency. The use of graded heterojunction enhances the charge collection and optical absorption efficiencies relative to uniformly mixed OPVs while maintaining a large exciton diffusion efficiency thus permitting further improvement in device performance. Using the graded architecture, we demonstrate $\eta_P = (5.4 \pm 0.2)\%$ for cells containing overall 80 wt.% C\textsubscript{70}. To our best knowledge, this peak efficiency is the highest reported efficiency based on SubPc as an electron donor material.\textsuperscript{161} Additionally, this device performance is among a few published thermally evaporated small molecule OPVs with $\eta_P >5\%$.\textsuperscript{114, 115, 119} The results of this chapter also confirm that the use of gradients is a general technique and can be applied to any D-A system.
Chapter 7-Characterizing the charge collection efficiency in bulk heterojunction organic photovoltaic cells

7.1 Introduction

As discussed in previous chapters, well-optimized organic photovoltaic cells (OPVs) often include a carefully engineered film morphology to simultaneously optimize exciton diffusion ($\eta_{\text{Diff}}$) and charge collection ($\eta_{\text{CC}}$) efficiencies. Typically, the $\eta_{\text{Diff}}$ in these efficient OPVs may be close to unity, as the vast majority of photogenerated excitons are able to reach the donor-acceptor (D-A) interface. Consequently, the $\eta_{\text{CC}}$ is an important parameter in these structures, quantifying the fraction of dissociated carriers that are collected at the electrodes. Interestingly, while numerous studies have attempted to characterize $\eta_{\text{Diff}}$ in OPVs, fewer approaches have been developed to assess the equally important $\eta_{\text{CC}}$. Most frequently, estimates of $\eta_{\text{CC}}$ require input from both simulation and experiment. This chapter demonstrates an alternative approach that permits calculation of $\eta_{\text{CC}}$ without any input from simulation.

7.2 Theory

As discussed in Chapter 2, optical absorption in an OPV leads to the creation of mobile, tightly bound excitons, with efficiency $\eta_A$. The exciton diffuses through the active layer to the D-A interface, where exciton dissociation and charge transfer occur with efficiency $\eta_{\text{CT}}$. The resulting charge carriers migrate away from the interface and
are collected at the respective electrodes with efficiency $\eta_{CC}$. The overall efficiency of photoconversion or the external quantum efficiency ($\eta_{EQE}$) is defined as:

$$\eta_{EQE} = \eta_A \eta_{Diff} \eta_{CT} \eta_{CC} \qquad (7.1)$$

Thus, with knowledge of $\eta_A$, $\eta_{Diff}$ and $\eta_{CT}$, $\eta_{CC}$ can be calculated from the $\eta_{EQE}$. The $\eta_A$, $\eta_{Diff}$ and $\eta_{CT}$ will differ for the donor and acceptor since these processes are governed by the absorption spectrum and exciton diffusion length of each material and the $\eta_{CT}$ for excitons generated on the donor (acceptor) will depend on the lowest unoccupied molecular orbital energy or LUMO (highest unoccupied molecular orbital energy level or HOMO) level offset of the donor and acceptor molecules. In contrast, the process of charge collection inherently involves electron transport along the acceptor and hole transport along the donor, regardless of where the exciton is created. Consequently, $\eta_{CC}$ is the same for excitons created on both donor and acceptor molecules and is independent of excitation wavelength and Equation 7.1 can be rewritten as:

$$\eta_{EQE}(\lambda) = \eta_{CC} [\eta_A^{Donor}(\lambda) \eta_{Diff}^{Donor} \eta_{CT}^{Donor} + \eta_A^{Acceptor}(\lambda) \eta_{Diff}^{Acceptor} \eta_{CT}^{Acceptor}] \qquad (7.2)$$

where $\eta_A^{Donor}$ ($\eta_A^{Acceptor}$), $\eta_{Diff}^{Donor}$ ($\eta_{Diff}^{Acceptor}$) and $\eta_{CT}^{Donor}$ ($\eta_{CT}^{Acceptor}$) represent the absorption, exciton diffusion and charge transfer efficiencies of the donor (acceptor), respectively. For a D:A system with large energy level offsets, the $\eta_{CT}$ for excitons generated on donor as well as acceptor can be approximated as 100%. As such, Equation 7.2 can be re-written as:

$$\eta_{EQE}(\lambda) = \eta_{CC} [\eta_A^{Donor}(\lambda) \eta_{Diff}^{Donor} + \eta_A^{Acceptor}(\lambda) \eta_{Diff}^{Acceptor}] \qquad (7.3)$$
In a uniform mixture, the individual absorption efficiencies (\(\eta_A^{\text{Donor}}\) or \(\eta_A^{\text{Acceptor}}\)) of Equation 7.3 can be expressed in terms of the donor and acceptor extinction coefficients (\(k_{\text{Donor}}\) or \(k_{\text{Acceptor}}\)) and \(\eta_A\) as: \(^{77}\)

\[
\eta_A^{\text{Donor}} = \frac{k_{\text{Donor}}}{k_{\text{Donor}} + k_{\text{Acceptor}}} \eta_A
\] (7.4)

where \(\eta_A\) includes the optical interference effects present in the OPV. \(^{172}\) An analogous expression can also be written for \(\eta_A^{\text{Acceptor}}\).

Multiple techniques have been previously used to determine the overall OPV absorption efficiency, \(\eta_A^{\text{QE}}\). \(^{26, 77, 124, 142}\) Even when the total device absorption is measured experimentally, the parasitic absorption in the electrodes is difficult to decouple from absorption in the organic active layers. \(^{142}\) In this work, the \(\eta_{\text{EQE}}\) is measured under reverse bias to estimate \(\eta_A\). Under a large enough reverse bias, all charge carriers are collected at the respective electrodes and the \(\eta_{\text{CC}}\) approaches 100%. \(^{171, 173}\) In addition, all the photogenerated excitons are dissociated at large reverse bias leading to \(\eta_{\text{Diff}} = 100\%\). \(^{174-176}\) This regime is experimentally reflected by a plateau in the \(\eta_{\text{EQE}}\) under reverse bias to a value that corresponds to \(\eta_A\). As such, the reverse-bias \(\eta_{\text{EQE}}\) can be a direct measurement of \(\eta_A\) for the absorbing active layers.

In order to estimate \(\eta_{\text{CC}}\), an estimate of \(\eta_{\text{Diff}}\) is also needed for at least one active material. For a fluorescent donor (acceptor) material, photoluminescence (PL) quenching measurements can be used to extract \(\eta_{\text{Diff}}^{\text{Donor}}\) (\(\eta_{\text{Diff}}^{\text{Acceptor}}\)). \(^{67, 68, 169, 177}\) Since the PL is directly proportional to the density of photogenerated excitons, \(^{68}\) the ratio of PL from a mixture to that of a neat donor (acceptor) film corresponds to the fraction of unquenched
excitons in the mixture. The $\eta_{\text{Diff, Donor}}/\eta_{\text{Diff, Acceptor}}$ is then calculated by subtracting this PL ratio from unity.\textsuperscript{12}

Based on the knowledge of $\eta_{\text{A, Donor}}$, $\eta_{\text{A, Acceptor}}$ and $\eta_{\text{Diff, Donor}}$, the $\eta_{\text{EQE}}$ can be fit using Equation 7.3 with the $\eta_{\text{Diff, Acceptor}}$ and $\eta_{\text{CC}}$ as fit parameters.

### 7.3 Charge collection efficiency in SubPc:C\textsubscript{60} mixtures

In order to estimate $\eta_{\text{CC}}$, bulk heterojunction OPVs based on the D-A pairing of boron subphthalocyanine chloride (SubPc):C\textsubscript{60} as well as SubPc:C\textsubscript{70} were fabricated using vacuum thermal co-sublimation (<8x10\textsuperscript{-7} Torr).\textsuperscript{133, 145, 177} A 10-nm-thick layer of MoO\textsubscript{3} was incorporated between the anode and the organic active layers to reduce the device dark current.\textsuperscript{92} A 10-nm-thick layer of bathocuproine (BCP) was deposited on top of the active layers to serve as an exciton and hole blocking layer.\textsuperscript{109} All devices were capped with a 65-nm-thick Al cathode through a shadow mask having 1 mm diameter openings. The $\eta_{\text{EQE}}$ measurements were performed at low illumination intensity (~5 mW/cm\textsuperscript{2}). However, the short-circuit current density ($J_{\text{SC}}$) as derived from the integrated $\eta_{\text{EQE}}$ is within 10% of the value measured under simulated AM1.5G solar illumination at all illumination intensities. Therefore, $\eta_{\text{CC}}$ values extracted using $\eta_{\text{EQE}}$ are assumed to be valid at an illumination intensity of 100 mW/cm\textsuperscript{2}. 

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The $\eta_{\text{EQE}}$ of uniformly mixed OPVs was measured at large reverse bias to estimate the $\eta_A$. Figures 7.1(a) and (b) show the $\eta_{\text{EQE}}$ as a function of applied negative voltage for uniformly mixed SubPc:C$_{60}$ OPVs containing 20 wt.% and 80 wt.% C$_{60}$, respectively. The $\eta_{\text{EQE}}$ at a wavelength of $\lambda$=355 nm corresponds primarily to exciton formation on C$_{60}$ while the $\eta_{\text{EQE}}$ at $\lambda$=585 nm corresponds to exciton formation on SubPc. For both compositions and excitation wavelengths, the $\eta_{\text{EQE}}$ is observed to plateau at large reverse bias to the respective absorption efficiency. Based on the $\eta_A$, the individual SubPc and C$_{60}$ absorption efficiencies are estimated using Equation 7.4.

Figure 7.1: The external quantum efficiency ($\eta_{\text{EQE}}$) as a function of reverse bias for OPVs comprising mixtures of SubPc:C$_{60}$ with (a) 20 wt.% C$_{60}$ and (b) 80 wt.% C$_{60}$. The $\eta_{\text{EQE}}$ at an excitation wavelength of $\lambda$=355 nm corresponds mainly to optical absorption in C$_{60}$ while the $\eta_{\text{EQE}}$ at $\lambda$=585 nm corresponds to optical absorption in SubPc.
As SubPc is fluorescent, PL quenching measurements were used to extract $\eta_{\text{Diff}}^{\text{Donor}}$. The ratio of PL from a SubPc:C$_{60}$ mixture to that of a neat film of SubPc was used to estimate the fraction of unquenched SubPc excitons in the mixture. In making this comparison, the amount of SubPc in the mixture is equal to that in the neat film. In addition, the slight overlap in absorption at the pump wavelength ($\lambda = 500$ nm) between SubPc and C$_{60}$ leads to a negligible difference in the SubPc exciton density between the neat and mixed films. Photoluminescence from SubPc is found to be completely quenched in mixed films containing at least 5 wt.% C$_{60}$ (Figure 7.2), suggesting $\eta_{\text{Diff}}^{\text{Donor}} = 100\%$ for this range of composition.

![Photoluminescence spectra for neat SubPc and uniform mixture containing 95 wt.% SubPc (5 wt.% C$_{60}$).](image)

Figure 7.2: Photoluminescence spectra for neat SubPc and uniform mixture containing 95 wt.% SubPc (5 wt.% C$_{60}$).

Based on the measurements of $\eta_A^{\text{Donor}}$, $\eta_A^{\text{Acceptor}}$ and $\eta_{\text{Diff}}^{\text{Donor}}$, the $\eta_{\text{Diff}}^{\text{Acceptor}}$ and $\eta_{\text{CC}}$ were estimated using Equation 7.3. Figures 7.3(a) and (b) show the $\eta_A$ and $\eta_{\text{EQE}}$ (data
and fit) for SubPc:C₆₀ mixtures containing 20 wt.% C₆₀ and 80 wt.% C₆₀, respectively. The experimental data is well-fit using the model, and $\eta_{\text{Diff, Acceptor}}$ and $\eta_{\text{CC}}$ can be extracted as fit parameters as a function of SubPc:C₆₀ composition. At compositions ranging from 20 wt.% C₆₀ to 90 wt.% C₆₀, $\eta_{\text{Diff, Acceptor}}$ is determined to be ~100%, reflecting the large D-A interface area. Figure 7.4a shows the $\eta_{\text{CC}}$ extracted from $\eta_{\text{EQE}}$ measurements both at short-circuit and under forward bias as a function of C₆₀ composition. Here, the forward bias for each composition corresponds to the maximum

![Graph](image)

Figure 7.3: External quantum efficiency ($\eta_{\text{EQE}}$) and absorption efficiency ($\eta_{\text{A}}$) for mixed SubPc:C₆₀ OPVs with active layers containing (a) 20 wt.% C₆₀ and (b) 80 wt.% C₆₀. The solid lines are fits to the $\eta_{\text{EQE}}$ data with the acceptor exciton diffusion efficiency and charge collection efficiency as fit parameters.
power point for each device. A peak $\eta_{CC}$ of $(79\pm2)\%$ is realized for SubPc:C$_{60}$ OPVs containing 80 wt.% C$_{60}$ under short-circuit conditions. The peak in $\eta_{CC}$ at 80 wt.% C$_{60}$ is attributed to the peak in hole and electron mobilities at this composition as discussed in Chapter 4. The combination of high $\eta_{CC}$ and $\eta_{Diff}$ also leads to a peak in the $J_{SC}$ at this composition (Figure 7.4b). Under forward bias, the $\eta_{CC}$ is reduced, contributing in part to a low device fill factor (Figure 7.4b), and as noted in Chapter 4, a reduction in the power conversion efficiency ($\eta_P$).

![Figure 7.4](a) The charge collection efficiency at short-circuit and under forward bias. Forward bias corresponds to the maximum power point for each device. The maximum power point for OPVs containing 20 wt.% and 50 wt.% C$_{60}$ occurs at 0.6 V, while for those containing 80 wt.% and 90 wt.% C$_{60}$, the maximum power point occurs at 0.75 V. (b) The $J_{SC}$ and FF for mixed SubPc:C$_{60}$ OPVs as a function of C$_{60}$ composition.
Additional insight on the dependence of $\eta_{CC}$ on composition can be gained by examining the effect of active layer thickness on $\eta_{CC}$. For this purpose, $\eta_{CC}$ was estimated in OPVs containing 50 or 80 wt.% $C_{60}$ as a function of active layer thickness. In uniform mixtures comprising 50 wt.% $C_{60}$, the $\eta_{CC}$ decreases with increasing active layer thickness reflecting increased resistance experienced by charge carriers to reach the respective electrodes. However, in uniform mixtures containing 80 wt.% $C_{60}$, the $\eta_{CC}$ is almost independent of active layer thickness up to 100 nm. This weak dependence of $\eta_{CC}$ on active layer thickness suggests some degree of connectivity in the donor and acceptor phases across the active layer.

![Figure 7.5: Effect of active layer thickness on $\eta_{CC}$ in OPVs containing 50 wt.% $C_{60}$ or 80 wt.% $C_{60}$](image-url)
7.4 Charge collection efficiency in graded heterojunction OPVs

Previous chapters have discussed the advantages of graded heterojunctions over conventional device architectures. For all the D-A pairings explored in this work, the optimized graded heterojunction OPV has a higher $\eta_{\text{EQE}}$ than the corresponding optimized mixed heterojunction. Previous work on graded heterojunctions has demonstrated that the graded heterojunction is expected to have a larger $\eta_A$ and $\eta_{\text{CC}}$ compared to a mixed heterojunction. In order to determine the origin of enhanced $\eta_{\text{EQE}}$ in graded heterojunctions, the $\eta_A$ and $\eta_{\text{CC}}$ of the optimized gradient was compared with the optimized mixed heterojunction in OPVs based on SubPc:C$_{60}$ and SubPc:C$_{70}$.

![Graph](image)

Figure 7.6: External quantum efficiency ($\eta_{\text{EQE}}$) and absorption efficiency ($\eta_A$) for optimized non-zero endpoint (NZEP 80 wt.% C$_{60}$) graded heterojunction OPV. The solid line is fit to the $\eta_{\text{EQE}}$ data using the model described in the text.
The $\eta_{\text{Diff}}^{\text{Donor}}$ of the optimized non-zero endpoint (NZEP) 80 wt.% C$_{60}$ graded heterojunction was calculated to be 100% using PL quenching measurements. The $\eta_{\text{CC}}$ was estimated to be (86±2)% at short-circuit using Equation 7.3 (Figure 7.6). Clearly, the $\eta_{\text{CC}}$ of optimized graded heterojunction is larger than optimized mixed 80 wt.% C$_{60}$ heterojunction (79±2)%. In addition, the $\eta_A$ of the gradient is slightly larger than uniform mixture of the same composition. The enhancement in $\eta_A$ and $\eta_{\text{CC}}$ lead to a higher $J_{\text{SC}}$ and hence, higher $\eta_P$ for the graded heterojunction containing SubPc:C$_{60}$.

Figure 7.7: External quantum efficiency ($\eta_{\text{EQE}}$) and absorption efficiency ($\eta_A$) for mixed SubPc:C$_{70}$ OPVs with active layers containing (a) optimized mixed heterojunction containing 80 wt.% C$_{70}$ (52 nm) and (b) graded heterojunction containing 80 wt.% C$_{70}$ (54 nm). The solid lines are fits to the $\eta_{\text{EQE}}$ data with the $\eta_{\text{Diff}}^{\text{Accept}}$ and $\eta_{\text{CC}}$ as fit parameters.
This analysis was also extended to OPVs based on SubPc:C$_{70}$. In SubPc:C$_{70}$ OPVs, the graded heterojunction shows a ~15% increase in $\eta_{\text{EQE}}$ across all wavelengths compared to a uniformly mixed heterojunction. Using PL quenching measurements, the $\eta_{\text{Diff}}^{\text{Donor}}$ in both mixed and graded OPVs was determined to be 100%. The experimentally measured $\eta_{\text{A}}$ for the gradient is ~5% larger across all wavelengths relative to a uniform mixture. Using estimates of the $\eta_{\text{Diff}}^{\text{Donor}}$ obtained from PL quenching and measurements of the $\eta_{\text{A}}$, the $\eta_{\text{CC}}$ was calculated in mixed and graded OPVs using Equation 7.3. The $\eta_{\text{CC}}$ was estimated to be (83±2)% and (91±2)% in the mixed and graded OPVs, respectively (Figure 7.7). As such, the enhancement in $\eta_{\text{EQE}}$ for the graded heterojunction OPV is attributed to increases in the $\eta_{\text{A}}$ and $\eta_{\text{CC}}$.

### 7.5 Conclusions

The $\eta_{\text{CC}}$ in an OPV can be thought of as a competition between charge transport to the electrodes and electron-hole recombination. The rates of charge collection and recombination depend in part on the mobility of the respective charge carriers.$^{129,178}$ As discussed in Chapter 4, the hole and electron mobilities in bulk heterojunction OPVs based on SubPc and C$_{60}$ are simultaneously maximized in a mixture comprising 80 wt.% C$_{60}$.$^{96}$ In contrast, mixed films containing 20 wt.% C$_{60}$ are characterized by reduced hole and electron mobilities, leading to an increased transit time for the charge carriers to reach the electrodes. This in turn results in higher hole and electron densities in the active layer, and hence a higher recombination rate.$^{173,179}$ Consequently, the device with 20 wt.% C$_{60}$ has a lower $\eta_{\text{CC}}$ compared to devices containing 80 wt.% C$_{60}$. This difference in
behavior is also reflected in the dependence of the $\eta_{\text{EQE}}$ on applied voltage. In films containing 20 wt.% $C_{60}$, a larger negative bias is required to collect all of the photogenerated charge carriers and observe a plateau in the $\eta_{\text{EQE}}$ (Figure 7.1a). In contrast, for mixtures comprising 80 wt.% $C_{60}$, a much smaller negative bias is needed to observe a plateau in the $\eta_{\text{EQE}}$ (Figure 7.1b). Due to the spatial distribution of donor and acceptor species across the active layer, the rate of recombination is expected to be lower in graded heterojunction compared to mixed heterojunction. This leads to a higher charge collection efficiency in the graded heterojunction.

This Chapter has demonstrated an approach to directly estimate the $\eta_A$ in an OPV by measuring the $\eta_{\text{EQE}}$ as a function of reverse bias. By coupling the $\eta_A$ with measurements of the $\eta_{\text{Diff}}$, the $\eta_{\text{EQE}}$ can be fit to extract the $\eta_{\text{CC}}$ in an OPV. This technique is used to study the $\eta_{\text{CC}}$ in OPVs containing mixtures of SubPc:$C_{60}$ as a function of composition and to compare the performance of graded heterojunctions with uniform mixtures based on SubPc:$C_{60}$ and SubPc:$C_{70}$. A peak in the $\eta_{\text{CC}}$ is realized in uniformly mixed films comprising 80 wt.% $C_{60}$, which correlates well with a peak in the charge carrier mobility and the $J_{\text{SC}}$. Additionally, the enhancement in the $\eta_{\text{EQE}}$ for the graded heterojunction OPV is attributed to increases in the $\eta_A$ and $\eta_{\text{CC}}$. Overall, this is a powerful technique that allows to decouple the efficiency of all the processes involved in photoconversion and permits estimates of the $\eta_{\text{CC}}$ to be made without requiring any input from optical field simulations.
Chapter 8-Metal naphthalocyanine complexes for infrared absorption in organic photovoltaic cells

8.1 Introduction

Previous chapters have discussed the use of novel device architectures as a means to improve organic photovoltaic cell (OPV) performance. In addition to improvements in the device design, the development of new materials is equally critical for continued improvement in device performance. This Chapter examines the properties of a new material and its potential as an electron donor material in OPVs.

To date, the highest performing single-cell bulk heterojunction OPVs are limited in their optical absorption to a wavelength range extending from roughly $\lambda=350$ nm to $\lambda=750$ nm. However, approximately 50% of the solar photon flux occurs at $\lambda>750$ nm. This potential limitation highlights the need for the further development of materials that efficiently absorb light in near infrared and infrared portions of the electromagnetic spectrum. In the past, low band gap polymers, metal phthalocyanines, carbon nanotubes as well as colloidal quantum dots have been used to extend OPV absorption further into the infrared. In this Chapter, use of tin naphthalocyanine dichloride (SnNcCl$_2$) as an electron donor material in OPVs is investigated (Figure 8.1a). Previous reports have examined a solution-processed derivative of SnNcCl$_2$ to enhance infrared absorption in organic photodetectors. We compare the optical properties and photovoltaic performance of SnNcCl$_2$ with those of tin phthalocyanine (SnPc), a previously studied, narrow energy gap small molecule, electron donor (Figure 8.1b).
Previous studies have demonstrated that SnPc owes its infrared absorption to the formation of physical dimers.\textsuperscript{187, 188}

Figure 8.1: Molecular structures of (a) tin naphthalocyanine dichloride (SnNcCl\textsubscript{2}) and (b) tin phthalocyanine (SnPc).

\section*{8.2 Optical characterization}

Efficient OPVs often consist of a bulk heterojunction designed to maximize the area of the exciton dissociating donor-acceptor (D-A) interface \textsuperscript{25, 26, 124, 126}. As such, we compared the optical properties of SnPc and SnNcCl\textsubscript{2} to determine if efficient infrared absorption could be realized in a bulk heterojunction based on SnPc or SnNcCl\textsubscript{2}. The absorption spectra of various mixed films of SnPc:C\textsubscript{60} and SnNcCl\textsubscript{2}:C\textsubscript{60} were measured on glass substrates using a OLIS Cary-14 spectrophotometer with reference to a clean glass substrate to account for absorption loss in the glass. Figure 8.2a shows the absorption coefficients of neat films of SnPc and SnNcCl\textsubscript{2} as estimated from absorbance data. The normalized absorption spectra of various mixed films of SnPc:C\textsubscript{60} and
SnNcCl$_2$:C$_{60}$ are shown in Figure 8.2b and c, respectively. The absorbance spectrum of SnPc has two prominent peaks centered at wavelengths of $\lambda=745$ nm and $\lambda=880$ nm. Previous work on SnPc has identified the peaks at $\lambda=745$ nm and $\lambda=880$ nm as originating from monomer and dimer absorption, respectively.$^{187, 188}$ Consequently, the

Figure 8.2: (a) Absorption coefficients of tin naphthalocyanine dichloride (SnNcCl$_2$) and tin phthalocyanine (SnPc) estimated using absorbance data. The measurement does not account for reflection losses. Normalized thin film absorption spectra for neat and mixed films of (b) SnPc and (c) SnNcCl$_2$ as a function of mixture composition.
peak at $\lambda=880$ nm decreases in intensity with increasing $C_{60}$ concentration due to the suppression of dimer formation. A similar red-shifting in the optical absorption edge has been also observed previously in substituted lead phthalocyanines.$^{195}$

Figure 8.2c shows the variation in optical absorption for SnNcCl$_2$ as a function of dilution with $C_{60}$. In contrast to the case of SnPc, the shape of the absorption spectrum for SnNcCl$_2$ does not exhibit a significant dependence on dilution. It is possible that in SnNcCl$_2$, the presence of two out-of-plane Cl atoms may frustrate dimer formation. Consequently, the absorption of SnNcCl$_2$ is likely intrinsically red-shifted compared to SnPc ($\lambda=745$ nm) due to extended conjugation present in SnNcCl$_2$. Since the infrared absorption feature in SnNcCl$_2$ does not depend on dimer formation, SnNcCl$_2$ could be a promising infrared absorbing material for use in bulk heterojunction OPVs.

### 8.3 Structural characterization

The thin film morphology of SnNcCl$_2$ was characterized using a combination of X-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD spectrum was collected from a 100-nm-thick organic film in the $\theta$-2$\theta$ geometry with Cu K$\alpha$ radiation ($\lambda=1.54$ Å). The film was deposited on a Si substrate at room temperature at a deposition rate of 0.2 nm/s. No diffraction peaks were observed in the XRD spectrum indicating that the film is amorphous. In addition, tapping mode AFM (repulsive regime) was conducted to quantify the roughness of SnNcCl$_2$ deposited on indium-tin-oxide (ITO). As shown in Figure 8.3, SnNcCl$_2$ has a fine granular structure with a root mean
square roughness of 4 nm. In contrast, previous studies have shown that SnPc film is polycrystalline. ¹⁸⁸,¹⁹⁶

8.4 Device performance

Organic photovoltaic cells were fabricated on glass substrates pre-coated with a 150-nm-thick ITO anode layer having a sheet resistance of 15 Ω/□. Prior to thin film deposition, substrates were treated using the procedure described in Appendix C. The donor and acceptor layer thicknesses were varied to determine the optimum layer thicknesses. Both optimized devices comprised a planar architecture containing a 15-nm-thick layer of the donor material and a 35-nm-thick acceptor layer of C₆₀. A 10-nm-thick exciton-blocking layer of bathocuproine (BCP) was grown on top of the active layers.¹⁰⁹ All devices were capped with a 65-nm-thick Al cathode that was deposited through a
shadow mask with 1 mm diameter openings. All layers were deposited at room temperature. The donor and $C_{60}$ layers were deposited at a growth rate of 0.2 nm/s, while BCP and Al were deposited at 0.25 nm/s and 0.3 nm/s, respectively.

The current density-voltage characteristics for optimized bilayer OPVs containing SnPc and SnNcCl$_2$ were compared both in the dark and under simulated AM1.5G solar illumination (134 mW/cm$^2$). As shown in Figure 8.4a, devices based on SnPc show a larger dark current density. Under illumination, both cells show comparable values of the short-circuit current density ($J_{SC}$) (Figure 8.4b). The device containing SnNcCl$_2$ has a larger open-circuit voltage ($V_{OC}$) compared to the device using SnPc.

Figure 8.4: Current density-voltage characteristics in (a) dark and (b) under simulated AM1.5G solar illumination at 134 mW/cm$^2$ for OPVs comprising (15 nm SnPc/35 nm $C_{60}$) or (15 nm SnNcCl$_2$/35 nm $C_{60}$) as active layer.
The operating parameters for optimized SnPc:C\textsubscript{60} and SnNcCl\textsubscript{2}:C\textsubscript{60} OPVs are shown in Figure 8.5 as a function of illumination intensity. The responsivity is defined as the ratio of J\textsubscript{SC} to the incident optical power. The responsivity for devices based on each donor material is comparable, and decreases at large illumination intensity (Figure 8.5a). The V\textsubscript{OC} increases linearly with the logarithm of illumination intensity for both devices (Figure 8.5b). The device containing SnNcCl\textsubscript{2} has a larger V\textsubscript{OC} than the device based on SnPc. The highest occupied molecular orbital (HOMO) energy level of SnPc has been previously measured using ultraviolet photoelectron spectroscopy to be 5.2 eV.\textsuperscript{188} Based

![Figure 8.5: The (a) responsivity, (b) open-circuit voltage (V\textsubscript{OC}), (c) fill factor (FF) and (d) power conversion efficiency (\eta\textsubscript{P}) for OPVs comprising (15 nm SnPc/35 nm C\textsubscript{60}) or (15 nm SnNcCl\textsubscript{2}/35 nm C\textsubscript{60}) as active layer as a function of illumination intensity.](image)
on the difference in $V_{OC}$ between OPVs based on SnPc and SnNcCl$_2$, the HOMO level of SnNcCl$_2$ is expected to be at $\sim$5.3 eV. The deeper HOMO level of SnNcCl$_2$ as inferred from $V_{OC}$ is consistent with the observation of a reduced dark current for OPVs based on SnNcCl$_2$ (Figure 8.4a).$^{79-81}$ The optimized SnNcCl$_2$ cell has a slightly larger fill factor (FF) relative to the optimized SnPc cell, possibly reflecting the lower dark current (Figure 8.5c).$^{79}$ Overall, a power conversion efficiency ($\eta_P$) of $(1.2\pm0.1)\%$ is obtained for the optimized SnNcCl$_2$ cell at 100 mW/cm$^2$ (AM1.5G), compared to $(0.8\pm0.1)\%$ for the optimized SnPc device (Figure 8.5d). Previous work has shown that further enhancements in device efficiency for OPVs based on SnPc can be realized through the use of organic and inorganic blocking layers between ITO and the active organic layer.$^{141}$ However, no similar improvement was observed in OPVs containing SnNcCl$_2$.

Figure 8.6 compares the external quantum efficiency ($\eta_{EQE}$) of optimized SnPc:C$_{60}$ and SnNcCl$_2$:C$_{60}$ based OPVs. The photoresponse occurring at $\lambda\leq$500 nm originates mainly from C$_{60}$ while the response at longer wavelengths corresponds to absorption in the donor material. A contribution to the photocurrent is clearly observed from both the monomer and dimer peaks in OPVs containing SnPc. Despite the high $\eta_{EQE}$ of C$_{60}$, both SnPc and SnNcCl$_2$ layers contribute approximately 50% to the $J_{SC}$ value of the respective device. The $\eta_{EQE}$ for each cell can be further enhanced by using bulk heterojunction active layers to increase the D-A interfacial area and hence, enhance the exciton diffusion efficiency. As such, SnNcCl$_2$ is an attractive material for realizing infrared absorption in a variety of applications such as tandem cells, organic photodetectors as well as building integrated photovoltaics.
This Chapter has presented the optical properties and OPV performance of a novel electron donor material SnNcCl\textsubscript{2} with sensitivity extending out to a wavelength of \(\lambda=1100\) nm. A comparison of the optical properties of SnPc and SnNcCl\textsubscript{2} reveals that while SnPc owes its infrared absorption to the formation of dimers, the infrared absorption of SnNcCl\textsubscript{2} is intrinsic to an extension in degree of conjugation of the molecule. In addition, a comparison of the device performance of OPVs based on SnPc and SnNcCl\textsubscript{2} demonstrates that a larger \(V_{OC}\) can be realized with the D-A pairing of SnNcCl\textsubscript{2}:C\textsubscript{60}. Both these factors make SnNcCl\textsubscript{2} an attractive candidate for fabricating

![Figure 8.6: External quantum efficiency (\(\eta_{\text{EQE}}\)) spectra for OPVs comprising (15 nm SnPc/35 nm C\textsubscript{60}) or (15 nm SnNcCl\textsubscript{2}/35 nm C\textsubscript{60}) as active layer.](image)
high efficiency bulk heterojunction tandem cells to extend the photoresponse of OPVs into the infrared. Overall, the results of this Chapter demonstrate that modifications in the molecular structure can be used to tune the optical properties of organic molecules and improve device performance.
Chapter 9-Conclusions and future work

The majority of this work has focused on developing novel device architectures and characterizing structure-property-performance relationships for organic photovoltaic cells (OPVs). The promising results obtained with graded heterojunctions to date have proved that this device architecture has the potential for high power conversion efficiency ($\eta_p$). Further optimization of this device architecture requires an understanding of the dependence of the exciton diffusion and charge collection efficiencies on film morphology. With this knowledge, the ultimate goal is to realize a high efficiency OPV cell. This Chapter will summarize the conclusions of work done so far and present the ideas for future research work.

9.1 Conclusions

This work has examined different approaches for overcoming the exciton diffusion bottleneck in OPVs using mixed and graded heterojunctions. Chapter 4 investigated the connection between device performance, charge transport properties and film morphology of uniform mixtures of boron subphthalocyanine chloride (SubPc):C$_{60}$. Structural characterization showed that while neat films of SubPc are amorphous, mixed films comprising 80 wt.% C$_{60}$ contains nanocrystalline domains of SubPc and C$_{60}$. As a result, both hole and electron mobilities are simultaneously optimized at 80 wt.% C$_{60}$ leading to optimum charge transport and hence, device performance at this composition.
A novel device architecture based on continuously graded donor-acceptor heterojunction was presented in Chapter 5. The large D-A interface area in a gradient increases the exciton diffusion efficiency relative to a planar heterojunction. In addition, the graded heterojunction enhances the charge collection and optical absorption efficiencies relative to a uniformly mixed OPV. The optimized graded heterojunction based on the D-A pairing of SubPc and C_{60} realized an increase in power conversion efficiency (\(\eta_P\)) of \(~35\%\) and \(~15\%\) relative to optimized planar and uniformly mixed heterojunction OPVs under simulated AM1.5G solar illumination at 100 mW/cm\(^2\), respectively. The use of gradients is a general technique and can be applied to any D-A system. As such, this work was extended to examine the device performance for mixed and graded heterojunction OPVs based on the D-A pairing of SubPc:C\(_{70}\). As an acceptor, C\(_{70}\) is a promising alternative to C\(_{60}\) due to its red-shifted absorption edge and large extinction coefficient, permitting increased photocurrent generation. In uniformly mixed OPVs based on SubPc:C\(_{70}\), peak \(\eta_P\) is realized in devices containing 80 wt.% C\(_{70}\). A continuously graded heterojunction OPV containing 80 wt.% C\(_{70}\) to realize further enhancement in device performance. A \(\eta_P = (5.4\pm0.2)\%\) was realized through the use of optimized graded heterojunction. To date, the peak efficiency of \((5.4\pm0.2)\%\) is the highest reported for this materials system.\(^{161}\) This high performance is made possible by the ability of the graded heterojunction to allow for the simultaneous optimization of the exciton diffusion efficiency and charge collection efficiency, representing a highly tunable device architecture for small molecule OPVs. The results of Chapter 3, 5 and 6
have demonstrated that the use of graded heterojunctions is not specific to any particular D-A pairing.

A novel approach to estimate the charge collection efficiency in an OPV without requiring any input from optical field simulations was discussed in Chapter 7. This technique was used to probe the compositional dependence of charge collection efficiency in uniform mixtures of SubPc:C$_{60}$ and compare the charge collection efficiency in optimized gradients with optimized uniform mixtures. Chapter 8 introduced a novel electron donor material for use in OPVs with sensitivity extending into the infrared. Its complimentary absorption with SubPc makes it an attractive candidate for fabricating tandem cells and hence, realizing further improvement in device performance.

### 9.2 Future work

In spite of the rapid improvement in OPVs over the last decade, further enhancement in device efficiency is required for OPVs to become a competitive and cost-effective technology. The use of graded heterojunctions is a promising route to high performance OPV. However, more work needs to be done to understand the limitations of this architecture and further optimize the film morphology. With further optimization of film morphology, additional enhancements in FF and J$_{SC}$ may be possible, leading to even higher efficiency. This section discusses some ideas for future research work.

#### 9.2.1 Broadband spectral coverage
The narrow absorption spectrum of many organic semiconductors makes it difficult to absorb the entire solar spectrum using a single D-A pair. As discussed in Chapter 8, long-wavelength absorbing materials need to be incorporated in the device, since approximately 50% of the total photon flux is in the red and near-infrared region.\textsuperscript{141, 197, 198} However, infrared absorbing materials in general result in lower open-circuit voltage ($V_{OC}$) owing to their lower energy gap. Therefore, it becomes imperative to use more than one D-A pair in the device to enhance spectral overlap while preserving the $V_{OC}$. One way to enhance the spectral overlap is the use of a multicell series stack of OPV cells, referred to as tandem cells (Figure 9.1a). In this architecture, the currents generated in each subcell flow in series to the opposing electrodes and therefore, the net current in the cell is limited by the smallest current generated by a particular subcell. The $V_{OC}$ of the tandem cell is equal to the sum of the $V_{OC}$ of the subcells. Significant

![Figure 9.1: (a) Simplified device architecture of a tandem cell. (b) The absorption spectra of SubPc and SnNcCl$_2$.](image)

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enhancement in $\eta_P$ has been realized in planar and mixed OPVs using tandem architectures.\textsuperscript{148, 166, 199-202} The idea with graded heterojunction tandem cells is to combine two optimized graded cells fabricated with different D-A pairs which absorb in different regions of the solar spectrum. The two donor materials explored in this work, SubPc and SnNcCl\textsubscript{2}, have complimentary absorption spectra (Figure 9.1b). While high efficiency was demonstrated for cells containing SubPc and C\textsubscript{70}, the performance of OPVs based on SnNcCl\textsubscript{2} needs to be further improved by using mixed or graded heterojunction OPVs. Using optimized single cells, a near addition of $\eta_P$ of single cells can be realized by careful optimization of this tandem architecture.

9.2.2 Optimizing film morphology

In polymer based OPVs, the phase separation of polymers during solvent evaporation or from annealing at elevated temperature creates donor and acceptor domains which help to achieve high charge collection efficiency in the active organic layer.\textsuperscript{120-122, 203-207} Atomic force microscopy (AFM) and transmission electron microscopy (TEM) studies indicate that annealing the device at high temperature creates nanoscale networks with high crystalline order. These morphological advantages account for high $\eta_P$ values realized with polymer bulk heterojunctions.

The effect of thermal treatment has not been explored in great detail in small molecule OPVs.\textsuperscript{63, 208} The results in Chapter 7 indicate that the charge collection efficiency in forward bias in the optimized mixed and graded heterojunction is low and ultimately limits the performance of these cells. The low charge carrier mobility in these
systems is partly responsible for the low charge collection efficiency. As discussed in Chapter 4, uniformly mixed films of SubPc and C$_{60}$ containing 80 wt.% C$_{60}$ contain nanocrystalline domains of SubPc and C$_{60}$ when the film is deposited at room temperature at a growth rate of 0.2 nm/s. Previous studies on thermal treatment have shown that

![Figure 9.2](image)

Figure 9.2: (a) X-ray diffraction spectrum (b) atomic force microscopy height image (c) transmission electron microscopy image and (d) transmission electron microscopy image of a different region of uniformly mixed SubPc:C$_{60}$ film containing 80 wt.% C$_{60}$ deposited at 0.02 nm/s and 100 °C.
heating the substrate during film growth and deposition at a slower growth rate promotes crystallization.\textsuperscript{186, 209} In order to probe the effect of growth rate and substrate heating, a uniformly mixed film of SubPc and C\textsubscript{60} film containing 80 wt.% C\textsubscript{60} was deposited at 0.02 nm/s and 100 °C. Structural characterization was performed using x-ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Figure 9.2). The XRD spectrum shows the diffraction peaks corresponding to the (111), (220) and (311) planes of C\textsubscript{60}.\textsuperscript{146, 154} However, the XRD pattern does not show evidence of SubPc crystallinity. As shown in the AFM image (Figure 9.2b), the annealed mixed film contains large crystalline domains on the order of ~100 nm. These large crystalline domains are also visible in the TEM images (Figure 9.2c and d). However, the large roughness of the film is detrimental to device performance. As such, the annealed film needs to be planarized before device fabrication. In addition, further characterization using selected area electron diffraction (SAED) is required to probe the existence of SubPc crystallinity in annealed mixed films. The presence of large crystalline domains of SubPc and C\textsubscript{60} can potentially increase both hole and electron mobilities resulting in improved charge collection efficiencies and therefore, $\eta_P$.

\textbf{9.2.3 Transient measurement of charge collection and recombination}

Chapter 7 emphasized the importance of characterizing the charge collection efficiency in OPVs. The results of work of chapter 7 show that both mixed and graded heterojunction OPVs have low charge collection efficiency in the forward bias. However, the reason for this low charge collection efficiency is not clearly understood. As
mentioned earlier, the charge collection efficiency in an OPV can be thought of as a competition between charge transport to the electrodes (Figure 9.3a) and electron-hole recombination (Figure 9.3b). Recombination leads to a loss of optically generated excitons and can significantly reduce the efficiency of the cell. However, there has been only limited attention given to these parasitic loss processes.

![Figure 9.3: Representation of the charge collection process in an OPV. (a) Charge carriers are collected at the respective electrodes generating photo-current. (b) Recombination of electron and holes is a possible loss mechanism in this device.](image)

The relative time scales (rates) of the charge collection and recombination processes can be determined by measuring time-dependent photo-current and photovoltage measurements. The rate of recombination is largest at the $V_{OC}$ and the rate of $V_{OC}$ decay is proportional to the rate of recombination. Thus, measurements of the $V_{OC}$ decay can be used to estimate the rate of recombination.$^{210}$ Similarly, the rate of photo-current decay at short-circuit corresponds to the average transit time of charge carriers.$^{210, 211}$ These measurements will allow estimates to be made of the charge collection efficiency ($\eta_{CC}$) which can be expressed as:
\[
\eta_{CC} = \frac{(1/\tau_{\text{transit}})}{(1/\tau_{\text{transit}}) + (1/\tau_{\text{recombination}})} \times 100
\]

(9.1)

where \(\tau_{\text{transit}}\) and \(\tau_{\text{recombination}}\) are characteristic time scales for charge transport to the electrode and recombination, respectively. A comparison of these time scales would determine the main limitation to the charge transport process thus, identifying the key areas important for further improvement of mixed and graded heterojunction OPVs.

The contributions made in this work have led to the realization of high efficiency OPVs and the development of new characterization techniques for OPVs. Further improvements in device design and materials selection may allow for additional enhancement in device performance. In addition to improving device efficiency, more work needs to be done to improve the lifetime of OPVs. With high efficiency and improved lifetimes, OPV commercialization may be possible in the near future.
Chapter 10-Bibliography


circuit voltage in organic photovoltaic cells with diindenoperylene as donor material," 


Appendix

A. List of Publications, Presentations and Patents

Publications


Presentations


2. Efficient organic photovoltaic cells using nanocrystalline donor-acceptor blends, Industrial Partnership for Research in Interfacial and Materials Engineering (IPrime), June 2012, Minneapolis, MN. (Poster)

4. Efficient organic photovoltaic cells using nanocrystalline donor-acceptor blends, *MRSEC Site visit*, February 2012, Minneapolis, MN. (Poster)


**Patents**


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Chapter 4

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Licensed content author: Richa Pandey, Russell J. Holmes
Licensed content date: Sep 24, 2010
Start page: 5301
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Type of use: Dissertation/Thesis
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License Number: 2956540432506
Order Date: July 26, 2012
Publisher: American Institute of Physics
Publication: Applied Physics Letters
Article Title: Efficient, bulk heterojunction organic photovoltaic cells based on boron subphthalocyanine chloride-C70
Author: Richa Pandey, Yunlong Zou and Russell J. Holmes
Online Publication Date: July 19, 2012
Volume number: 101
Issue number: 3
Type of Use: Thesis/Dissertation
Requestor type: Author (original article)
Format: Print and electronic
Portion: Excerpt (> 800 words)
Will you be translating?: No
Title of your thesis / dissertation: Nanoscale Engineering of thin film morphology for efficient organic photovoltaic cells
Expected completion date: Jul 2012
Estimated size (number of pages): 200
Total: 0.00 USD
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Order Date: May 18, 2012
Publisher: American Institute of Physics
Publication: Applied Physics Letters
Article Title: Characterizing the charge collection efficiency in bulk heterojunction organic photovoltaic cells
Author: Richa Pandey, Russell J. Holmes
Online Publication Date: Feb 22, 2012
Volume number: 100
Issue number: 8
Type of Use: Thesis/Dissertation
Requestor type: Author (original article)
Format: Print and electronic
Portion: Excerpt (> 800 words)
Will you be translating?: No
Title of your thesis / dissertation: Nanoscale Engineering of thin film morphology for efficient organic photovoltaic cells
Expected completion date: Jul 2012
Estimated size (number of pages): 200
Total: 0.00 USD

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C. Substrate Preparation

All organic photovoltaic cells in this work were fabricated on glass substrates pre-coated with a 150-nm-thick indium-tin-oxide (ITO) anode layer having a sheet resistance of 15 $\Omega/\square$. The standard procedure used for cleaning substrates involved sonication in tergitol solution for five minutes followed by sonication in deionized water for another five minutes. Subsequently, the substrates were sonicated in acetone for five minutes. Finally, the substrates were boiled in isopropyl alcohol solution for five minutes. The substrates were exposed to UV-ozone treatment for 5 minutes prior to deposition.
D. Derivation of Poole-Frenkel Mobility

Derivation of current density-voltage relationship for space charge limited current model in the presence of a strong applied electric field adapted from Reference 210. This derivation is done for inorganic semiconductors.

Assuming the semiconductor consists of a single set of traps situated at energy (Δ) below the conduction band, the fraction of free charges (θ₀) is given by:

\[ θ₀ = \frac{ρ_f}{ρ_f + ρ_t} = \frac{N_c}{N_t} \exp\left(\frac{-Δ}{kT}\right) \]  

where \( ρ_f \) and \( ρ_t \) are the free and trapped charge densities, respectively, \( N_c \) is the effective density of states in the conduction band, \( N_t \) is the density of traps, \( k \) is the Boltzmann’s constant and \( T \) is the temperature. In the presence of an applied electric field, the

![Figure 1: The effect of applied electric field on the depth of trap states. The zero of x is at the trap center. Adapted from Reference 116.](image-url)
effective depth of a trap may be reduced. The potential energy (PE) of the electron with an applied electric field can be written as:

\[ PE(x) = -\frac{e^2}{4\pi\varepsilon\varepsilon_0 x} - eEx \]  

(2)

where \( e \) is the electronic charge, \( \varepsilon \) is the relative dielectric constant of the material, \( \varepsilon_0 \) is the relative permittivity of free space, \( E \) is the applied electric field in the \( x \)-direction and \( x \) is the distance from the trap center. The maximum value of the potential energy can be calculated by setting the derivative of \( PE \) with respect to \( x \) equal to zero (Figure 1). The maximum value of \( PE \) is:

\[ PE_{\text{max}} = -\left( \frac{e^3 E}{\pi\varepsilon_0} \right)^{\frac{1}{2}} \]  

(3)

The effective depth of the trap is reduced by \( PE_{\text{max}} \) and thus, the fraction of free charge carriers is increased. As such, Equation 1 is modified as follows:

\[ \frac{\rho_f}{\rho_f + \rho_i} = \frac{N_c}{N_i} \exp \left( -\frac{\Delta}{kT} + \frac{1}{kT} \left( \frac{e^3 E}{\pi\varepsilon_0} \right)^{\frac{1}{2}} \right) = \theta_0 \exp \left( \beta E^{\frac{1}{2}} \right) \]  

(4)

where

\[ \beta = \frac{1}{kT} \left( \frac{e^3}{\pi\varepsilon_0} \right)^{\frac{1}{2}} \]  

(5)

If the contribution of diffusion is neglected, the current density (\( J \)) is given by
\[ J = \mu_0 \rho_f E \]  

(6)

where \( \mu_0 \) is the mobility. Additionally, the Poisson’s equation can be written as

\[
\frac{dE}{dx} = \frac{\rho_f + \rho_t}{\varepsilon \varepsilon_0} 
\]

(7)

Substituting for \( \rho_f \) using Equation 4 and \( (\rho_f + \rho_t) \) based on Equation 7, Equation 6 can be re-written as

\[
J = \mu_0 \theta_0 \varepsilon \varepsilon_0 E \exp(\beta E^{1/2}) \frac{dE}{dx}
\]

(8)

Integrating Equation 8 by-parts yields

\[
\frac{Jx}{\mu_0 \theta_0 \varepsilon \varepsilon_0} = \frac{2}{\beta^4} \left[ \exp(\beta E^{1/2}) \left\{ \beta^3 E^{3/2} - 3\beta^2 E + 6\beta E^{1/2} - 6 \right\} + 6 \right]
\]

(9)

where the injecting electrode is at \( x=0 \), \( E(0) \) is assumed to be zero. In this equation, \( E = \frac{dV}{dx} \) where \( V \) is the voltage. Equation 9 cannot be solved analytically. A numerical solution has been demonstrated for Equation 9 as follows:\(^{212}\)

\[
J = \frac{9}{8} \mu_0 \varepsilon \varepsilon_0 \theta_0 \frac{V^2}{L^3} \exp \left\{ 0.891 \left( \frac{e^3 V}{kT \left( \frac{\varepsilon \varepsilon_0 L}{\pi} \right)^{3/2}} \right) \right\}
\]

(10)

or

\[
J = \frac{9}{8} \mu_\varepsilon \varepsilon_0 \theta_0 \frac{V^2}{L^3}
\]

(11)
with
\[ \mu = \mu_0 \exp \left\{ \frac{0.891 \left( e^\gamma V \right)^{1/2}}{kT \left( \frac{\pi \varepsilon \varepsilon_0 L}{12} \right)} \right\} = \mu_0 \exp \left\{ \gamma \left( \frac{V}{L} \right)^{1/2} \right\} \] (12)

where \( \mu \) is the Poole Frenkel mobility, \( \gamma \) is the field-activation parameter and \( L \) is the thickness of the layer.
E. Photocurrent Simulation Code

Optical model developed by Petterson et al. was used to simulate the photocurrent in a planar device architecture. The following code was written in MATLAB for this optical model.

clear all
close all
clc
m=7;
phi=0;
charge=1.6*10^(-19);
E0=1;
x1(1)=0;
x2(1)=0;

d(1)=0;
d(2)=130*10^(-9);
d(3)=13*10^(-9);
d(4)=35*10^(-9);
d(5)=10*10^(-9);
d(6)=50*10^(-9);
d(7)=0;

% Diffusion length of donor and acceptor materials
Ld(3)=8.5*10^(-9);
Ld(4)=17*10^(-9);
beta(3)=(1/(Ld(3)));
beta(4)=(1/(Ld(4)));
D(3)=(Ld(3)*Ld(3))/(10^(-9));
D(4)=(Ld(4)*Ld(4))/(10^(-9));

for i=1:m
   dx(i)=0.01*d(i);
end

load intensity.txt
load constants.txt

for k=1:326
   lam(k)=constants(k,1);
   lambda(k)=constants(k,1)*(10^(-9));
   Intensity(k)=intensity(k,1);
Npho(k)=((Intensity(k)*lambda(k))/(1.9878*10^(-25)));

for i=1:m
    n(i,k)=constants(k,2*i)+j*constants(k,2*i+1);
end

for i=1:m
    nr(i,k)=real(n(i,k));
    alpha(i,k)=((4*pi*imag(n(i,k)))/lambda(k));
end

for i=1:m
    q(i,k)=sqrt((n(i,k)*n(i,k))-(real(n(1,k))*real(n(1,k))*sin(phi)));
end

for i=1:m
    e(i,k)=((2*pi*q(i,k))/lambda(k));
end

for i=1:(m-1)
    r(i,k)=((q(i,k)-q(i+1,k))/(q(i,k)+q(i+1,k)));
    t(i,k)=((2*q(i,k))/(q(i,k)+q(i+1,k)));
    I(:,:,i,k)=(1/t(i,k))*[1 r(i,k);r(i,k) 1];
end

for i=1:m
    L(:,:,i,k)=[exp(-j*e(i,k)*d(i)) 0;0 exp(j*e(i,k)*d(i))];
end

S(:,:,k)=eye(2,2);

for i=1:(m-2)
    S(:,:,k)=S(:,:,k)*I(:,:,i,k)*L(:,:,i+1,k);
end

S(:,:,k)=S(:,:,k)*I(:,:,m-1,k);

R(k)=S(2,1,k)/S(1,1,k);
T1(k)=1/S(1,1,k);

RC(k)=R(k)*conj(R(k));
TC(k)=T1(k)*conj(T1(k));
Abs(k)=1-RC(k)-TC(k);
for n=2:(m-1)
S1(:,:,n,k)=eye(2,2);
S2(:,:,n,k)=eye(2,2);
for a=1:(n-2)
S1(:,:,n,k)=S1(:,:,n,k)*I(:,:,a,k)*L(:,:,a+1,k);
end
S1(:,:,n,k)=S1(:,:,n,k)*I(:,:,n-1,k);
for a=n:(m-2)
S2(:,:,n,k)=S2(:,:,n,k)*I(:,:,a,k)*L(:,:,a+1,k);
end
S2(:,:,n,k)=S2(:,:,n,k)*I(:,:,m-1,k);
end

for i=2:(m-1)
    r1(i,k)=S1(2,1,i,k)/S1(1,1,i,k);
    t1(i,k)=1/S1(1,1,i,k);
    r2(i,k)=S2(2,1,i,k)/S2(1,1,i,k);
    t2(i,k)=1/S2(1,1,i,k);
    tplus(i,k)=(t1(i,k)/(1+(r2(i,k)*exp(j*2*e(i,k)*d(i))*(S1(1,2,i,k)/S1(1,1,i,k)))));
    tminus(i,k)=tplus(i,k)*r2(i,k)*exp(j*2*e(i,k)*d(i));
    rho(i,k)=abs(r2(i,k));
    delta(i,k)=angle(r2(i,k));
    T(i,k)=(nr(i,k)/nr(1,k))*(abs(tplus(i,k))^2);
end

for i=2:(m-1)
    for p=(i-2)*100+1:(i-1)*100
        for l=1:101
            x(i,l)=0.01*(l-1)*d(i);
        end
    end
end

E1(i,l,k)=E0*((S2(1,1,i,k)*exp(-j*e(i,k)*(d(i)-x(i,l)))+S2(2,1,i,k)*exp(j*e(i,k)*(d(i)-x(i,l))))/(S1(1,1,i,k)*S2(1,1,i,k)*exp(j*e(i,k)*d(i))+S1(1,2,i,k)*S2(2,1,i,k)*exp(j*e(i,k)*d(i))));

E(i,l,k)=E1(i,l,k)*conj(E1(i,l,k));
    E1(i,l,k)=E0*tplus(i,k)*(exp(j*e(i,k)*x(i,l))+r2(i,k)*exp(j*e(i,k)*(2*d(i)-x(i,l))));
    E(i,l,k)=E1(i,l,k)*conj(E1(i,l,k));
    x1(p+1)=x1(p)+dx(i);
end
end
for i=3:3
C1(i,k)=((rho(i,k)^2)*exp(-2*alpha(i,k)*d(i)));
C2(i,k)=(((beta(i)^2)-alpha(i,k)^2))/((beta(i)^2)+((4*pi*nr(i,k)/lambda(k))^2)))*
(2*rho(i,k)*exp(-alpha(i,k)*d(i)));
B(i,k)=(((alpha(i,k)*exp(-beta(i)*d(i))-beta(i)*exp(-alpha(i,k)*d(i)))+C1(i,k)*
(exp(-beta(i)*d(i))+alpha(i,k)*exp(alpha(i,k)*d(i)))-C2(i,k)*((4*pi*nr(i,k))/lambda(k))*
((4*pi*nr(i,k)*d(i))/lambda(k))+delta(i,k)+beta(i)*cos(delta(i,k)))/
(beta(i)*exp(-beta(i)*d(i)))+beta(i)*exp(beta(i)*d(i)));
A(i,k)=((-beta(i)*exp(beta(i)*d(i))-alpha(i,k)*exp(-alpha(i,k)*d(i)))+C1(i,k)*
(exp(beta(i)*d(i)))+alpha(i,k)*exp(alpha(i,k)*d(i)))+C2(i,k)*
((4*pi*nr(i,k))/lambda(k))*sin(delta(i,k)))/(beta(i)*exp(-beta(i)*d(i)))+
beta(i)*exp(beta(i)*d(i)));
kappa(i,k)=((alpha(i,k)*T(i,k)*Npho(k))/(D(i)*((beta(i)^2)-alpha(i,k)^2)));
end
for i=4:4
C1(i,k)=((rho(i,k)^2)*exp(-2*alpha(i,k)*d(i)));
C2(i,k)=(((beta(i)^2)-alpha(i,k)^2))/((beta(i)^2)+((4*pi*nr(i,k)/lambda(k))^2)))*
(2*rho(i,k)*exp(-alpha(i,k)*d(i)));
B(i,k)=((-beta(i)*exp(-beta(i)*d(i))-alpha(i,k)*exp(-alpha(i,k)*d(i)))+C1(i,k)*
(exp(-beta(i)*d(i))+alpha(i,k)*exp(alpha(i,k)*d(i)))+C2(i,k)*
((4*pi*nr(i,k))/lambda(k))*cos(delta(i,k)))/(beta(i)*exp(-beta(i)*d(i)))+
beta(i)*exp(beta(i)*d(i)));
A(i,k)=((-beta(i)*exp(beta(i)*d(i))-alpha(i,k)*exp(-alpha(i,k)*d(i)))+C1(i,k)*
(exp(beta(i)*d(i)))+alpha(i,k)*exp(alpha(i,k)*d(i)))+C2(i,k)*
((4*pi*nr(i,k))/lambda(k))*sin(delta(i,k)))/(beta(i)*exp(-beta(i)*d(i)))+
beta(i)*exp(beta(i)*d(i)));
kappa(i,k)=((alpha(i,k)*T(i,k)*Npho(k))/(D(i)*((beta(i)^2)-alpha(i,k)^2)));
end
for i=3:4
for p=(i-3)*100+1:(i-2)*100
for l=1:101
x(i,l)=0.01*(l-1)*d(i);
Gex(i,l,k)=(alpha(i,k)*T(i,k)*2.3*lambda(k)/(6.63*10^(-34)*3*10^8))*(exp(-alpha(i,k)*
x(i,l))+rho(i,k)*rho(i,k)*exp(-alpha(i,k)*(2*d(i)-x(i,l)))+C1(i,k)*cos(((4*pi*nr(i,k)*(d(i)-
x(i,l)))/lambda(k))+delta(i,k)));

Gex(i,l,k)=((alpha(i,k)*T(i,k)*Intensity(k)*lambda(k))/(19.89*10^(-26)))*(exp(-
alpha(i,k)*x(i,l))+rho(i,k)*rho(i,k)*exp(-alpha(i,k)*(2*d(i)-x(i,l)))+C1(i,k)*cos(((4*pi*nr(i,k)*(d(i)-x(i,l)))/lambda(k))+delta(i,k)));

x2(p+1)=x2(p)+dx(i);
end
end
end

for i=3:4
for p=(i-3)*100+1:(i-2)*100
for l=1:101
x(i,l)=0.01*(l-1)*d(i);
next(i,l,k)=(kappa(i,k))*(A(i,k)*exp(-beta(i)*x(i,l))+B(i,k)*exp(beta(i)*x(i,l))+exp(-
alpha(i,k)*x(i,l))+C1(i,k)*exp(alpha(i,k)*x(i,l))+C2(i,k)*cos(((4*pi*nr(i,k)*(d(i)-x(i,l)))/lambda(k))+delta(i,k)));
x2(p+1)=x2(p)+dx(i);
end
end
end

Jphoto(3,k)=D(3)*charge*kappa(3,k)*(beta(3)*A(3,k)*exp(-beta(3)*d(3))-beta(3)*B(3,k)
*exp(beta(3)*d(3))+alpha(3,k)*exp(-alpha(3,k)*d(3))-alpha(3,k)*C1(3,k)*exp(alpha(3,k)*
d(3))-((4*pi*nr(3,k))/lambda(k))*C2(3,k)*sin(delta(3,k)));

Jphoto(4,k)=D(4)*charge*kappa(4,k)*(-beta(4)*A(4,k)+beta(4)*B(4,k)-alpha(4,k)
+alpha(4,k)*C1(4,k)+((4*pi*nr(4,k))/lambda(k))*C2(4,k)*sin(((4*pi*nr(4,k)*d(4))/lamb
da(k))+delta(4,k)));

Jtotal(k)=Jphoto(3,k)+Jphoto(4,k);
EQE(k)=1240*((Jtotal(k)*(100))/(lambda(k)*10^9*Intensity(k)));
end

Jsctotalcum=cumtrapz(lambda,Jsc);
Jsctotal=trapz(lam,Jsc);
% % in Units of mA/cm2
Jsc=0.1*Jsctotal

plot(lambda,EQE)