Transport, material characterization, and device applications of photovoltaic polymers used in bulk heterojunction solar cells

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Transport, Material Characterization, and Device Applications of Photovoltaic Polymers Used in Bulk Heterojunction Solar Cells

LEE Ka Hin

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Principal Supervisor: Prof. SO Shu Kong
Hong Kong Baptist University
November 2014
Declaration

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

Signature: __________________

Date: November 2014
Abstract

This thesis presents the transport, material characterization, and device applications of photovoltaic polymers used in bulk heterojunction solar cells. These three areas were found to be well correlated. Materials properties affect charge transport behaviors. Charge transport behaviors affect organic photovoltaic (OPV) cell performances. Two typical PV polymers were selected for investigation. They were poly(3-hexylthiophene) (P3HT) and poly[N-9”-heptadecanyl-2,7- carbazole-alt-5,5-(4’,7’-di-2- thienyl-2’,1’,3’- benzothiadiazole)] (PCDTBT).

Different charge transport measurement techniques were employed to study how charge carriers move in OPV materials including space-charge-limited current (SCLC) measurement, dark-injection space-charge-limited current (DI-SCLC) measurement, and admittance spectroscopy (AS). For hole transport measurement on P3HT, electron leakages were found in a presumed hole-only device structure resulting in ill-defined DI-SCLC and AS signals. After inserting a thin electron blocking and trapping (EBT) layer between the active layer and the Au cathode, the electron leakages can be significantly suppressed leading to well-defined transport measurement signals. Applying the EBT layer to the polymer:fullerene bulk heterojunction (BHJ) blends, the transport properties can also be studied.

Charge transport measurements were carried out at different temperatures for Gaussian Disorder Model (GDM) analysis to extract energetic disorders $\sigma$ and high-temperature limit mobilities $\mu_{\infty}$. For P3HT BHJ films, $\sigma$ were found to be
much smaller than PCDTBT BHJ films. Within the same polymer system, similar \( \sigma \) were extracted. \( \sigma \) can be correlated to the device parameters such as open-circuit voltage \( V_{OC} \) and fill factor \( FF \). Large \( \sigma \) was found to limit both \( V_{OC} \) and \( FF \).

With the experience of transport measurement for PV materials gained, we focused on a common problem of batch-to-batch variations in device performance. Five batches of amorphous polymers PCDTBT were purchased from two vendors. From gel permeation chromatography, bimodal distributions of molecular weight were observed in all five batches of PCDTBT with different fraction of small molecular weight component. The corresponding charge carrier mobilities and device performances drop significantly with the small molecular weight component. From GDM, all five batches of polymers have similar \( \sigma \). However, \( \mu_\infty \) for each batch of PCDTBT appear to have significant differences. The differences originate from the variation of charge carrier hopping distances caused by different amounts of the small molecular weight component of PCDTBT.

At last, ZnO prepared by low temperature annealing sol gel method was used as functional layers for OPV cells and charge transport measurements. Structural, elemental, energetic, optical, and electrical characterizations were performed to examine the ZnO. The results suggested that the ZnO should be suitable for organic device applications. The applications of the ZnO on inverted OPV cells and charge transport measurements were demonstrated.
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Chapter 1
Introduction

Organic electronics is a fast-growing research field in the past three decades because of the unique properties of organic materials. Devices fabricated from organic materials can be lightweight, semi-transparent, compatible with flexible substrates, processable at low temperatures, and potentially low cost. Organic light-emitting diode (OLED), organic photovoltaic (OPV) cell, and organic field-effect transistor (OFET) are the three main categories of organic devices.

In 1986, Tang published the first organic photovoltaic (OPV) cell paper using a two-layer structure of copper phthalocyanine (CuPc) and a perylene tetracarboxylic derivative as an electron donor and an electron acceptor, respectively. The power conversion efficiency (PCE) is about 1 %. Figure 1.1 shows the corresponding current-voltage (J-V) characteristic.[1.1] One year later, he and VanSlyke published the first organic light-emitting diode (OLED) paper using an aromatic diamine and 8-hydroxyquinoline aluminum (Alq3) in a bilayer device configuration resulting in a luminous efficiency of 1.5 Im/W and the corresponding J-V characteristic is shown in Figure 1.2.[1.2] In this bilayer OLED, the diamine acts as the hole transporting layer while Alq3 acts both as the electron transporting and emissive layer. Although OLED was invented later than OPV cell, the development of OLED was much faster. OLEDs have been integrated into different kinds of electronic devices we use every day including mobile phones, tablets, digital cameras, and televisions as shown in Figure 1.3. There are several advantages of using OLEDs as displays compared to commonly
used liquid crystal displays (LCD). OLED is self-emitting light source while LCD requires liquid crystal placed in front of a back light panel. Therefore, OLEDs can display real black colour by turning off pixels while LCDs cannot, resulting a higher contrast ratio for OLED displays. Due to the self-emitting nature of OLED, the viewing angle of OLED display is usually larger than that of LCD.

The research and industrial application of OLEDs are still growing. There are many opportunities for OLEDs other than the existing OLED products such as flexible displays, transparent displays, lightings, etc. Besides improving the power efficiency, obtaining better colour emission such as blue light and longer device lifetime are also very important and challenging issues for future development of OLED.

Parallel to the development of OLEDs, efficiencies of single junction OPV cells have been improved considerably from about 1 % in 1986 to about 11 % in 2014. Some of the best performing OPV cells were recorded by National Renewable Energy Laboratory (NREL) in the best research-cell efficiency chart as shown in Figure 1.4. The improvement over these years can be attributed to two main reasons.
Figure 1.1 The first OPV cell published by Tang in 1986.[1.1]
Figure 1.2   The first OLED published by Tang and VanSlyke in 1987.[1.2]
Figure 1.3Examples of OLED integrated electronic devices. Curved OLED displays in (a) Samsung Galaxy Note Edge and (b) LG G Flex mobile phones. OLED electronic viewfinder in (c) Fujifilm X-E1 digital camera. Curved OLED display in (d) Samsung OLED S9C Series Smart TV television.
Figure 1.4 Best research-cell efficiency chart from National Renewable Energy Laboratory.
First, bulk-heterojunction (BHJ) structure consisting of a mixture of donor and acceptor, which was first proposed by Heeger in 1995, is used instead of the bilayer structure.\[1.3\] In a bilayer structure, as the diffusion length of the bound electron hole pairs is only in the order of 10 nm, free charge carriers can only be generated by the absorbed photons within the short diffusion length from the donor-acceptor (DA) interface.\[1.4 – 1.6\] However, a BHJ blend mixes the donor and acceptor together. As a result, DA interfaces are dispersed over the whole active layer and lead to increase in the overall DA interfacial area by allowing more charge separation.

Second, the improvement of the donor materials also drives the field forward. The chemical structures of some important donor materials are shown in Figure 1.5. In the early stage, metal phthalocyanines (Pc) or poly(p-phenylenevinylene) (PPV) derivatives such as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) were used as donor materials in the OPV cells and the corresponding \( \text{PCE} \) are around 1 – 3 \%.\[1.1, 1.3, 1.7, 1.8\] Later, but before 2009, poly(3-hexylthiophene-2,5-diyl) (P3HT) was the most promising donor with \( \text{PCE} \) of 3 – 5 \%.\[1.9\] Since 2009, several donor-acceptor copolymers such as poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) were found to perform better than P3HT with \( \text{PCE} \) of 5 – 9 \%.\[1.10, 1.11\] Generally, energy level engineering of the donor materials is the key strategy that leads to the improvement. In particular, the bandgaps of the donor material are reduced from about 2.2 eV for PPV type polymer to 2.0 eV for P3HT. The bandgaps
of copolymer donor materials are further reduced to 1.9 eV and 1.6 eV for PCDTBT and PTB7, respectively. A smaller bandgap causes the optical absorption red-shift. From 2.2 eV to 1.6 eV bandgap, the cutoff absorption shifts from green light to near infrared and covers a larger portion of the solar spectrum.

Although there is a rapid improvement in the efficiency of OPV cells over the past two decades, large scale commercial products are not yet available. However, there are some OPV cell products for conceptual demonstrations as shown in Figure 1.6. There are multiple issues to be overcome which may include cost, stability, and efficiency. In particular, there are two main challenges of achieving high efficiency.[1.12] First, the bandgap of donor material should be further reduced to have broader solar absorption. Dennler et al. estimated the limit of $PCE$ as a function of donor bandgap with reasonable assumptions as shown in Figure 1.7.[1.9] For a donor material with bandgap close to 1.24 eV (1000 nm) and reasonable loss (the middle curve in Figure 1.7), the $PCE$ can exceed 20 %. Second, the mobilities of BHJ blend are not high enough. Higher mobilities can improve sweep out of the charge carriers before recombination. In addition, higher mobilities enable thicker active layer which can absorb more sunlight. For the state of the art BHJ system, PTB7 and [6,6]-phenyl C\textsubscript{71} butyric acid methyl ester (PC\textsubscript{71}BM), the optimized active layer thickness is only around 100 nm.[1.11]
Figure 1.5  Chemical structures of some important donor materials used in the past two decades.
Figure 1.6 Conceptual products of OPV cells from Solarmer Energy Inc. and Konarka Inc.: (a) portable power, (b) photovoltaic roof, (c) off-grid, and (d) building-integrated photovoltaics.
Figure 1.7  Estimation of power conversion efficiency as a function of donor bandgap. A external quantum efficiency (EQE) of 90 % and a fill factor (FF) of 0.7 were used for calculation. CT stands for charge transfer.[1.9]
In organic electronics, despite the successes of OLEDs and rapid growth in the efficiencies of OPV cells, there is still room for improvement especially in OPV cells. For electronic devices, the study of charge carrier transport can be viewed as the most fundamental and yet relevant issue for understanding device operations. Through better understanding, we may further improve the device performance and the stability.

In this thesis, we employ different transport measurement techniques to study the transport properties of polymeric PV materials and correlate the transport properties to device performances. Due to the latest development of the donor materials, we focus on the hole transport in both PV polymers and their BHJ blends. Chapter 2 covers the basic concepts for organic semiconductors and devices. Chapter 3 provides the details of the experimental work. Chapters 4 to 6 present the results and discussions. In Chapter 4, we report the problem of minority carrier leakage in the transport measurement and how it can be overcome to extract reliable transport information. Chapter 5 discusses the origin of a well-known problem in polymer solar cells, i.e. batch-to-batch variations of polymer from commercial vendors and the impacts on the PCE. We trace the origin of the variations to the molecular weight variations of polymers and the corresponding transport properties. Chapter 6 provides a solution processable method to fabricate ZnO to act as a functional layer for OPV cells and electron transport characterization for OPV materials. Finally, Chapter 7 concludes the work of this thesis.
References:


Chapter 2

Basic Concepts for Organic Semiconductors and Devices

2.1. Electronic Structure of Organic Materials

Organic materials are hydrocarbon molecules. Atomic orbitals of adjacent carbon atoms, sp$^2$, overlap and form a bonding and an antibonding molecular orbitals, $\sigma$ and $\sigma^*$, respectively. $\sigma$ bonds are the strongest type of covalent bond because of the head-on overlapping of the atomic orbitals. The remaining atomic orbitals of the adjacent carbon atoms overlap to form bonding and antibonding molecular orbitals, $\pi$ and $\pi^*$. Owing to lesser degree of orbital overlap, $\pi$ bond is weaker than $\sigma$ bond in bond strength. Therefore, electrons in $\pi$ bond are loosely bound.[2.1, 2.2] Figure 2.1 shows three examples of organic molecules with different $\sigma$ and $\pi$ bonds between two carbon atoms.

In the ground state, all the bonding orbitals are filled with electrons up to the highest occupied molecular orbital (HOMO). Each orbital can be filled with two electrons with antiparallel spins, i.e. spin down and spin up. On the other hand, empty orbitals are formed by the antibonding orbitals from the lowest unoccupied molecular orbital (LUMO). Borrowing the concept in inorganic semiconductors, HOMO is the valence band maximum (VBM) while LUMO is the conduction band minimum (CBM). If an electron is excited by optical absorption from the HOMO to the LUMO, an excited state is formed in which a missing electron is in a bonding orbital, a hole, and an electron is in an antibonding orbital. Figure 2.2 shows a diagram of molecular orbitals of in the ground state and the neutral excited states. In an excited state, the excited electron and the hole attract each other via Coulomb’s force. For organic materials, the dielectric constant, $\varepsilon_r$, is
around 3 which is relatively small comparing with that of silicon of 11.7. According to the Coulomb’s law,

\[ F = \frac{1}{4\pi\varepsilon_0 \varepsilon_r \frac{q_1 q_2}{r^2}} \]  

(2.1)

where \( F \) is the Coulomb’s force, \( \varepsilon_0 \) is the permittivity of free space, \( q_1 \) and \( q_2 \) are the charges, \( r \) is the distance between two charges. The Coulomb’s attraction between the excited electron and the hole is relatively strong due to the relatively small \( \varepsilon_r \) for organic materials. The bound electron-hole pair can be regarded as a quasi-particle known as an exciton, with a binding energy of 0.5 eV or more.[2.2]

Conductivity of a material, \( \kappa \), can be expressed as the product of three parameters:

\[ \kappa = e n \mu \]  

(2.2)

where \( e \) is the elementary charge, \( n \) is the charge carrier concentration, and \( \mu \) is the charge carrier mobility. From Equation 2.2, for a material, if there are no charges or they are immobilized, the material is an insulator. A typical example of an insulator with no charges is quartz. The bandgap of quartz is about 10 eV, equivalent to a wavelength of about 120 nm.[2.3] Therefore, at room temperature and in the absence of external excitation, there are no free charge carriers inside. However, charge carriers can be generated by radiation with energy higher than 10 eV. Then, the charge carriers can move with a high mobility in the order of \( 10^3 \) cm\(^2\)/Vs which is comparable to that of silicon. For organic materials, inherently, they are insulators. However, if there are free charge carriers generated by optical excitation, electrical injection, or doping, organic materials can be converted into organic semiconductors (OSs).[2.2]
Bonding between two carbon atoms:

\[
\begin{align*}
\text{Ethane} & \quad \text{Ethylene} & \quad \text{Ethyne} \\
\text{H} \quad \text{C} \quad \text{H} & \quad \text{C} \quad \equiv \quad \text{C} \quad \text{H} & \quad \text{H} \quad \text{C} \quad \equiv \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

1 \sigma \text{ bond} \quad 1 \pi \text{ bond} \quad 2 \pi \text{ bonds}

Figure 2.1 Three examples of organic molecules, ethane, ethylene, and ethyne, with different \(\sigma\) and \(\pi\) bonds between two carbon atoms.

Figure 2.2 Molecular orbitals illustrating electronic configurations for ground state \(S_0\), first spin-singlet excited state \(S_1\), and first spin-triplet excited state \(T_1\). Electron spin is indicated by the direction of arrows. Coulomb’s attraction is taken into consideration with the aid of the grey line.[2.2]
2.2. Classification of Organic Materials

Organic materials can be classified according to their structural complexities and molecular weights. In general, there are three categories. They are small molecules, polymers, and biological molecules.[2.4] Among these three classes of organic materials, small molecules have the lowest complexities with well-defined molecular weights while biological molecules have the highest complexities. Polymers, in general, consist of chains of repeating units and the complexities are in between small molecules and biological molecules with distributions of molecular weights. In particular, small molecules and polymers are widely used in organic electronics. In most cases, the structures of small molecules and polymers are synthesized so that they possess suitable charge mobility, luminescent property, or light absorption property for device applications. Figure 2.3 shows some examples of these three classes of organic materials.
Figure 2.3 Examples of small molecule, polymer, and biological molecule[2.4]. The full names of the materials: \(N,N'\)-Bis(naphthalen-1-yl)-\(N,N'\)-bis(phenyl)-benzidine (NPB), polystyrene (PS), poly(3-hexylthiophene-2,5-diyl) (P3HT), and poly\{4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl\} (PTB7).
2.3. Charge Carrier Transport and Injection Mechanisms

2.3.1. Hopping Transport

For organic semiconductors (OSs), they are usually amorphous or polycrystalline. Also, they are bound by weak van der Waals force and therefore the intermolecular separation is large. As a result, the overlapping of molecular orbitals is small compared to inorganic crystals. Therefore, we may expect the energy levels of a single molecule can be retained in solid state for a crude approximation. In reality, due to mutual interactions of molecules, their energy levels slightly spread out. Charge conduction occurs when charge carriers hop from one molecule to another molecule as shown in Figure 2.4.[2.5]. The energetic sites for hopping are assumed to possess a Gaussian distribution. With the aid of thermal excitation, charge carriers can overcome the energetic barrier between nearest transport sites. Therefore, charge carrier mobility increases with the temperature.
Figure 2.4 Schematic diagram of hopping transport in an OS.
2.3.2. Gaussian Disorder Model

Gaussian disorder model (GDM) was proposed by H. Bässler in 1993.[2.6] This model describes charge carriers transport in a disorder organic solid. There are several assumptions in GDM. First, the energetic transporting sites in HOMO and LUMO of a disorder solid possess Gaussian distributions which can be expressed in the following equation:

\[ g(E) = \frac{1}{\sqrt{2\pi}} \sigma e^{-\frac{E^2}{2\sigma^2}} \]  

(2.3)

where \( E \) is the energy of the site and \( \sigma \) is the energetic disorder. Energetic disorder reveals the spread of the Gaussian distribution in which \( \sigma \) equals to the standard derivation of the distribution as shown in Figure 2.5. Second, there are no interactions between energetic hopping sites. Third, the coupling between electron and phonon is weak such that the influences of polaron are insignificant. Therefore, the hopping process can be described by Miller-Abrahams expression,[2.7]

\[ \nu_{ij} = v_0 \exp\left(-2\frac{a_{ij}}{L}\right) \begin{cases} \exp\left(-\frac{\epsilon_j - \epsilon_i}{kT}\right) & \text{for } \epsilon_j < \epsilon_i \\ 1 & \text{for } \epsilon_j \geq \epsilon_i \end{cases} \]  

(2.4)

where \( \nu_{ij} \) is the hopping rate of a charge carrier hops from site \( i \) to neighboring site \( j \), \( v_0 \) is the attempt-to-hop frequency, \( a_{ij} \) is the hopping distance between site \( i \) to neighboring site \( j \), \( L \) is the localization radius, \( \epsilon_j \) and \( \epsilon_i \) are the site energies of site \( j \) and site \( i \), respectively, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. The hopping rate, \( \nu_{ij} \), is the product of the frequency prefactor, \( v_0 \), the wavefunction overlap factor, \( \exp\left(-2\frac{a_{ij}}{L}\right) \), and either the Boltzmann factor, \( \exp\left(-\frac{\epsilon_j - \epsilon_i}{kT}\right) \), for \( \epsilon_j < \epsilon_i \), or 1, for \( \epsilon_j \geq \epsilon_i \). The last part of the expression means charge carriers can hop directly between energetic sites if the
next site energy is equal or lower. However, the hoping rate will drop exponentially with the site energies difference if the next site has a higher energy.

Although the equation of the hopping rate of charge carriers between neighboring sites is available, it is difficult to measure the hopping rate experimentally. As a result, Monte Carlo (MC) simulations are used to simulate carrier mobility, $\mu$, which is temperature, $T$, and electric field, $F$, dependent. The carrier mobility, $\mu$, can be expressed in the following equation:[2.6]

$$\mu(F, T) = \mu_\infty \exp \left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp \left(\beta F^\frac{1}{2}\right)$$  \quad (2.5)

where $\mu_\infty$ is the high-temperature limit mobility, $\sigma$ is the energetic disorder, $\beta$ is the Poole-Frenkel (PF) slope. The last part of Equation 2.5, $\mu \propto \exp \left(\beta F^\frac{1}{2}\right)$, follows the PF model.[2.8] In fact, under MC simulation, $\beta$ is related to the energetic disorder, $\sigma$, and positional disorder, $\Sigma$:

$$\beta = C \left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]$$  \quad \text{for } \Sigma \geq 1.5;  \quad (2.6a)$$

$$\beta = C \left[\left(\frac{\sigma}{kT}\right)^2 - 2.25\right]$$  \quad \text{for } \Sigma \leq 1.5  \quad (2.6b)$$

where $C$ is a numerical constant depending on the site separation. $C$ is $2.9 \times 10^{-4}$ cmV$^{1/2}$ for a lattice constant of 0.6 nm. Equation 2.5 can be simplified if the electric field is zero:

$$\mu(F = 0, T) = \mu_\infty \exp \left[-\left(\frac{2\sigma}{3kT}\right)^2\right]$$  \quad (2.7)

Instead of Equation 2.5, Equation 2.7 is widely applied to experimental data of zero-field mobility at different temperatures, $\mu(F = 0, T)$ or $\mu_0$. By plotting $\mu_0$ vs $1/T^2$, $\mu_\infty$ and $\sigma$ can be extracted from the y-intercept and the slope, respectively.
Figure 2.5 Gaussian distributions of energetic hopping sites in the HOMO and the LUMO of an organic semiconductor.
2.3.3. Electrical Injection of Charge Carriers

As mentioned in section 2.1, electrical injection is one of the charge generation methods. For some of the charge transport measurement techniques and device application such as OLEDs and OFETs, charges are injected from an appropriate contact electrode. However, the classical inorganic semiconductor mechanisms for charge injection based on Richardson-Schottky emission or Fowler-Nordheim tunneling[2.9] cannot be applied to OSs as the electronic coupling between molecules is the weak van de Waals type.[2.2] Thus, the injection to OSs is usually based on hopping. Figure 2.6 shows the injection processes through different mechanisms in inorganic semiconductors or OSs.
Figure 2.6  Schematic diagrams of electron injection from a metallic electrode into a semiconductor through (a) Richardson-Schottky emission, (b) Fowler-Nordheim tunneling, and (c) hopping in a disordered organic semiconductor. $E_F$ is the Fermi-level energy of the electrode, $F$ is the applied electric field, and $r$ is the distance from the electrode.\[2.2\]
Metal/organic interface is common in organic devices. Figure 2.7 shows the energy level diagrams of a metal and an OS when they are separated from each other. The reference level of the energy is called the vacuum level, $E_{\text{vac}}$ which is defined as the energy that an electron is at rest. Usually, $E_{\text{vac}}$ is taken to be zero. $\varphi$ is the work function of a metal while HOMO and LUMO are the energy levels for holes and electrons conduction respectively. $\varphi$ or $IP$ are the energies needed to remove an electron from a metal or organic molecule respectively. $EA$ is the energy released by adding an electron to an organic molecule. For undoped organic semiconductor, the Fermi-level energy, $E_F$, is located at the middle of the HOMO and LUMO.

When a metal and an OS are in contact, $E_{\text{vac}}$ of the metal and the OS can be aligned directly as shown in Figure 2.7. The alignment of $E_{\text{vac}}$ is known as the Mott-Schotty limit. The injection barriers for holes and electrons, $\Phi_h$ and $\Phi_e$, can be written as,

\begin{align*}
\Phi_h &= IP - \varphi \\
\Phi_e &= \varphi - EA
\end{align*}

(2.8a)
(2.8b)

Theoretically, an electrical contact between a metal electrode and an OS is Ohmic if $\Phi_h$ or $\Phi_e$ are zero for holes or electrons injection respectively.
In reality, the vacuum levels do not necessarily aligned under thermal equilibrium.[2.10] Charge transfer happens at the metal/organic interface and a layer of interfacial dipoles is formed. The presence of these interfacial dipoles causes an abrupt shift in potential, $\Delta$, at the metal/organic interface as shown in Figure 2.8. Hence, the injection barriers for holes and electrons are modified to,

$$\Phi_h = IP - \varphi + \Delta \quad (2.9a)$$

$$\Phi_e = \varphi - EA - \Delta \quad (2.9b)$$
Figure 2.7  Energy level diagram of an isolated (a) metal and (b) organic semiconductor.
Figure 2.8  Energy level diagrams of a metal/organic interface under the thermo-dynamic equilibrium with Fermi level alignment.
2.4. Charge Transport Characteristics of Organic Semiconductors

2.4.1. Space-Charge-Limited Current

Space-charge-limited current (SCLC) model describes the current-voltage \((J-V)\) characteristic of an insulator and it is the most common model to describe electrical conduction in an organic semiconductor.\[2.11\] According to Poisson’s equation, we have,

\[
\frac{\partial F}{\partial x} = \frac{\rho}{\varepsilon}
\]

(2.10)

where \(\rho = nq\) \((q \text{ is the elementary charge})\), and \(\varepsilon = \varepsilon_0 \varepsilon_r\) is the product of permittivity of free space, \(\varepsilon_0\), and the dielectric constant, \(\varepsilon_r\), therefore,

\[
\frac{\partial F}{\partial x} = \frac{nq}{\varepsilon} = \left(\frac{q}{\varepsilon}\right)\left[n - n_0 + \sum_i(n_t - n_{t,0})\right]
\]

(2.11)

where \(n\) and \(n_t\) are the free and trapped electron concentrations, respectively, and \(n_0\) and \(n_{t,0}\) are thermally generated free electron and trapped electron concentrations in the absence of an external electric field. The free electron concentration, \(n(x)\), can be expressed as,

\[
n(x) = N_{LUMO} \exp\left(\frac{E_F - E_{LUMO}}{kT}\right)
\]

(2.12)

where \(N_{LUMO}\) is the effective density of states (DOS) of electrons in the LUMO, \(E_{LUMO}\) is the energy of LUMO. The trapped electron concentration, \(n_t(x)\), with the trap energy, \(E_t\), is given by the Fermi-Dirac expression,

\[
n_t(x) = N_t\left[1 + \frac{1}{g} \exp\left(\frac{E_t - E_F}{kT}\right)\right]^{-1} = N_t\left[1 + \frac{1}{g} N_{LUMO} \exp\left(\frac{E_t - E_{LUMO}}{kT}\right)\right]^{-1}
\]

(2.13)

where \(N_t\) is the concentration of traps and \(g\) is the degeneracy factor for the traps. The drift current of the transporting charge carriers in a material is given by,

\[
J = nq\mu F
\]

(2.14)

where \(\mu\) is the carrier mobility. For an insulator with no trap, \(n_t\) and \(n_{t,0}\) vanish. At low electric field, thermally generated free carriers are the majority
carriers and the current density obeys Ohm’s law. However, at high electric field, the injected free carriers are dominant, e.g. \( n \gg n_0 \). Equation 2.11 becomes,

\[
\frac{\varepsilon \partial F}{q \partial x} = n
\]  

(2.15)

With Equations 2.11 and 2.15, \( n \) can be eliminated,

\[
F \partial F = \frac{J}{\varepsilon \mu} \partial x
\]  

(2.16)

By integrating both sides, Equation 2.16 becomes,

\[
F(x) = \left( \frac{2J}{\varepsilon \mu} \right)^{1/2} x^{1/2} + \text{constant}
\]  

(2.17)

For the boundary condition, \( F(0) = 0 \), the integrating constant is found to be zero. By integrating Equation 2.17 from \( x = 0 \) to \( x = d \), where \( d \) is the thickness of an organic material, the \( J-V \) characteristic for a trap-free organic material can be obtained,

\[
V(x) = \int_0^d F(x) \, dx = \left( \frac{2J}{\varepsilon \mu} \right)^{1/2} \int_0^d x^{1/2} \, dx = \left( \frac{8J}{\varepsilon \mu} \right)^{1/2} d^{3/2}
\]

\[
J_{\text{SCL}} = \frac{9}{8} \varepsilon_0 \varepsilon \mu_0 \frac{v^2}{d^3}
\]  

(2.18)

According to the PF model, mobilities of organic materials are dependent on the electric field. Equation 2.18 is modified by Murgatoryd:[2.12]

\[
J_{\text{SCL}} = \frac{9}{8} \varepsilon_0 \varepsilon \mu_0 \exp \left( 0.89 \beta \sqrt{F} \right) \frac{v^2}{d}
\]  

(2.19)

where \( \mu_0 \) is the zero-field mobility.

From Equation 2.19, \( J_{\text{SCL}} \) is thickness dependent. In real devices for transport measurement, the films were usually prepared by spin-coating technique. The thickness obtained by spin-coating technique may vary from time to time. In order to have a meaningful comparison on the \( J-V \) characteristic between different samples with different thicknesses, \( J_{\text{SCL}}d \), instead of \( J_{\text{SCL}} \), is usually plotted against \( F \) to get rid of the effect of the thickness, \( d \).
So, by fitting the experimentally obtained $J$-$V$ data with the SCLC (Equation 2.19 or 2.20), $\mu_0$ and $\beta$ can be extracted.

2.4.2. Dark-Injection Space-Charge-Limited Current

In this section, we review the phenomenon of dark-injection space-charge-limited current (DI-SCLC).[2.11] We assume that a trap-free insulator forms an Ohmic contact at its cathode. Furthermore, the anode is hole-blocking but permits the flow of electrons. The sample is then subject to a forward bias step voltage as shown in Figure 2.9. A time and position dependent current $J(x, t)$ will arise and it can be expressed as,

$$J(x, t) = J_{\text{cond}} + J_{\text{displ}}$$

$$J(x, t) = \epsilon \mu_0 n(x, t) F(x, t) + \epsilon \frac{\partial F(x, t)}{\partial t}$$

where $J_{\text{cond}}$ and $J_{\text{displ}}$ are the conduction and displacement currents, respectively. The electric field is described by the Poisson’s equation,

$$\epsilon \frac{\partial F(x, t)}{\partial x} = en(x, t)$$

Substituting Eq. 2.23 into Eq. 2.22, we have,

$$J(t) = \epsilon \left[ \frac{\mu}{2} \frac{\partial F^2(x, t)}{\partial x} + \frac{\partial F(x, t)}{\partial t} \right]$$

Integrating Eq. 2.24 from $x = 0$ (cathode) to $x = d$ (anode), we have,

$$\int_0^d J(t) dx = \epsilon \left[ \frac{\mu}{2} \int_0^d dF^2(x, t) + \frac{\partial}{\partial t} \int_0^d F(x, t) dx \right]$$

where the last term vanishes in which $\int_0^d F(x, t) dx = V$ and $\frac{\partial V}{\partial t} = 0$. Eq. 2.25 becomes,

$$J(t) = \frac{\epsilon \mu}{2d} \left[ F^2(d, t) - F^2(0, t) \right]$$

$$J_{\text{SCLC}} = \frac{9}{8} \frac{\epsilon_0 \epsilon_r \mu_0}{\beta} \exp\left(0.89 \beta \sqrt{F} \right) F^2$$

(2.20)
By substituting the boundary condition, the relation of the electric field between the anode and cathode,

\[ F(d, t) - F(0, t) = \frac{Q(t)}{\varepsilon} \]  
(2.27a)

\[ F^2(d, t) - F^2(0, t) = \frac{Q(t)}{\varepsilon} [F(d, t) + F(0, t)] \]  
(2.27b)

\[ F^2(d, t) - F^2(0, t) = \frac{Q(t)}{\varepsilon} \left[ 2F(d, t) - \frac{Q(t)}{\varepsilon} \right] \]  
(2.27c)

where \( Q(t) \) is the total charge per unit area and therefore we have,

\[ J(t) = \frac{\mu Q(t)}{2d} \left[ 2F(d, t) - \frac{Q(t)}{\varepsilon} \right] \]  
(2.28)

For an electrode with Ohmic contact and a non-injecting counter electrode, carriers are injected from the former electrode under presence of electric field and hence space-charge-limited current (SCLC) transient can be obtained as shown. The SCLC transient can be described in three parts as shown in Figure 2.9: (i) an instantaneous current, \( J_0 \), at \( t = 0 \), (ii) a monotonic rise to a maximum, \( J_{D1} \), at \( t = \tau_{D1} \), and (iii) a current drop with a discontinuous change of slope after the maximum to the steady-state current, \( J_{SCL} \).

From the boundary condition,

\[ F(d, t) = 0 \]  
(2.29)

Eq. 2.26 gives a differential equation,

\[ \frac{dF(d, t)}{F^2(d, t)} = \frac{\mu}{2L} dt \]  
(2.30)

with solution,

\[ \frac{L}{V} - \frac{1}{F(d, t)} = \frac{\mu t}{2L} \Rightarrow F(d, t) = \frac{L}{V} \left( 1 - \frac{1}{2t_0 \mu V} \right) \]  
(2.31)

where \( t_0 = \frac{d^2}{\mu V} \). From Eq. 2.27a, 2.29, and 2.31,
\[ Q(t) = \varepsilon F(d, t) = \frac{Q_0}{1-t/2t_0} \quad (2.32) \]

where \( Q_0 = \frac{eL}{V} \).

Differentiating Eq. 2.32 with respect to \( t \), we have,

\[ J(t) = J_0 \frac{1}{[1-(t/2t_0)]^2} \quad (2.33) \]

where \( J_0 = J(0) = \frac{e\mu v^2}{2L^3} \).

The leading injected charges arrive at the anode at \( t = \tau_{DI} \). Using Eq. 2.31, we have,

\[ L = \mu \int_0^{\tau_{DI}} F(d, t) dt = \frac{2\mu t_0 v}{L} \ln \left[ 1 - \frac{t}{2t_0} \right]^{-1} \quad (2.34) \]

From the definition of \( t_0 \), it gives,

\[ \tau_{DI} = 2 \left( 1 - e^{-1/2} \right) t_0 \approx 0.786 t_0 \quad (2.35) \]

Letting \( J_{DI} = J(\tau_{DI}) \) and \( J_{SCL} = J(\infty) = \frac{9}{8} \frac{e\mu v^2}{L^3} \), the following current ratios can be calculated,

\[ \frac{J_{DI}}{J_0} = e \approx 2.72 \quad (2.36) \]
\[ \frac{J_{DI}}{J_{SCL}} = \frac{4e}{9} \approx 1.21 \quad (2.37) \]

Equation 2.37 will be employed in Chapter 4 of this thesis to examine if a semiconducting polymer forms an Ohmic contact with selected anode materials.
Figure 2.9  An ideal DI-SCLC transient under a step voltage.
2.4.3. Admittance Spectroscopy

Admittance Spectroscopy (AS) can be used to measure the carrier mobilities of organic semiconductors in the frequency domain.[2.13] In an AS experiment, the target material is sandwiched between a cathode and an anode. The resulting device can be treated as a RC parallel circuit. Below, we assume that after the application of a dc voltage, holes can be injected from the anode and then transport through the organic layer, and the cathode is electron-blocking. With a small ac modulation, $\nu_{ac}$, is superimposed on the dc bias. The frequency dependent complex admittance, $Y(\omega)$, can be expressed as,

$$Y(\omega) = G + i\omega C$$

(2.38)

where $G$ is the conductance, $i$ is the imaginary number, $\omega$ is the angular frequency, and $C$ is the capacitance. From Poisson's equation, the position and time dependent hole density $\rho(x,t)$ can be written as,

$$\rho(x,t) = \frac{\varepsilon}{q} \frac{\partial F(x,t)}{\partial x}$$

(2.39)

The total current density is given by,

$$J(t) = e\rho(x,t)\mu(t)F(x,t) + \varepsilon \frac{\partial F(x,t)}{\partial t}$$

(2.40)

When there is no ac modulation, the last term in Eq. 2.40 vanishes. Substituting Eq. 2.39 into Eq. 2.40, the dc current density is obtained,

$$J_{dc} = \varepsilon \mu_{dc} F_{dc}(x) \frac{\partial F_{dc}(x)}{\partial x}$$

(2.41)
Integrating Eq. 2.41 with the boundary condition $F_{dc}(0) = 0$, we have,

$$F_{dc}(x) = \left(\frac{2/L_{dc}}{\varepsilon \mu_{dc}}\right)^{1/2} x^{1/2}$$  \hspace{1cm} (2.42)

Substituting Eq. 2.42 in Eq. 2.39, the dc hole density is obtained,

$$\rho_{dc}(x) = \frac{1}{q} \left(\frac{\varepsilon J_{dc}}{2 \mu_{dc}}\right)^{1/2} x^{-1/2}$$  \hspace{1cm} (2.43)

According to Child’s law, the $J_{dc}$ can be written as,

$$J_{dc} = \frac{9}{8} \varepsilon \mu_{dc} \frac{V^{2}}{d^{3}}$$  \hspace{1cm} (2.44)

With Eq. 2.44 and $\mu_{dc} = \frac{d^{2}}{V_{dc} x_{dc}}$, Eq. 2.42 and 2.43 can be rewritten as,

$$F_{dc}(x) = \frac{3d^{1/2}}{2 \mu_{dc} x_{dc}} x^{1/2}$$  \hspace{1cm} (2.45)

$$\rho_{dc}(x) = \frac{3d^{1/2}}{4 \mu_{dc} x_{dc}} x^{-1/2}$$  \hspace{1cm} (2.46)

In presence of an additional small ac signal $\nu_{ac}$, the electric field, charge density, and current density can be rewritten as the sum of the respective dc component and ac component in the forms:

$$F(x, t) = F_{dc}(x) + f(x, t)$$  \hspace{1cm} (2.47)

$$\rho(x, t) = \rho_{dc}(x) + \varphi(x, t)$$  \hspace{1cm} (2.48)

$$J(x, t) = J_{dc}(x) + j(x, t)$$  \hspace{1cm} (2.49)

Substituting Eq. 2.40, 2.41, 2.47, and 2.48 into Eq. 2.49, the time-dependent ac current density can be expressed as,

$$j(t) = q\mu(t)\rho_{dc} f(x, t) + \varepsilon \mu(t) F_{dc} \frac{\partial f(x, t)}{\partial x} + \varepsilon \frac{\partial f(x, t)}{\partial x}$$  \hspace{1cm} (2.50)
Applying Fourier transform for Eq. 2.50, the time-dependent current density is transformed to frequency-dependent ac current density $j(\omega)$,

$$
j(\omega) = q\mu(\omega)\rho_{dc} f(x, \omega) + \varepsilon\mu(\omega)F_{dc}\frac{\partial f(x, \omega)}{\partial x} + i\omega\varepsilon f(x, \omega)
$$

(2.51)

Putting Eq. 2.45 and 2.46 into Eq. 2.51, we have,

$$
j(\omega) = \frac{3\varepsilon d^{1/2}\bar{\mu}(\omega)}{4\tau_{dc}} x^{-1/2} f(x, \omega) + \frac{3\varepsilon d^{1/2}\bar{\mu}(\omega)}{2\tau_{dc}} x^{1/2} \frac{\partial f(x, \omega)}{\partial x} + i\omega\varepsilon f(x, \omega)
$$

(2.52)

where $\bar{\mu}(\omega) = \frac{\mu(\omega)}{\mu_{dc}}$ is the normalized mobility. Since Eq. 2.52 is a first-order differential equation with respect to $f(x, \omega)$, the solution can be written as,

$$
f(x, \omega) = \frac{j(\omega)}{i\omega\varepsilon} \left(1 - \frac{3d^{1/2}\bar{\mu}(\omega)}{4\omega\tau_{dc}} x^{-1/2} \left\{1 - \exp\left[-\frac{-i4\omega\tau_{dc}}{3d^{1/2}\bar{\mu}(\omega)} x^{-1/2}\right]\right\}\right)
$$

(2.53)

Since $v_{ac} = \int_0^d f(x, \omega) \, dx$, we have,

$$
v_{ac}(\omega) = \frac{j(\omega)}{i\omega\varepsilon} \left(d - \frac{3d\bar{\mu}(\omega)}{i2\omega\tau_{dc}} - 2d \frac{3\bar{\mu}(\omega)}{i4\omega\tau_{dc}} \left\{1 - \exp\left[-\frac{-i4\omega\tau_{dc}}{3\bar{\mu}(\omega)}\right]\right\}\right)
$$

(2.54)

By defining the normalized frequency $\Omega = \omega\tau_{dc}$, Eq. 2.54 becomes,

$$
v_{ac}(\Omega) = \frac{j(\Omega)\tau_{dc}d}{\Omega^2\varepsilon} \left(-i\Omega^2 + 1.5\bar{\mu}(\Omega)\Omega + i2[0.75\bar{\mu}(\Omega)]^2 \left\{1 - \exp\left[-\frac{-i4\Omega}{3\bar{\mu}(\Omega)}\right]\right\}\right)
$$

(2.55)

As the admittance $Y(\Omega) = \frac{i_{ac}}{v_{ac}}$ with $i_{ac} = Af$ where $A$ is the active area of the device, the admittance can be expressed as,

$$
Y(\Omega) = \frac{\varepsilon A}{\tau_{dc}d} \left(-\Omega^2 + 1.5\bar{\mu}(\Omega)\Omega + i2[0.75\bar{\mu}(\Omega)]^2 \left\{1 - \exp\left[-i4\Omega/3\bar{\mu}(\Omega)\right]\right\}\right)
$$

(2.56)

Figure 2.10 shows the frequency dependent capacitance based on Eq. 2.56 with $V_{dc} > 0$. The plot can be separated in three regions, region I: $f \gg f_r$, region II: $f \approx f_r$, and region III: $f \ll f_r$. Considering only the ac response, in region I,
since $f$ is too high, injected charge carriers cannot go into the organic layer and capacitance equals to geometric capacitance, $C_{geo} = \frac{\varepsilon A}{d}$. In region II, $f$ becomes smaller and injected charge carriers can go into the organic layer. Thus, the capacitance drops with the decreasing frequency. For non-dispersive situation, the capacitance will drop until it reaches $0.75C_{geo}$ which can be determined from Eq. 2.56 for $\Omega \ll 1$. For dispersive situation, owing to trapping of charges and releasing of charges from the traps, the capacitance rise with the decreasing frequency.[2.14, 2.15] For $V_{dc} = 0$, the capacitance is independent of frequency and equals to $C_{geo}$. Plotting the corresponding negative differential susceptance, $-\Delta B$, from the frequency dependent capacitance plot is required to extract the carrier mobility,

$$-\Delta B = -2\pi f (C - C_{geo}) \quad (2.57)$$

In the $-\Delta B$ vs $f$ plot, there is a maximum of $-\Delta B$ at $f = f_r$ where $f_r$ can be used to calculate the average carrier transit time $\tau$,

$$\tau = \frac{0.56}{f_r} = 0.56\tau_r \quad (2.58)$$

Therefore, the average mobility, $\mu$, can be calculated,

$$\mu = \frac{f_r d^2}{0.56V} \quad (2.59)$$
Figure 2.10 AS signals for frequency-dependent capacitance (upper plot) and the negative differential susceptance (lower plot) for non-dispersive and dispersive situations.
2.5. Organic Photovoltaic Cells

2.5.1. Working Principles

OPV cells, like other types of PV cells, can convert light energy into electricity. The mechanism behind OPV cell can be divided into five steps.[2.17, 2.18] Figure 2.11 shows these steps at short-circuit condition. Step (i) is light absorption and exciton generation. When a donor material absorbs light with photon energies larger than the bandgap of the donor material, electrons are excited to the LUMO of donor. Holes are left behind in the HOMO. An electron in the LUMO and a hole in the HOMO may attract each other to form a bound electron-hole pair known as an exciton. Step (ii) is exciton diffusion. Exciton is neutral, but they can move by diffusion. As the concentration of excitons inside the donor material is much higher than at the boundary of the donor and acceptor, a concentration gradient is formed. Then, the excitons in donor tend to diffuse toward the acceptor material. Step (iii) is charge separation. During diffusion, an exciton may reach the donor-acceptor (DA) interface. Then the exciton has a large chance of dissociation because the LUMO of the acceptor is chosen to have an energy level lower than the donor. So, electron and hole are separated. Step (iv) is charge transport. After charge separation, the electrons will transport through the acceptor material towards cathode while the hole transports through the donor material towards anode due to the presence of internal electric field. Step (v) is charge extraction. Electrons and holes are collected at the cathode and the anode, respectively, and then they are extracted to the circuit outside the cell.
Figure 2.11  Schematic diagram of the working principles of an OPV cell, (i) light absorption and exciton generation, (ii) exciton diffusion, (iii) charge separation, (iv) charge transport, and (v) charge extraction.
2.5.2. Current-Voltage Characteristic

$J$-$V$ measurement is the most popular means of characterizing an OPV cell. In such a measurement, the OPV cell is usually subject to an illumination standard, air mass 1.5 global (AM1.5G) solar spectrum. The number “1.5” is equal to $\frac{1}{\cos z}$ where $z = 48.2^\circ$ is the solar zenith angle as shown in Figure 2.12. At this solar zenith angle, the light intensity from the sun is equal to 100 mW/cm². Furthermore, the measurement temperature in this standard is set to be 25 °C. This measurement condition is known as “one sun condition”.

Figure 2.13 shows the typical $J$-$V$ data of an OPV cell. In this plot, there are three points of interest. They are the short-circuit current density $J_{SC}$ at $V = 0$, open-circuit voltage $V_{OC}$ at $J = 0$, and maximum power point where the product of $J$ and $V$ reaches the maximum, i.e. $J_{max}$ and $V_{max}$. Under the short-circuit condition, $J = J_{SC}$, free charge carriers are subject to the full internal electric field of the active materials. When $V = V_{OC}$, charge carriers experience zero electric field because the internal electric field is canceled by the external electric field, and there is no current flowing out from the solar cell. The maximum power point is the location in which maximum energy can be extracted from the solar cell. With these three parameters extracted from the $J$-$V$ plot, the performance of a solar cell can be evaluated.
Figure 2.12  Schematic diagram illustrating AM1.5G solar spectrum.
Figure 2.13 Typical $J-V$ curve of an OPV cell showing the short-circuit current (open square), open-circuit voltage (open circle), and the maximum power point (cross).
Power conversion efficiency (PCE) of a solar cell can be expressed as,

\[ PCE = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{max}}V_{\text{max}}}{P_{\text{in}}} \]  \hspace{1cm} (2.60)

where \( P_{\text{max}} \) is the maximum power output, and \( P_{\text{in}} \) is the incident light intensity of AM1.5G. In order to have a better description of the curvature of the \( J-V \) data between short-circuit and open-circuit condition, fill factor \( (FF) \) is introduced as,

\[ FF = \frac{I_{\text{max}}V_{\text{max}}}{J_{\text{SC}}V_{\text{OC}}} \]  \hspace{1cm} (2.61)

From Eq. 2.61, \( FF \) can be understood as the ratio of the area defined by \( I_{\text{max}}V_{\text{max}} \) to the area defined by \( J_{\text{SC}}V_{\text{OC}} \). With this definition, \( PCE \) can be rewritten as,

\[ PCE = \frac{J_{\text{SC}}V_{\text{OC}}FF}{P_{\text{in}}} \]  \hspace{1cm} (2.62)

### 2.5.3. Losses in Organic Photovoltaic Cells

#### 2.5.3.1. Photocurrent Losses

If all the above steps are operating ideally, all photons can be converted into free charge carriers, and the carriers can be collected to become the current in the circuit. In reality, there are always losses in this energy conversion process. External quantum efficiency \( (EQE) \) or Incident-photon-to-electron conversion efficiency \( (IPCE) \) is a parameter to describe the energy conversion in percentage at different wavelength \( (\lambda) \). There is an efficiency for each of the step and the product of these efficiencies is the \( EQE(\lambda) \),

\[ EQE(\lambda) = \eta_{\text{abs}}\eta_{\text{diff}}\eta_{\text{cs}}\eta_{\text{ct}}\eta_{\text{cc}} = \eta_{\text{abs}}IQE \]  \hspace{1cm} (2.63)

In Eq. 2.63, \( \eta_{\text{abs}} \) is the light absorption efficiency, \( \eta_{\text{diff}} \) is the exciton diffusion efficiency, \( \eta_{\text{cs}} \) is the charge separation efficiency, \( \eta_{\text{ct}} \) is the charge transport efficiency, and \( \eta_{\text{cc}} \) is the charge collection efficiency. Excluding the photons absorption, the product of remaining four parameters is known as internal
quantum efficiency (IQE) which describes the efficiency of absorbed photons converting into electrons.

In a real PV device, there must be some optical loss due to the device geometry such as optical reflection and transmission which is included in to the term $\eta_{\text{abs}}$.

The photo-excited excitons are, in fact, the geminate electron-hole pair. In general, the diffusion lengths for excitons vary from a few to around ten nanometers due to the strong coulomb force caused by the low dielectric constant for OPV materials.[2.19, 2.20] By overcoming the Coulomb force, the geminate pair can be separated. For these electron-hole pairs that cannot be separated, they will recombine as shown in Figure 2.14. This process is called geminate recombination. Since the recombination may occurs during exciton diffusion and charge separation, it affects the values of $\eta_{\text{diff}}$ and $\eta_{\text{cs}}$.[2.21]

After exciton dissociation, electrons and holes are affected by the net electric field which is superposition of the internal electric field and the external electric field. In between the short-circuit condition and the open-circuit condition, the net electric field drives electrons and holes towards the cathode and the anode, respectively. During charge transport process, free charges may recombine as shown in Figure 2.15. Two kinds of recombination may occur, (i) trap-assisted recombination, and (ii) bimolecular recombination. They are classified as nongeminate recombination.[2.21] Both recombinations influence the value of $\eta_{\text{ct}}$. 
Figure 2.14  Schematic diagram showing geminate recombination.
Figure 2.15 Schematic diagram showing two kinds of nongeminate recombination: trap-assisted and bimolecular. SRH expression (first order) is used to describe trap-assisted recombination. Langevin expression (second order) is used to describe bimolecular recombination.

\[
R_t = \frac{n_{OC}}{\tau_R}
\]

\[
R_b = \frac{e}{\varepsilon} (\mu_e + \mu_h)n_e n_h
\]
Trap-assisted recombination describes the process that free electrons or holes recombine with the trapped holes or electrons, respectively. This recombination can be modeled by Shockley-Read-Hall (SRH) recombination with the recombination rate,\[2.21, 2.22\]

\[ R_t = \frac{n_e n_h - n_i^2}{\tau_e (n_e + n_{e,\text{trap}}) + \tau_h (n_h + n_{h,\text{trap}})} \]  (2.64)

where \(n_e\) is the density of photogenerated electrons, \(n_h\) is the density of photogenerated holes, \(n_i\) is the density of the intrinsic carriers, \(\tau_e\) is the recombination lifetime of mobile electrons, \(\tau_h\) is the recombination lifetime of mobile holes, \(n_{e,\text{trap}}\) is the density of trapped electrons, \(n_{h,\text{trap}}\) is the density of trapped holes. It can be assumed that \(n_e n_h \gg n_i^2\), \(n_e \gg n_{e,\text{trap}}\), \(n_h \gg n_{h,\text{trap}}\), and \(n_e \sim n_h\) in organic OPV materials.\[2.21, 2.22\] By defining \(n_e n_h = n_{\text{OC}}^2\) and \(\tau_R = \tau_e + \tau_h\), Eq. 2.64 becomes,

\[ R_t = \frac{n_{\text{OC}}}{\tau_R} \]  (2.65)

The recombination rate \(R_t\) is a first order process provided that one carrier is first trapped and then a mobile and oppositely charged carrier finds and recombines with the trapped carrier. Finally, the recombination rate is proportional to the density of charge carrier and inversely proportional to the recombination lifetime.

Bimolecular recombination rate, \(R_b\), can be described by Langevin expression,\[2.21 – 2.23\]

\[ R_b = \zeta \frac{e}{\epsilon} (\mu_e + \mu_h) (n_e n_h - n_i^2) \]  (2.66)

where \(\zeta\) is reduction factor for the theoretical Langevin recombination coefficient, \(\mu_e\) is the electron mobility in the LUMO of acceptor, and \(\mu_h\) is the hole mobility in the HOMO of the donor. With the same assumptions mentioned above, \(n_{e,n_h} \gg n_i^2\), and \(n_e \sim n_h\), Eq. 2.66 becomes,
\[ R_b = \gamma n_e n_h = \gamma n^2_{0c} \]  

(2.67)

where \( \gamma = \zeta \frac{e}{\varepsilon} (\mu_e + \mu_h) \) is bimolecular recombination rate constant. Obviously, bimolecular recombination depends on both carrier mobility and carrier density. For higher mobility, oppositely charged carriers can reach one another faster. Similarly, higher carrier concentration leads to higher probability for oppositely charged carriers to meet. Unlike trapped-assisted recombination, this is a second order process in which it involves two carriers. For a number of optimized polymer:fullerene systems, bimolecular recombination is found to be the dominant recombination mechanism.[2.21, 2.22]

Finally, after charge generation, separation, and transportation, the charges reach the interface between BHJ and electrodes and then they may be collected at the electrodes. The loss in this process is reflected on \( \eta_{ee} \). Figure 2.16 surmises the main operation steps and the recombinations of OPV cells.
Figure 2.16  Operation flowchart of OPV cells.
2.5.3.2. Open-Circuit Voltage Losses

Before discussing $V_{OC}$ losses, we should know the origin of $V_{OC}$. In 2011, Blakesley et al. reported an expression of $V_{OC}$ with the consideration of the DOS distribution. For organic materials, it is commonly accepted that the DOS is Gaussian distribution. Thus, $V_{OC}$ can be expressed as,

$$V_{OC} = \frac{1}{e} \left( E_{\text{LUMO}}^{\text{acceptor}} - E_{\text{HOMO}}^{\text{donor}} - \frac{\sigma^2}{kT} \right) + \frac{kT}{e} \ln \left( \frac{n_e n_h}{N_e N_h} \right)$$  \hspace{1cm} (2.68)

where $E_{\text{LUMO}}^{\text{acceptor}}$ is the LUMO of the acceptor, $E_{\text{HOMO}}^{\text{donor}}$ is the HOMO of the donor, $N_e$ is the DOS for electrons, and $N_h$ is the DOS for holes. From Eq. 2.68, $V_{OC}$ is mainly governed by the effective bandgap of the donor and acceptor, i.e. energy difference between the LUMO of the acceptor and the HOMO of the donor.

In Eq. 2.68, the last term in the first bracket, $-\frac{\sigma^2}{kT}$, is the loss arising from the energetic disorder which is the standard deviation of the Gaussian distributed DOS. The last term in Eq. 2.68, $\frac{kT}{e} \ln \left( \frac{n_e n_h}{N_e N_h} \right)$, is the loss in $V_{OC}$ arising from the unfilled DOS for electrons and holes.

With the $V_{OC}$ expression, the two kinds of nongeminate recombination, trapped-assisted recombination and bimolecular recombination, can be further elaborated.[2.21 – 2.24] At open-circuit condition, there is no current flowing out from the solar cell. The generation rate, $G$, is equal to the recombination rate, $R_{Voc}$,

$$G = R_{Voc} \hspace{1cm} (2.69)$$

Considering only trapped-assisted recombination, $R_{Voc} = R_t = \frac{n_{OC}}{\tau_R}$ (Eq. 2.65), Eq. 2.69 becomes,

$$G = \frac{n_{OC}}{\tau_R} \Rightarrow n_{OC}^2 = G^2 \tau_R^2$$  \hspace{1cm} (2.70)
Since \( n_e n_h = n_{OC}^2 \), substituting Eq. 2.70 into Eq. 2.68, we have,

\[
V_{OC} = \frac{1}{e} \left( E_{\text{LUMO}} - E_{\text{HOMO}} - \frac{\sigma^2}{kT} \right) + \frac{kT}{e} \ln \left( \frac{G^2 \tau_R}{N_e N_h} \right)
\]  
(2.71)

As \( G \) is proportional to the incident light intensity \( I \), \( G \propto I \), \( V_{OC} \) with only trapped-assisted recombination can be written as,

\[
V_{OC} = 2 \frac{kT}{e} \ln I + \text{constant}
\]  
(2.72)

As a result, if we plot \( V_{OC} \) against \( \ln I \), the slope is equal to \( 2 \frac{kT}{e} \).

Similarly, starting again from Eq. 2.69, considering only bimolecular recombination, \( R_{\text{Voc}} = R_b = \gamma n_{OC}^2 \) (Eq. 2.67), Eq. 2.69 becomes,

\[
G = \gamma n_{OC}^2 \Rightarrow n_{OC}^2 = \frac{G}{\gamma}
\]  
(2.73)

Since \( n_e n_h = n_{OC}^2 \), substituting Eq. 2.73 into Eq. 2.68, we have,

\[
V_{OC} = \frac{1}{e} \left( E_{\text{LUMO}} - E_{\text{HOMO}} - \frac{\sigma^2}{kT} \right) + \frac{kT}{e} \ln \left( \frac{\gamma N_e N_h}{G} \right)
\]  
(2.74)

Thus, as \( G \propto I \), \( V_{OC} \) with only bimolecular recombination can be written as,

\[
V_{OC} = \frac{kT}{e} \ln I + \text{constant}
\]  
(2.75)

As a result, if we plot \( V_{OC} \) against \( \ln I \), the slope is equal to \( \frac{kT}{e} \).

From Eq. 2.72 and 2.75, the slope of \( V_{OC} \) vs \( \ln I \) plot for only trapped-assisted recombination and only bimolecular recombination is different. Experimentally, if we measure the \( V_{OC} \) at different \( I \), the slope of \( V_{OC} \) vs \( \ln I \) plot can tell which recombination mechanism is dominant or both are contributing. If both recombinations occur, \( R_{\text{Voc}} = R_t + R_b \), Eq. 2.69 becomes,

\[
G = \frac{n_{OC}}{\tau_R} + \gamma n_{OC}^2
\]  
(2.76)

\( n_{OC} \) in Eq. 2.76 can be solved in term of \( \tau_R \) and \( G \).
\[(n_{OC})^2 = \frac{1}{4\gamma} \left[ 1 + (1 + 4\gamma G\tau_R^2) - 2(1 + 4\gamma G\tau_R^2)^{1/2} \right] \quad (2.77)\]

Based on Eq. 2.77, generation rate dependent \(V_{OC}\) is simulated in Figure 2.17.[2.24] The simulation considers both bimolecular and trap-assisted recombinations in which trap densities increase logarithmically. We will apply such an analysis in Chapter 5 of this thesis.
Figure 2.17  Generation rate dependent open-circuit voltage with consideration of trap-assisted and bimolecular recombinations. Colour scale from purple (up) to brown (down) indicates logarithmical increase in trap densities with slope varying from $kT/e$ (upper purple dash line) to $2kT/e$ (lower tan dash line) [2.24]
2.6. Material Characterizations

2.6.1. X-Ray Crystallography – X-Ray Diffraction

X-ray diffraction (XRD) is the most popular technique to study the crystal structure of a solid.[2.25, 2.26] In a single crystal, atoms are located periodically in a lattice. If a monochromatic X-ray beam is irradiated on the crystal, constructive interference will occur in accordance with Bragg’s law

\[ n\lambda = 2d \sin \theta \]  

\( n \) is a positive integer, \( \lambda \) is the wavelength of the X-ray, \( d \) is the lattice spacing, and \( \theta \) is the diffraction angle. As shown in Figure 2.18, the path difference of two X-ray beams is \( 2d \sin \theta \). Constructive interference occurs when the path difference equals to an integral multiple of the incident X-ray wavelength. For crystalline materials, diffraction peaks on top of background signals can be obtained after XRD measurement. However, for amorphous materials, no diffraction peak but only the background signals can be obtained after XRD measurement. From the position of the diffraction peaks, the lattice spacing can be calculated.
Figure 2.18  Schematic diagram of Bragg’s diffraction on a crystalline solid.
2.6.2. Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a kind of size exclusion chromatography used to separate molecules with different sizes when these molecules are dissolved in a solvent.[2.27] GPC is often used to analyze the polymers with distributed molecular weights. Figure 2.19 shows a molecular weight distribution of a polymer, indicating the weight average molecular weight, $M_w$, and the number average molecular weight, $M_n$. The former is the average molecular weight with consideration of the weight of polymer chain. The latter is the average molecular weight with only consideration of the number of polymer chain. From these two numbers, polydispersity index ($PDI$) can be calculated,

$$PDI = \frac{M_w}{M_n}$$  \hspace{1cm} (2.79)

$PDI$ describes the spread of the distribution. If the numbers of repeating unit for all the polymer chains are the same, there will be no dispersity, i.e. $M_w = M_n$ and $PDI = 1$.

The principle of GPC is illustrated in Figure 2.20. Dissolved polymers with different molecular weights enter the GPC column. Low molecular weight polymer (smaller molecules) diffuses into the porous particles and resides there temporarily. However, high molecular weight polymer (larger molecules) cannot diffuse into the porous particles due to the larger molecular size and they elute in the interstitial region. The smaller the molecules, the longer the distances and times are needed to travel from one end to the other end of the GPC column. As a result, higher molecular weight polymer comes out first from the column and then lower molecular weight polymer gets out.
Figure 2.19 Molecular weight distribution of a polymer indicating the corresponding weight average molecular weight, $M_w$, and number average molecular weight, $M_n$. 
Figure 2.20  Schematic diagram of how GPC separating high and low molecular weight polymers.[2.27]
References:


Chapter 3
Experimental Details

This chapter describes the sample preparation, fabrication, and characterization procedures.

3.1. Sample Preparation

3.1.1. Substrate Patterning and Preparation

Indium tin oxide (ITO) is the most common transparent conducting oxide used in organic electronics devices. Different patterns and sheet resistances of ITO glass substrates were used for different experiments (see Table 3.1). All the ITO glass substrates were purchased from Tinwell.

ITO glass substrates were first cleaned with acetone soaked cotton tips. Then, they were cleaned by a brush with detergent. After that, they were immersed in deionized (DI) water diluted Deconex cleaner (Borer Chemie, Deconex 12 PA) at 80 °C for 10 minutes in order to remove residual detergent. The volume ratio of Deconex to DI water is 1:20. Then, the ITO glasses were further cleaned by a series of solvents in an ultrasonic bath as shown in Table 3.2. The solvents used for cleaning were at least analytical reagent grade. After that, they were dried in air before use. Normally, ITO glass substrates were cleaned one day before device fabrication. Finally, right before fabrication, they were treated with an ultra-violet ozone (UVO) cleaner (Jelight, UVO cleaner, Model 42-220) to remove hydrocarbon contamination on the surface.[3.1]
<table>
<thead>
<tr>
<th>Experiment</th>
<th>ITO Pattern</th>
<th>Dimension (mm x mm)</th>
<th>Sheet resistance (Ω/□)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCLC, DI-SCLC, AS</td>
<td><img src="image" alt="Pattern" /></td>
<td>25×25</td>
<td>40</td>
</tr>
<tr>
<td>TOF</td>
<td><img src="image" alt="Pattern" /></td>
<td>25×25</td>
<td>25</td>
</tr>
<tr>
<td>OPV cell</td>
<td><img src="image" alt="Pattern" /></td>
<td>32×32</td>
<td>15 – 20</td>
</tr>
<tr>
<td>XPS, UPS</td>
<td><img src="image" alt="Pattern" /></td>
<td>14×14</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3.1 ITO substrates of different ITO patterns and conductivities. The shaded area represents ITO covered area. Abbreviation keys: space-charge-limited current (SCLC), time-of-flight (TOF), organic photovoltaic (OPV), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS).

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Solvent</th>
<th>Duration (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DI water</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>DI water</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Acetone</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>2-propanol</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>2-propanol</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 3.2 Sequence of substrates cleaning in an ultrasonic bath.
3.1.2. Deposition Methods

3.1.2.1. Spin-Coating and Drop-Casting

Spin-coating are the most commonly used method to make solid films from solutions in laboratory. The thickness of the resulting film can be controlled by the viscosity of the solution, spin speed, and spin duration. Water soluble poly(3,4-ethylenedioxythiophene):poly(styrene) (PEDOT:PSS) (H. C. Starck GmbH, Clevios P VP Al 4083) is often used to modify the ITO surface, increasing the work function from -4.8 eV to -5.2 eV.[3.2, 3.3] PEDOT:PSS is a blend of two polymers and in this thesis, the PEDOT:PSS ratio was 1:6. In order to have a better mixture, sonication was needed for PEDOT:PSS solution before using it. To remove large particles or aggregation in the solution, PEDOT:PSS was filtered by a 0.45 µm hydrophilic PVDF syringe filter right before use. The filtered PEDOT:PSS was spin coated onto the cleaned ITO substrates by a spin-coater (Specialty Coating System, Model 6708D) with 5000 rpm for 90 s. The PEDOT:PSS coated substrates were then dried at 150 °C on a hotplate for 30 mins. The resulting film thickness was around 30 nm. Although the fabrication of PEDOT:PSS was done in air, the PEDOT:PSS coated substrates had to be transferred immediately to either N₂ filled glove box or vacuum chamber after drying in order to avoid absorption of moisture from air as PEDOT:PSS is water soluble.

Fabrication of polymers and fullerene derivatives such as (6,6)-phenyl C₆₁ butyric acid methyl ester (PCBM) (nano-c-PCBM-BF, [60]PCBM, 99.5% purity) or (6,6)-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) (nano-c-PCBM-SF, [70]PCBM 99+% purity; mixture of isomers) also employed spin coating technique. These materials have to be dissolved by an organic solvent such as
chloroform (CF), or 1,2-dichlorobenzene (DCB) as they are in solid form. First, materials were taken out from a glove box or desiccator for weighting. The weighted materials were put into a vial together with a magnetic stir bar. Second, the vial was then transferred into a glove box for making a solution. Plas Labs glove box (Model 855-AC) was used for the experiments in Chapters 4 and 6 as shown in Figure 3.2. Vigor glove box (Model SG1200/750TS) was used for the experiments in chapter 5 as shown in Figure 3.3. The operation of the Vigor glove box is covered in the appendix of this thesis. The solution was placed on a hot plate for heating and stirring overnight. Similar to spin coating PEDOT:PSS, the solution was filtered by a 0.45 μm hydrophobic PTFE syringe filter right before spin coating. Depending on the thickness required, different spin speeds and durations would be used to control the thickness by a spin coater (Chemat Technology, Model KW-4A) inside the glove box. The spin coating procedures are outlined in Figure 3.1. The film would be dried with or without annealing on a hot plate for different purposes. The details of solution preparation, spin coating, and drying conditions for a particular experiment will be covered in Chapters 4, 5, and 6. The thicknesses of the resulting films can be measured by a profilometer (Veeco, Dektak 150).
Figure 3.1  Schematic diagram of solution preparation, solution filtering, and spin coating.
Figure 3.2  Plas lab glove box, Model 855-AC.
Figure 3.3 Vigor glove box, Model SG1200/750TS.
3.1.2.2. Thermal Evaporation

Thermal evaporation is another film deposition technique frequently used in fabricating organic materials, metals, metal oxides, and metal salts. This deposition technique requires heating materials in high vacuum of around $10^{-6}$ Torr. For the work in this thesis, two thermal evaporators are used for fabricating different materials. Denton, Model DV-502 V, was used to evaporate organic materials and metal oxides at pressure of $4 \times 10^{-6}$ Torr. Edwards, Model AUTO 306, was used to evaporate metals and metal salts at pressure of $4 \times 10^{-6}$ mbar. For these two evaporators, since both of them employ diffusion pumps to achieve the required pressure, liquid nitrogen is needed to suppress the evaporated diffusion pump oil flowing from the pump to the chamber. Therefore, liquid nitrogen should be added before pumping the chamber by the diffusion pump. Different kinds of metal containers were used for evaporating different materials and they were listed in Table 3.3. When a current was applied to the conducting container, heating occurred. As a result, the material inside would be heated up and either sublimed or melted. The vapor of the material was then evaporated onto the substrate as shown in Figure 3.4. Different shadow masks were used during metal deposition to define the active area. New containers were pre-heated in order to drive out residual gases or solvents. The material coating rate can be monitored by a quartz-crystal sensor. The coating rate can be calibrated by measuring the actual thickness of the film by a profilometer.
<table>
<thead>
<tr>
<th>Materials</th>
<th>Containers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic materials</td>
<td>Molybdenum boats</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Boron nitride crucibles with tungsten filament</td>
</tr>
<tr>
<td></td>
<td>(R.D. Mathis, C9-BN, B8B-3X.025W)</td>
</tr>
<tr>
<td>Au, Al</td>
<td>Tungsten baskets for Au</td>
</tr>
<tr>
<td></td>
<td>(R.D. Mathis, B12B-3X.030W)</td>
</tr>
<tr>
<td></td>
<td>Tungsten filaments for Al</td>
</tr>
<tr>
<td></td>
<td>(R.D. Mathis, ME11-3x.025W)</td>
</tr>
<tr>
<td>LiF</td>
<td>Tungsten baskets</td>
</tr>
<tr>
<td></td>
<td>(R.D. Mathis, B12B-3X.030W)</td>
</tr>
</tbody>
</table>

Table 3.3 Evaporation containers for different materials.
Figure 3.4  Schematic diagram of thermal evaporation.
3.1.2.3. Sample Patterning

The effective device area of a sample for electrical measurement is defined by the overlapping area of the cathode and the anode. The final device geometries are shown in Table 3.4.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample configurations</th>
<th>Device geometry</th>
<th>Number of devices</th>
<th>Area of each device (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCLC, DI-SCLC, AS</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>4</td>
<td>0.035</td>
</tr>
<tr>
<td>TOF</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>1</td>
<td>0.250</td>
</tr>
<tr>
<td>OPV cell</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>4</td>
<td>0.108</td>
</tr>
</tbody>
</table>

Table 3.4  Sample configurations of (a) J-V, DI-SCLC, AS, (b) TOF, and OPV devices.

3.2. Charge Carrier Transport Measurement

In this section, experimental details of several charge carrier transport measurement techniques will be presented. All the samples were measured under vacuum (10-20 mbar) in a Cryostat (Oxford Instruments, Optistat DN-V) which was connected to a temperature controller (Oxford Instruments, ITC 502) to
regulate the temperature of the sample. The sample temperatures were calibrated by a thermal couple with direct contact to a substrate. For temperatures lower than room temperature, liquid nitrogen was used to absorb heat from the sample. Normally, room temperature data were taken both before and after the sample was cooled down. After cooling down and going back to the room temperature, the temperature of the sample was raised for elevated temperature measurements. Usually, two days were needed for the whole temperature dependent measurements with the first day for low temperatures and the second day for high temperatures. The temperature of the sample was changed in a step of around 10 K. About 40 minutes was needed for each temperature change.
Figure 3.5 Schematic diagram of an Oxford Cryostat illustrating connections to a mechanical pump, a temperature controller, and electrical feedthroughs for transport measurements.
3.2.1. Current-Voltage Measurement

A Source Measure Unit (SMU), Keithley Instruments, Model 236 SMU, was used to perform current-voltage (J-V) measurements of organic semiconductors. Different dc voltages are applied to inject charge carriers into the organic film and the resulting currents are recorded by the SMU. Figure 3.6 shows the experimental setup of the J-V measurement. The J-V data of a single carrier device with Ohmic charge injection can be fitted by the SCLC model (Equation 2.19 or 2.20) in Chapter 2 in which charge carrier transport parameters, $\mu_0$ and $\beta$, can be extracted. The fitting process is done by the nonlinear curve fit function in the software Origin.
Figure 3.6  Schematic diagram of the $J-V$ measurement setup.
3.2.2. Dark-Injection Space-Charge-Limited Current Technique

Dark-injection space-charge-limited current (DI-SCLC) is a current transient technique which captures the current transient passing through an insulator or organic semiconductor after the application of a step voltage.[3.4] The sample requires unipolar carrier transport and Ohmic injection. A Hewlett Packard pulse generator, Model HP214B, was used to provide voltage steps while an Agilent oscilloscope, Model 54622A - 100 MHz, was used to capture both applied step voltage transients and voltage transients from a sensing resistor. With the resistance value, the current transients passing through the sensing resistor could be calculated. For the pulse generator, the width of the voltage pulse was set at 4 ms. It is important to choose a suitable sensing resistor in order to obtain a reliable transient. In general, always avoid using large resistance values. It is because large resistance causes long RC decay at the beginning of the transient which may affect the carrier transit time extraction. So, it is suitable to a small resistance (usually 10-1k Ω) to obtain an acceptable signal-to-noise transient. Figure 3.7 shows the experimental setup of DI-SCLC.
Figure 3.7  Schematic diagram of the DI-SCLC measurement setup.
3.2.3. Admittance Spectroscopy

Similar to the SCLC fitting and DI-SCLC, the sample for admittance spectroscopy (AS) measurements requires single carrier transport and Ohmic injection. So, in the thesis, the samples were probed separately by DI-SCLC and AS techniques. A dc bias, superimposed with a small ac modulation is applied to the sample for AS measurement. A dc supply (Manson Engineering Industrial, Model DPS-3030) is used to provide the dc bias while an impedance analyzer (Hioki, Model 3535-50 LCR meter) is used to provide the ac modulation. The amplitude of the modulation is 0.05 V and the capacitance was measured between 42 and $5 \times 10^6$ Hz. Figure 3.8 shows the experimental setup of AS.

After measuring the frequency ($f$) dependent capacitance ($C$) of a sample, negative differential susceptance ($-\Delta B$) can be calculated with the following equation to extract carrier mobility:

\[-\Delta B = -2\pi f (C - C_{geo})\]

(3.2)

From the $-\Delta B$ vs $f$ plot, the frequency corresponding to the maximum point, \(f_r\), can be used to calculate the mobility, \(\mu_{AS}\):[3.5]

\[\mu_{AS} = \frac{f_r d^2}{0.56V}\]

(3.3)
Figure 3.8  Schematic diagram of AS measurement setup.
3.3. Organic Photovoltaic Cell Measurement

\( J-V \) characteristic of an OPV cell is recorded by a sourcemeter (Keithley Instruments, Model 2400 SourceMeter) with exposure to simulated AM1.5G illumination (Newport, Model 96000 150W solar simulator, AM1.5G filter, Newport, Model 81094). The electrical power output of the solar simulator has to be set at 150 W in order to maintain stable light illumination. Although the light spectrum is modified by the AM1.5G filter, the intensity may exceed 100 mW/cm². An optical density (OD) 1.0 filter is inserted between the solar simulator and the sample to obtain the required intensity. The solar simulator is calibrated by a power meter (Thorlabs, Model PB100D). Figure 3.9 shows the experimental setup for OPV cells measurements. There are four basic parameters to describe an OPV cell performance. They are the short-circuit current density \( (J_{SC}) \), the open-circuit voltage \( (V_{OC}) \), the fill factor \( (FF) \), the power conversion efficiency \( (PCE) \). These four parameters can be simply obtained from the \( J-V \) plot. \( J_{SC} \) and \( V_{OC} \) are the y-intercept and x-intercept, respectively. \( FF \) can be calculated by the following equation:

\[
FF = \frac{J_{max}V_{max}}{J_{sc}V_{oc}} \tag{3.6}
\]

\( PCE \) can be expressed in the following form:

\[
PCE = \frac{P_{max}}{P_{in}} = \frac{J_{max}V_{max}}{P_{in}} = \frac{J_{sc}V_{oc}FF}{P_{in}} \tag{3.7}
\]
Figure 3.9 Schematic diagram of OPV cell measurement setup.
Figure 3.10  Experimental setup for OPV cells measurements.
3.4. Characterization

3.4.1. Grazing Incident X-Ray Diffraction

The materials for grazing incident X-ray diffraction (GIXRD) measurements were prepared on ITO glass substrates. Due to the grazing incident angle, the thickness of the material under investigation can be as thin as 10 nm. It is suitable to study samples with the thicknesses less than 200 nm.

GIXRD measurements were performed by an X-ray diffractometer (Bruker AXS, Model D8 Advanced X-ray Diffractometer) in the Institute of Advanced Materials (IAM) in Hong Kong Baptist University. The CuKα X-ray source provides the X-ray irradiation with wavelength $\lambda = 1.54$ Å. The incident angle of the X-ray is fixed at 0.3° while the detector can scan from 3° to 65° with step of 0.05°. The sample dimension should be around 25 mm × 25 mm. Figure 3.11 shows the experimental setup of GIXRD. The measured signals were plotted against $2\theta$. 

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Figure 3.11  Schematic diagram of the GIXRD setup.
Figure 3.12  GIXRD measurement of P3HT:PCBM(1:1) sample.
3.4.2. Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed in Department of Chemistry, Hong Kong Baptist University (HKBU) and in National Research Council Canada (NRCC) (Waters Breeze HPLC system with 1525 Binary HPLC Pump and 2414 Differential Refractometer). Chloroform and chlorobenzene were used as eluent in HKBU and NRCC. Commercial polystyrene standards were used to calibrate the molecular weight and polydispersity index (PDI). A series of PS standard with different known molecular weights, where the PDI are assumed to be 1, were used for calibration.

Figure 3.13 and Figure 3.14 show the experimental setup for GPC measurement in HKBU. Before turning on the pump, make sure there is enough eluent and the GPC column is well connected. Once the pump is turned on, the eluent will be pumped through the whole system including the GPC column. By turning on the refractometer which is connected to a computer, you can see the background signal from the refractometer. Normally, there may be some residual materials from the previous measurements and therefore 30 minutes or more are needed to rinse the whole system with the eluent in order to obtain a steady background signal for measurement.

The polymers under test and the PS standards should be dissolved in an solvent that is same as the eluent used in the system. HPLC grade solvent is required for the measurement to avoid any signal arose from the impurities in the solvent. The concentration of the polymer solution should not be too high and usually 1 – 5 mg/ml is enough for measurement. The solution should be fully dissolved and must be filtered to avoid large particles remaining in the solution.
Finally, ~0.05 μl solution is injected to the system for analysis. For each scan, it took 30 – 60 minutes. Figure 3.15 shows the calibration from four PS standards and the measurement of five batches of PCDTBT.
Figure 3.13  Schematic diagram of the GPC setup.
Figure 3.14  Experimental setup of GPC in HKBU.
Figure 3.15  GPC data obtained in HKBU (a) PS standard calibration and (b) examples of the measurements on five batches of PCDTBT.
References:


Chapter 4

Electron Blocking and Trapping Layer for Hole Transport Measurement on Photovoltaic Polymers and Their Bulk Heterojunction Blends

4.1. Introduction

Charge carrier mobility, $\mu$, is a key parameter that can be used to quantify the transport properties of an organic semiconductor (OS).[4.1] Using $\mu$, one can estimate the current that can go through an OS, and make some predictions about device characteristics. For example, $\mu$ can be used to estimate the carrier drift length in an organic photovoltaic (OPV) cell, and to optimize the thickness of an OPV cell.[4.2] Several techniques can be used for extracting $\mu$. For semiconducting PV polymers, current-voltage ($I-V$) fitting is, perhaps, the most popular.[4.3] However, the method can be error-prone if the sample is not fulfilling the assumptions used in the space-charge-limited current (SCLC) model. For example, the charge injection contact is non-Ohmic or the sample is not unipolar.[4.4] Another popular technique is photo-charge-extraction by linearly-increasing voltage (photo-CELIV). Photo-CELIV measurement can be carried out on samples in an OPV configuration.[4.5] Nevertheless, photo-CELIV cannot distinguish what kind of charge carrier that we are measuring.

This study looks into two transport characterization techniques: dark-injection space-charge-limited current (DI-SCLC) and admittance

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spectroscopy (AS),[4.6, 4.7] and explores their applicabilities to OPV polymers. DI-SCLC probes the transient current response (by electrons or holes) of a thin film after the application of a step voltage. AS measures the frequency dependent capacitance under a dc bias and a small ac signal. The principles of this technique are well-known [4.8 – 4.12]. Detailed theories on DI-SCLC and AS are also given in Chapter 2 of this thesis. However, applications of DI-SCLC or AS to OPV polymers are rather scarce. Below, we demonstrate that achieving unipolar transport measurement is the key for DI-SCLC and AS experiments. We outline a means of excluding electron leakage in a hole-only device for a PV polymer by inserting an interlayer between the polymer and the cathode. With the aid of this interlayer, we obtained well-defined DI-SCLC and AS signals for reliable carrier mobility determination.

4.2. Experimental Details

Three transport techniques, current-voltage (J-V) measurement, DI-SCLC, and AS are used in the chapter. A hole-only device structure is required for these three techniques which is ITO / PEDOT:PSS / polymer / (interlayer) / Au. In the first part of this chapter, two hole-conducting semiconducting polymers are studied. One is a light-emitting polymers, poly[(9,9-dioctylfluorenyl-2,7-diyl) -co-(N,N’-diphenyl)-N,N'-di(p-butylphenyl)-1,4-diamino-benzene)] (PFB). Another one is a PV polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT). They were obtained from American Dye Source and Rieke (P200), respectively, and used as-received. PFB is widely used as a hole-injection and -transporting layer in polymer light-emitting diodes while P3HT is one of the most popular materials for OPV cell.[4.13, 4.14]
PEDOT:PSS of 25 nm was spin-coated on a cleaned ITO glass substrate as the anode. PFB and P3HT was dissolved in toluene and 1,2-dichlorobenzene (DCB), respectively, for a concentration of 40 mg/ml. Then, the solution was spin-coated on the top of the PEDOT:PSS layer and dried naturally for around 18 hours in N₂ atmosphere to form the polymer films. The film thicknesses were between 300-420 nm. P3HT films were then thermally annealed at 120 °C for 10 minutes. Subsequently, 100 nm of gold was coated on the polymer by thermal evaporation. For P3HT samples, a 10 nm of hole-transporting, but electron blocking and/or trapping, interlayer was sometimes inserted in between P3HT and the Au cathode. Three types of interlayer were used: (i) electron-blocking (EB), (ii) electron-trapping (ET), and (iii) electron-blocking and -trapping (EBT). For the EB layer, two materials were used, 4,4’,4”-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (m-MTDATA) and N,N’-Bis(3-methylphenyl)-N,N’-bis(phenyl)-9,9-Spirobifluorene (Spiro-TPD). For the ET layer, copper phthalocyanine (CuPc) was picked. For the EBT layer, m-MTDATA doped with 2% of CuPc [m-MTDATA:CuPc(2%)] and spiro-TPD:CuPc(2%) were tried. Table 4.1 lists the types of interlayer and the materials chosen. The chemical structures of the polymers and the interlayer are shown in Figure 4.1. The HOMO and LUMO values of the polymers and the EB and ET materials are shown in the Figure 4.2.
<table>
<thead>
<tr>
<th>Type</th>
<th>Nature of the interlayer</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Electron-blocking (EB)</td>
<td>m-MTDATA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spiro-TPD</td>
</tr>
<tr>
<td>ii</td>
<td>Electron-trapping (ET)</td>
<td>CuPc</td>
</tr>
<tr>
<td>iii</td>
<td>Electron-blocking and -trapping (EBT)</td>
<td>m-MTDATA:CuPc (2%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spiro-TPD:CuPc (2%)</td>
</tr>
</tbody>
</table>

Table 4.1 Types of interlayer and the corresponding materials.
Figure 4.1  Chemical structures of PFB, P3HT, m-MTDATA, spiro-TPD and CuPc.

Figure 4.2  Energy levels of different polymers and interlayers.
4.3. Results and Discussion

4.3.1. Electron Leakage in a Nominally Hole-Only Structure

PFB and P3HT are first probed by DI-SCLC. Figure 4.3 shows the experimentally determined DI-SCLC signals for samples with the structure ITO / PEDOT:PSS / polymer / Au at room temperature (RT). The HOMOs of PFB and P3HT are -5.1 and -5.2 eV, respectively. These values are very similar to the work function of PEDOT:PSS. Therefore, the anode contact is Ohmic for hole conduction. On the other hand, Au has a work function of about -5.2 eV, and is well below the LUMOs of PFB (-1.9 eV) and P3HT (-3.2 eV). Therefore, the Au cathode is expected to be electron-blocking. Under the conditions of Ohmic contact and unipolar transport, the standard theory of DI-SCLC predicts, after the application of a voltage step $V$, at $t = 0$, a transient current $J(t)$ that bears a characteristic temporal profile as indicated in Figure 4.3(a).[4.6] At $t = \tau_{D1}$, $J(t)$ reaches a maximum value of $J_{D1}$. For $t > \tau_{D1}$, the transient current decays to a steady state value of the space-charge-limited current $J_{SCL}$. Figure 4.3(b) shows that for PFB, the DI-SCLC signal follows the expected $J(t)$ quite well, with a well-defined $J_{D1}$, $\tau_{D1}$, and a clear steady state $J_{SCL}$. The hole mobility is found to be $7.3 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ under 117 kV/cm electric field at RT, in general agreement to those in the literature.[4.15] On the other hand, the DI-SCLC signal in Figure 4.3(c) for P3HT deviates significantly from Figure 4.3(a). The severe departure of DI-SCLC signal for P3HT can be understood as follows. Only hole current should be expected. However, the intrinsic density-of-states (DOS) distribution can be quite broad.[4.16] Besides the intrinsic DOS, defect states can be produced in the energy gap during hot Au atoms deposition. These defect states may effectively broaden the intrinsic electron DOS. Under a high enough electric field, the effective tailed states of the electron DOS can be accessible for electron injection.
from the Au cathode. The injected electrons transport under the applied field, and they result in an electron current. The current measured is actually the superposition of the hole and electron currents. In contrast, for PFB, the LUMO level is located at about -1.9 eV, and presents a significantly higher barrier for electron injection. Thus, much better DI-SCLC transient can be obtained for PFB as shown in Figure 4.3(b).
Figure 4.3 DI-SCLC transients at room temperature. (a) PFB (418 nm) at 4.9 V. (b) P3HT (292 nm) at 3.9 V.
4.3.2. DI-SCLC Results with an Interlayer

In this part, three types of interlayer were inserted between P3HT and Au to prevent electron injection or leakage from the cathode. However, the interlayer should allow holes to transport with sufficient hole mobility. In addition, the HOMO of the interlayer should match with that of P3HT. Also, the interlayer should be thin relative to the active layer in order to minimize the effect on the transit time. Thus, the thicknesses of all the interlayers were restricted to 10 nm. Meanwhile, the thickness of P3HT is about 300 nm.

For electron-blocking (EB) interlayer, the materials should have high-lying LUMO. M-MTDATA and Spiro-TPD were chosen for blocking electrons from the cathode. Both materials have high-lying LUMOs of about -1.9 eV, and their HOMO values match with that of P3HT (Figure 4.2). For electron-trapping (ET) interlayer, the materials should have the ability to trap electron. CuPc was chosen for ET material. Pristine CuPc is known to be ambipolar with comparable electron and hole mobilities of $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$.[4.17] After air exposure, CuPc films can preserve its hole transport, but its electron transport is severely hindered due to electron traps induced by moisture or oxygen.[4.17] For the EBT interlayer, 2% of CuPc was doped into the m-MTDATA or spiro-TPD by thermal co-evaporation.

Figure 4.4 shows selected DI-SCLC transients of P3HT with and without interlayer. The plots on the left column are the DI-SCLC transients at RT, 292 K, while those on the right column are the transient at low temperature (LT), 246 K. The signals without using an interlayer are also shown in Figure 4.4(a). Figure 4.4(b) and (c) show the results with m-MTDATA and Spiro-TPD as an EB layer. The transient spikes at RT do not really improve suggesting that m-MTDATA and
Spiro-TPD are not effective in EB. However, at LT, current spikes appear to emerge. This points out that electrons can still leak from the Au cathode but, at a lower temperature, the electrons have less thermal energy. So, the electron leakages are reduced. Figure 4.4(d) shows the result for an ET layer of CuPc. A clear but small peak can be observed at RT. The spike is sharper at LT. So, CuPc is useful in suppressing electron leakage. However, the signal is still not desirable. Figure 4.4(e) and (f) show the results with m-MTDATA:CuPc (2%) or spiro-TPD:CuPc (2%) as an EBT layer. Much sharper transient peaks were obtained compared to Figure 4.4(a-d). In fact, the results mimic the classic DI-SCLC signal quite well [Figure 4.3(a)]. At RT, the transit times, $\tau_{DI}$, are 0.68 $\mu$s and 0.61 $\mu$s corresponding to hole mobility values of $3.2 \times 10^{-4}$ and $4.3 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for using m-MTDATA:CuPc and Spiro-TPC:CuPc, respectively. Among these three types of interlayer, the combined EBT interlayer scheme is the most effective in suppressing electron leakages.

The ratio of $J_{DI}$ to $J_{SCL}$ allows us to further evaluate the DI-SCLC signals. The ratios are 1.09 and 1.22 for m-MTDATA:CuPc and Spiro-TPD:CuPc respectively. The latter, 1.22, is practically the same as the ideal value of 1.21 in DI-SCLC theory.[4.6] As a result, Spiro-TPD:CuPc is the most effective interlayer in suppressing electron leakage.
Figure 4.4 DI-SCLC transients of P3HT with an interlayer ($V \sim 3.9$ V) at room temperature (left) and low temperature (right) with (a) no interlayer, (b) m-MTDATA, (c) spiro-TPD, (d) CuPc, (e) m-MTDATA:CuPc (2%), (f) Spiro-TPD:CuPc (2%).
We use Spiro-TPD:CuPc interlayer to explain how this kind of EBT interlayer functions. The LUMO of CuPc is located at about -3.5 eV, which is lower than those of both Spiro-TPD (-1.9 eV) and P3HT (-3.2 eV). After the application of the voltage step, the high-lying LUMO of Spiro-TPD presents a high barrier for electron injection. For those electrons that manage to cross this barrier, they are trapped by the CuPc dopants. Electron conduction within the CuPc dopants is not feasible due to low dopant concentration of 2%. Alternatively, detrapping to the LUMO of the Spiro-TPD host is also not favorable due to the 1.6 eV offset in the LUMO levels of the host and the dopant (Figure 4.2). Figure 4.5 is a schematic diagram, illustrating how electrons are trapped by the CuPc dopants in the Spiro-TPD host within the interlayer. On the other hand, transport of holes is effectively barrier-free throughout the entire sample.
Figure 4.5  Schematic diagram illustrating how leakage electrons from the Au electrode are blocked by Spiro-TPD or trapped by the CuPc dopants in the Spiro-TPD host within the interlayer.
Figure 4.6 summarizes the hole mobilities of P3HT at room temperature extracted from DI-SCLC by using EBT interlayer m-MTDATA:CuPc and Spiro-TPD:CuPc. The mobilities extracted with m-MTDATA:CuPc are generally slightly smaller than that with Spiro-TPD:CuPc which can be attributed to the hole mobility of the interlayer. Spiro-TPD has a hole mobility of $\sim 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is one to two orders higher than that of m-MTDATA, $\sim 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.\[4.18, 4.19\] The low hole mobility of m-MTDATA will probably affect the transit time and therefore a lower mobility is extracted. For comparison, we also measured hole mobilities of a thick film (6.8 $\mu$m) of P3HT using time-of-flight (TOF) technique. We can see there is a good agreement between the two techniques with $\mu$ in the range between $3 \times 10^{-4}$ and $6 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The experimental values also agree to those in the literatures.[4.16, 4.20] In the case of P3HT for DI-SCLC measurement, we only need $\sim 300$ nm for measurements. However, in TOF, a much thicker film is required for measurements.
Figure 4.6 Hole mobilities of P3HT at room temperature from TOF and DI-SCLC experiments. The film thicknesses for TOF and DI-SCLC experiments were 6.8 µm and ~300 nm, respectively. The solid lines represent the best linear fits to the data. The inset shows a typical TOF signal. The vertical dashed line indicates the position of the hole transit time $\tau$. 
4.3.3. Admittance Spectroscopy with an Interlayer

Besides DI-SCLC, we also probe hole transport in P3HT films by admittance spectroscopy (AS). Figure 4.7 shows the expected AS signal and the normalized capacitance against frequency plot of P3HT. As shown in Figure 4.7(b), some experimental AS data clearly depart from the expected signal as suggested in Figure 4.7(a). For the sample without using interlayer, capacitance decreases with decreasing frequency due to electron injection at the cathode as illustrated in Figure 4.8. This negative contribution to the capacitance is the result of minority carrier injection and this is also a key evidence of the electron leakage.[4.21 – 4.24] So, after inserting a 10 nm interlayer, all the signals at low frequencies are improved. With a m-MTDATA interlayer, the signal has a notable improvement at low frequencies. However, with a Spiro-TPD interlayer, this signal at low frequencies barely improved compared to the control sample (without interlayer). When CuPc is used as the ET layer, the negative contribution to the capacitance is also improved at low frequencies. Finally, with EBT layers of m-MTDATA:CuPc or Spiro-TPD:CuPc, well-defined AS signals similar to the ideal signal in Figure 4.7(a) can be obtained.

Figure 4.9 shows the AS mobilities. Using the same interlayer Spiro-TPD:CuPc, the mobilities from AS are very similar to those from DI-SCLC. Furthermore, the mobilities extracted using m-MTDATA:CuPc as interlayer are slightly lower than the mobilities extracted using Spiro-TPD:CuPc as interlayer. The results obtained from AS is consistent with that from DI-SCLC. Therefore, the presence of the EBT interlayer can suppress the electron leakage resulting in meaningful mobilities extraction.
Figure 4.7  (a) Expected AS plot showing the capacitance response of an organic semiconductor at different frequencies. (b) Normalized capacitances against frequencies of P3HT under 2 V bias at room temperature with different interlayers.
Figure 4.8  Negative contribution to the capacitance due to electron leakage in a hole-only device.
Figure 4.9 Hole mobilities of P3HT at room temperature extracted from TOF, DI-SCLC, and AS experiments. The solid lines represent the best linear fits to the data.
4.3.4. Gaussian Disorder Model Analysis

To study the energetic disorder of P3HT, Gaussian disorder model (GDM) is used to analyze the field dependent mobility at different temperatures.[4.25] In GDM, carriers transport in a disordered molecular material by hopping through the density-of-states (DOS) with Gaussian distribution. The field and temperature dependent mobility in GDM can be expressed as:

$$\mu(F, T) = \mu_\infty \exp \left[-\left(\frac{2\sigma}{3kT}\right)\right] \exp \left(\frac{1}{\beta F^2}\right)$$

(4.1)

where $\mu_\infty$ is the high-temperature limit mobility, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\sigma$ is the energetic disorder. The energetic disorder is the standard derivation of the Gaussian DOS. From a semi-log plot of $\mu(0, T)$ against $1/T^2$, $\mu_\infty$ and $\sigma$ can be found. Figure 4.10 shows the mobilities extracted by DI-SCLC. The zero-field mobilities $\mu(0, T)$ can be found from y-intercepts shown in Figure 4.10. Figure 4.11 is a semi-log plot of $\mu(0, T)$ vs $1/T^2$. $\mu_\infty$ and $\sigma$ are found to be 0.12 cm$^2$V$^{-1}$s$^{-1}$ and 86 meV, respectively.
Figure 4.10 Field dependent hole mobilities of P3HT at different temperatures extracted by DI-SCLC with spiro-TPD:CuPc as EBT interlayer. The solid lines represent the best linear fits to the data.
Figure 4.11  Zero-field mobilities of P3HT vs $1/T^2$. The solid line represents the best linear fitting to the data.

$\mu_\infty = 0.12 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

$\sigma = 86 \text{ meV}$
4.3.5. Application of Electron Blocking and Trapping Layer in Polymer:Fullerene Bulk Heterojunction Blends

The EBT Spiro-TPD:CuPc (2%) interlayer can be applied for the transport characterization of bulk-heterojunction (BHJ) thin films used in OPV cells. Two OPV polymers, P3HT and poly[N-9’’-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’’,1’’,3’’-benzothiadiazole)] (PCDTBT), were separately blended with [6,6]-phenyl C61 butyric acid methyl ester (PCBM) and [6,6]-phenyl C71 butyric acid methyl ester (PC71BM). These two BHJ blends can be denoted by P3HT:PCBM and PCDTBT:PC71BM, respectively. The transport properties of the BHJ films were studied by AS. In these films, we expect more serious electron leakage if an electron-blocking and -trapping (EBT) layer is absent. Electrons can inject directly from the metal cathode into PCBM or PC71BM due to their low lying LUMOs. Figure 4.12 shows the capacitance-frequency characteristics of P3HT:PCBM (1:1 mass ratio dissolved in DCB) and PCDTBT:PC71BM (1:2 mass ratio dissolved in CF). For P3HT:PCBM, the raw data still deviate from a typical AS signal in which the onset of the capacitance drop is shifted from higher frequency to lower frequency regime. This suggests that part of the electron leakage is suppressed with the presence of the EBT interlayer. Although the EBT layer cannot completely prevent all the electron leakage, carrier mobility can still be extracted with the improved AS signal. On the other hand, for PCDTBT:PC71BM, the improvement is more obvious. A standard AS signal can be obtained indicating efficient suppression of the electron leakage.
Figure 4.12 Normalized capacitance against normalized frequency plots of (a) P3HT:PCBM (350 nm, 1:1 mass ratio in dissolved in DCB) and (b) PCDTBT:PC$_{71}$BM (200 nm, 1:2 mass ratio in dissolved in CF) under 3 V bias at room temperature with a Spiro-TPD:CuPc(2%) EBT interlayer.
Figure 4.13 shows the extracted field dependent mobilities of P3HT:PCBM and PCDTBT:PC\textsubscript{71}BM BHJ blends with different blend ratios. For comparison, charge carrier mobilities of pristine polymers are also shown in the same plot. For P3HT and its BHJ blends, the hole mobilities extracted are insensitive to the presence of PCBM and the mobilities are about $2 - 3 \times 10^{-4}$ cm\textsuperscript{2}/V\textit{s}. This result is consistent with a previous report.[4.19] For P3HT containing films, sharp peaks were observed by grazing incident X-ray diffraction (GIXRD) indicating polycrystalline nature of P3HT films as shown in Figure 4.14(a). As the polymer chains of P3HT are well-connected, holes can transport through the BHJ blend via the distinct percolation pathways. In contrast, for PCDTBT containing films, the hole mobilities extracted strongly depends on the blend ratio. As the PC\textsubscript{71}BM content increases, more hole transporting pathways are blocked by PC\textsubscript{71}BM in the amorphous PCDTBT films as indicated by GIXRD in Figure 4.14(b). Therefore, holes are required to hop, on average, longer distances among PCDTBT domains, resulting in reduced hole mobilities with increasing PC\textsubscript{71}BM content.
Figure 4.13 Extracted field dependent mobilities of P3HT:PCBM (open symbols) and PCDTBT:PC71BM (solid symbols) with different blend ratios at room temperature. The solid lines represent the best linear fits to the data.
Figure 4.14  GIXRD spectra of the BHJ blends with different blend ratios.
4.3.6. Correlations between Device Performances and Energetic Disorder

The GDM can be used to analyze the mobilities of the BHJ blend samples with different blend ratios at different temperatures. From the analysis, the high-temperature limit mobility, $\mu_\infty$, and the energetic disorder, $\sigma$, can be extracted. Figure 4.15 shows $\mu_0$ vs $1/T^2$ plot of different BHJ blends with different blend ratios. With the y-intercepts and slopes obtained from the data in Figure 4.15, $\mu_\infty$ and $\sigma$ can be calculated. They are listed in Table 4.2.

<table>
<thead>
<tr>
<th>BHJ blend</th>
<th>Blend ratio (Donor:acceptor)</th>
<th>$\mu_\infty$ (cm$^2$/Vs)</th>
<th>$\sigma$ (meV)</th>
</tr>
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<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>1:0</td>
<td>$3.0 \times 10^{-3}$</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>$1.1 \times 10^{-3}$</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>$5.7 \times 10^{-3}$</td>
<td>88</td>
</tr>
<tr>
<td>PCDTBT:PC$_{71}$BM</td>
<td>1:0</td>
<td>$3.4 \times 10^{-1}$</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>$2.9 \times 10^{-3}$</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>$3.3 \times 10^{-3}$</td>
<td>122</td>
</tr>
</tbody>
</table>

Table 4.2 High-temperature limit mobilities and energetic disorders of the BHJ blends with different blend ratios.
Figure 4.15  Zero-filed mobilities of BHJ blends with different blend ratios vs $1/T^2$. The solid lines represent the best linear fits to the data.
As shown in Table 4.2 and Figure 4.15, for P3HT:PCBM blends, $\mu_\infty$ is insensitive to the presence of PCBM where $\mu_\infty$ are in the range of $1 \sim 6 \times 10^{-3}$ cm$^2$/Vs. However, for PCDTBT:PC$_{71}$BM blends, $\mu_\infty$ is sensitive to the portion of PC$_{71}$BM. $\mu_\infty$ of PCDTBT:PC$_{71}$BM blend drops from $10^{-1}$ to $10^{-3}$ cm$^2$/Vs for blend ratio from 1:0 to 1:4 respectively. These results can be explained as discussed in the last section. Different film properties of these two BHJ blends were found by the GIXRD. Well-resolved diffraction peaks at about 6° for P3HT containing films (Figure 4.14) indicating that P3HT forms nano-crystalline domains. These crystalline domains are well-connected even though half of the blend film is PCBM. Therefore, the hole transport are not affected in the case of P3HT. For PCDTBT containing films, the GIXRD spectra are featureless (Figure 4.14) indicating that these films are amorphous. The connection between PCDTBT is strongly affected by the presence of PC$_{71}$BM. Higher portion of PC$_{71}$BM results in longer average hopping distance for holes to hop and leading to reduced $\mu_\infty$.

Unlike $\mu_\infty$, the energetic disorders, $\sigma$, are almost the same within the same donor BHJ blend even with different blend ratios. The $\sigma$ for P3HT containing films are around 82 meV and the $\sigma$ for PCDTBT containing films are around 120 meV. For the hole transport in the BHJ film, holes mainly transport via the HOMO of the donor without entering the HOMO of the acceptor. Therefore, the extracted $\sigma$ only indicate the HOMO width of the donor. Meanwhile, the acceptor acts as scatterer in the BHJ blend.[4.26]

With these transport properties of the BHJ blends, we further investigate the performance of the corresponding OPV cells. The devices are optimized and with
active layer thicknesses of 150 and 70 nm for the active layer of P3HT:PCBM and PCDTBT:PC71BM, respectively. The PV performances are listed in Table 4.3 and the $J-V$ characteristics of the OPV cells are shown in Figure 4.16.

<table>
<thead>
<tr>
<th>BHJ Blend</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>8.1</td>
<td>0.62</td>
<td>71</td>
<td>3.5</td>
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<tr>
<td>PCDTBT:PC71BM</td>
<td>10.2</td>
<td>0.90</td>
<td>59</td>
<td>5.5</td>
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Table 4.3 Performances of optimized OPV cells with different BHJ blends.
Figure 4.16  $J$-$V$ characteristics of OPV cells with different BHJ blends under AM1.5G illumination.
The $J_{SC}$ of P3HT OPV cell is 7.5 mA/cm$^2$ which is smaller than that of PCDTBT OPV cell of 10.2 mA/cm$^2$. The difference is due to the smaller bendgap of PCDTBT which has a better optical absorption in solar spectrum. Although the hole mobility for PCDTBT:PC$_{71}$BM is around 1 order lower than that of P3HT (Figure 4.13), this seems not to affect much on the charge carrier extraction. In fact, the optimized active layer thickness reflects the influence of the hole mobility. For PCDTBT:PC$_{71}$BM, with lower hole mobility, the optimized active layer thickness is only 70 nm which is much smaller than that of P3HT:PCBM of 150 nm. So, with reasonable mobility, charge carrier extraction can be efficient. However, with higher mobility, the optimized active layer thickness can be thicker for more light absorption.

For the $V_{OC}$, it is directly proportional to the donor-acceptor interface energy gap ($\Delta E_{DA}$) and can be expressed as: [4.27, 4.28]

$$qV_{OC} = \Delta E_{DA} + kT\ln\left(\frac{G}{\gamma N_h N_e}\right) - \frac{\sigma^2}{kT}$$  \hspace{1cm} (4.1)

where $q$ is the elementary charge, $G$ is the generation rate, $\gamma$ is the recombination rate coefficient, $N_h$ and $N_e$ are the total density of states for holes and electrons, respectively. In Eq. 4.1, it is clear that the last term with the energetic disorder, $-\frac{\sigma^2}{kT}$, suppresses the $V_{OC}$. The suppressed values for the two BHJ blends are calculated in Table 4.4 together with measured $V_{OC}$ and the energetic disorders. For PCDTBT:PC$_{71}$BM, with higher $\sigma$ of 115 meV, the loss in $V_{OC}$ is higher than that of P3HT:PCBM by 0.21 V.
<table>
<thead>
<tr>
<th>BHJ blend</th>
<th>Measured $V_{OC}$ (V)</th>
<th>$\sigma$ (meV)</th>
<th>$-\sigma^2/kT$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>0.60</td>
<td>87</td>
<td>-0.30</td>
</tr>
<tr>
<td>PCDTBT:PC$_{71}$BM</td>
<td>0.90</td>
<td>115</td>
<td>-0.51</td>
</tr>
</tbody>
</table>

Table 4.4  Calculated $V_{OC}$ loss due to energetic disorder.

$V_{OC}$ aside, $FF$ is also found to be limited by $\sigma$. For P3HT:PCBM, a smaller $\sigma$ of 87 meV, the $FF$ is higher with 67% while for PCDTBT:PC$_{71}$BM, a larger $\sigma$ of 115 meV, the $FF$ is lower with 59%. In BHJ blend, a small $\sigma$ results in reduced recombination [4.27 – 4.30]. For a large $\sigma$ (such as PCDTBT:PC$_{71}$BM), holes can be more easily trapped at the tailed states of the broadened DOS and recombine with the electrons. As a result, the loss in photocurrent will be enhanced which leads to poor $FF$.

Blakesley et al. simulated a series of $J$-$V$ characteristic of OPV cell based on different energetic disorders as shown in Figure 4.17. For a higher $\sigma$, a lower $V_{OC}$ and $FF$ are achieved. Their result agrees with our observation that high energetic disorder, $\sigma$, is one of the origin in suppressing $V_{OC}$ and $FF$.  

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Figure 4.17 Simulations of a series of $J$-$V$ characteristic of OPV cells based on different energetic disorders.[4.27]
4.4. Summary

DI-SCLC and AS techniques were used to study the transport properties of PFB, P3HT, and PCDTBT. When a nominally hole-only device structure, PEDOT:PSS / polymer / Au was used, well-defined DI-SCLC signals for PFB but ill-defined DI-SCLC and AS signals for P3HT were obtained. The ill-defined signals for P3HT arise from electron leakages from the cathode. Three kinds of layer, EB (m-MTDATA and spiro-TPD), ET (CuPc), and EBT (m-MTDATA:CuPc and spiro-TPD:CuPc), were used to prevent electron leakages. Among these interlayers, only EBT can effectively prevent the electron leakages and result in a meaningful DI-SCLC and AS measurements. With a suitable interlayer to suppress undesirable carrier injection and transport, DI-SCLC and AS techniques should find broad applications in the transport characterization of PV-based polymers and the corresponding BHJ blends.

The application of EBT layer to BHJ blends of P3HT:PCBM and PCDTBT:PC$_{71}$BM are also demonstrated. From Gaussian disorder model analysis, the high-temperature limit mobility, $\mu_\infty$, and energetic disorder, $\sigma$, of the BHJ blends can be obtained. For a well-connected polymer such as P3HT, $\mu_\infty$ is insensitive to the acceptor portion. However, for an amorphous polymer such as PCDTBT, $\mu_\infty$ drops with increasing acceptor portion. On the other hand, $\sigma$ is independent of composition within the tested blend ratios as holes only transport via the HOMO of the donors. The $\sigma$ extracted for P3HT and PCDTBT containing samples are around 87 and 115 meV, respectively. $\sigma$ can be correlated to OPV cell performances. Large $\sigma$ is found to suppress both $V_{OC}$ and FF.
References:


Chapter 5

Batch-to-Batch Variation of Polymeric Photovoltaic Materials: its Origin and Impacts on Charge Carrier Transport and Device Performances

5.1. Introduction

Nowadays, low bandgap photovoltaic (PV) co-polymers with power conversion efficiency ($PCE$) in the range of 5% to 7% are readily available. [5.1-5.3] With further optimization, $PCE$ of 7% to 9% can be achieved. [5.4, 5.5] Some of these polymers are now commercially available in small amounts for laboratory scale research. Normally, vendors provide little information on the physical properties of the polymers. Data such as trace metal contents, impurities, molecular weight distributions are generally lacking. These factors may have significant impacts on device performance. However, it is difficult to control these factors during synthesis. As a result, the device performance may vary from one batch to the other. Obviously, batch-to-batch variation is a stumbling block for the development of polymeric PV cells in both research and in industry. Therefore, it is of paramount importance to understand the origin of batch-to-batch variation in photovoltaic polymers.

In this chapter, an amorphous photovoltaic polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) was used to study the origin of batch-to-batch variation. PCDTBT was probably the first polymer to achieve a $PCE$ exceeding 6%, and it has captured tremendous attention in the past five years.[5.1] Five different batches of PCDTBT were

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b Parts of this Chapter have appeared in Adv. Energy Mater. 2014, 4, 1400768.
purchased from two companies. Their photovoltaic performances turned out to be very different. We discovered that the molecular weight distribution of these polymers have deep impacts on their transport behaviors and device performance.

5.2. Experimental Details

Five batches of PCDTBT, labeled A to E, were used as-received without further purification. Batches A to D were purchased from 1-Material and batch E was purchased from Luminescence Technology. PC\textsubscript{71}BM was purchased from Nano-C. Anhydrous 1,2-dichlorobenzene (DCB) was obtained from Sigma Aldrich. These materials were used as-received.

Gel permeation chromatography (GPC) can reveal the molecular weight distribution of polymers. In this experiment, Waters Breeze HPLC system with 1525 Binary HPLC Pump and 2414 Differential Refractometer was used for GPC measurement to obtain molecular weight information of polymers, including number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity index (PDI).\textsuperscript{c} Absorption spectra were measured for samples A to E. In general, thin PCDTBT films (30 – 40 nm) were spun (700 rpm, 120 s) on quartz substrates with PCDTBT concentration of 5 mg/ml in DCB. PerkinElmer Lambda 750 UV/Vis Spectrometer was used for the measurement. Grazing incident X-ray diffraction (GIXRD) measurements were performed by the Bruker D8 Advance X-ray Diffractometer. The incident angle of X-ray was fixed at 0.3 °, while the detector was scanned from 3 ° to 30 °. The PCDTBT thin films were prepared in a way similar to the absorption samples except Si wafers rather than quartz substrates were used.

\textsuperscript{c} The GPC measurements were performed by Dr. Zhao Li in National Research Council Canada.
For organic photovoltaic (OPV) cell fabrication, 15 nm of MoO₃ (99.998%, Strem Chemical) was thermally evaporated on a cleaned ITO substrate under high vacuum (~10⁻⁶ Torr). The MoO₃ coated substrate was then transferred into a nitrogen filled glove box (oxygen and moisture less than 1 ppm). PCDTBT and PC₇₁BM were dissolved in DCB with a mass ratio of 1:4. The total concentration of PCDTBT:PC₇₁BM blend solution was 40 mg/ml. The solution was stirred at 90 °C for at least 16 hours and then filtered with a 0.45 μm PTFE syringe filter right before spin-coating. The solution was spin-coated onto the MoO₃ coated ITO glass substrate with 900 rpm for 120 s resulting in ~70 nm thick blend layer. The films were dried naturally for at least 30 minutes. The samples were then transferred to a vacuum evaporator with exposure to air. Finally, 1 nm of lithium fluoride (LiF) and 130 nm of aluminum (Al) were thermally evaporated on the blend layer under high vacuum. The resulting device area was 0.108 cm². As a result, the OPV cells had a structure of ITO / MoO₃(15 nm) / PCDTBT:PC₇₁BM(~70 nm) / LiF(1 nm) / Al. OPV cell characterization was carried out in air using an AM1.5G solar simulator with an intensity of 100 mW/cm². For light intensity dependent OPV cell measurement, different neutral density filter was added to achieve different incident light intensities and devices in these measurements were encapsulated in order to minimize the effect of degradation. Keithley 2400 sourcemeter was used for the current-voltage measurement under illumination.

Hole-only devices were fabricated for the transport measurement with the structure of ITO / MoO₃(20nm) / PCDTBT(250-350nm) / Au. To obtain film thicknesses between 250 nm and 350 nm, the concentration of PCDTBT solution
and the spin speed were varied from 35 to 60 mg/ml and 700 to 1200 rpm respectively. The fabrication procedure was similar to that of OPV cells. Finally, instead of LiF/Al electrode, 100 nm of gold (Au) was thermally evaporated on PCDTBT to serve as a high work function electrode to prevent electron injection. The resulting device area was 0.035 cm². Transport data were taken in an Oxford cryostat with pressure of less than 20 mTorr. The temperatures of the samples were regulated between 244 and 314 K.

5.3. Results and Discussion

5.3.1. Basic Characterization of the Polymers

GPC was performed to characterize the molecular weight distributions on the five different batches of as-received PCDTBT, namely A to E. The results are shown in Figure 5.1. All five batches of PCDTBT show two peaks in the GPC data. For these bimodal molecular weight distributions, the peak at shorter time corresponds to a higher molecular weight component; the peak at longer time corresponds to a lower molecular weight component. The high molecular weight component has a number average molecular weight ($M_n$) in the range of 70-110 kDa for different batches as shown in Table 5.1. Recently, Beaupré et al summarized the effect of molecular weight of PCDTBT on PV device performances.[5.6] They showed that PCEs larger than 5% can be obtained with polymers having $M_n$ larger than 25 kDa. Therefore, the high molecular weight component of different batches should be within the desirable range for efficient PV devices. However, the major difference among different batches is the amount of the low molecular weight component. In general, the amount of low molecular weight peak is increasing (peak intensity) from batch A to E as shown in Figure 5.1. The low molecular weight component corresponds to $M_n$ in the range of
2-10 kDa. To summarize the whole distributions, the overall average of $M_n$, $\bar{M}_n$, were calculated varying from 27 kDa to 5 kDa. All the GPC results are listed in Table 5.1.
Figure 5.1 GPC results of five different batches (labeled A to E) of PCDTBT showing bimodal distributions of the molecular weight. A shorter time indicates higher molecular weight. The data were normalized to the high molecular weight peak. The inset shows the chemical structure of PCDTBT.
<table>
<thead>
<tr>
<th></th>
<th>High molecular weight peak [PDI]</th>
<th>Low molecular weight peak [PDI]</th>
<th>Overall average, $\overline{M_n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110.0 [2.2]</td>
<td>2.8 [1.2]</td>
<td>27.3</td>
</tr>
<tr>
<td>B</td>
<td>98.8 [2.0]</td>
<td>2.6 [1.3]</td>
<td>23.6</td>
</tr>
<tr>
<td>C</td>
<td>75.4 [1.4]</td>
<td>8.2 [1.1]</td>
<td>11.6</td>
</tr>
<tr>
<td>D</td>
<td>74.6 [1.2]</td>
<td>6.4 [1.3]</td>
<td>6.0</td>
</tr>
<tr>
<td>E</td>
<td>70.6 [1.3]</td>
<td>6.8 [1.2]</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 5.1 GPC analysis of PCDTBT for sample A to E showing the number average molecular weight ($M_n$) of the high and low molecular weight peaks. The overall average of the entire distribution ($\overline{M_n}$) is shown in the last column. Numbers within square parenthesis are the polydispersity indices (PDI) of the individual peaks.

Figure 5.2 shows $\overline{M_n}$ and the peak ratio of the high-to-low molecular weight peaks of different batches of PCDTBT. It is well known that such combination of high and low molecular weight components is typical during polymerization. For instance, for PCDTBT, the polymers can be synthesized by condensation polymerization and the polydispersity depends on both the monomer ratio and the reaction conditions.[5.7] Particularly in high concentration, cyclization may take place and results in low molecular weight part. Consequently, without further extraction, the as-received polymers might have an uncertainty of such molecular weight distribution. Although the high $M_n$ component is desirable for efficient PV device, the additional low $M_n$ component would strongly affect the device performance. We note that when these polymers were acquired from the vendors, only the average molecular weights for some polymer batches were given. However, the vendors did not provide information of the molecular weight...
distributions. Our data clearly suggests that molecular weight screening is essential for full characterization of the polymers.

To check the ordering of PCDTBT molecules in thin films prepared by spin coating, grazing incident X-ray diffraction (GIXRD) measurements were performed. Figure 5.3 shows the GIXRD results of five PCDTBT thin films. There is absence of any notable diffraction peak in different batches of samples. This confirms the amorphous nature of PCDTBT films.
Figure 5.2  (a) Overall average molecular weight, $\bar{M}_n$. (b) Peak height ratio (high-to-low molecular weight) of PCDTBT samples A to E. Samples A and B have higher fractions of the high weight component.
Figure 5.3 Grazing incident X-ray diffraction (GIXRD) data of PCDTBT samples A to E.
Figure 5.4 shows the absorption coefficients of five different PCDTBT films. All spectra are comparable in shapes, positions and the cut-off absorptions. These results are different from previously reported polymers possessing strong $\pi-\pi$ stacking.[5.8, 5.9] In those cases, thin films casted with high molecular weight polymers had higher optical absorption coefficients and had the cut-off absorptions towards longer wavelengths. Although PCDTBT A to E have different molecular weight distributions, the optical absorptions of their films are still very similar. This can be explained by the amorphous nature of PCDTBT films.

Figure 5.5 shows the 2 $\mu$m $\times$ 2 $\mu$m atomic force microscope (AFM) images of five different PCDTBT films. From the height images (left column) with the scale bar from 0 to 20 nm, the surfaces of all PCDTBT films are quite smooth with root-mean-square roughnesses between 0.37 and 0.54 nm. From the phase images (right column) with the scale bar from 0 to 60°, it is expected that all the films appear to be very uniform.

Summarizing the results in this section, we note that all five polymers samples have very similar optical, structural, and morphological properties. Without the GPC analysis, it would appear that these polymers are similar and should have similar device properties.
Figure 5.4  Absorption coefficients of PCDTBT A to E.
Figure 5.5  Atomic force microscope images (2 μm × 2 μm) of PCDTBT samples A to E. Left column shows the height profiles with scale bar from 0 to 20 nm. Right column shows the phase profiles with scale bar from 0 to 60 °.
5.3.2. **Organic Photovoltaic Cell Performances**

The performance of PCDTBT PV cells using batch A to E were tested under AM1.5G condition. The current density-voltage ($J-V$) characteristics are shown in Figure 5.6. The highest PCE of 5.7 % has been achieved with batch A, which has the least amount of low molecular weight component. The $PCE$ is reduced with increasing amount of the low molecular weight component, and a $PCE$ of only 2.5 % can be obtained for batch E. The PV device performances are summarized in Table 5.2. The correlation between the device performance and $M_n$ is summarized in Figure 5.7. For samples A to D, the reduced $PCE$ is mainly attributed to the lower $J_{SC}$ and $FF$ of the devices. The $J_{SC}$ and $FF$ were reduced from 10.7 mA/cm$^2$ to 9.1 mA/cm$^2$ and 58.5 % to 47.8 %, respectively. We also note that there is an abrupt drop in device performance for sample E despite its molecular weight is similar to D. Sample E has a much reduced open-circuit voltage ($V_{OC}$) of 0.77 V compared to samples A – D. As companies might have different synthetic routes for a given polymer, a strict and quantitative comparison between sample E and the other four samples may not be reasonable. However, we still incorporate sample E in our discussion because it supports the notion that higher fraction of low molecular weight in PCDTBT suppresses the PV device performance.
Figure 5.6  $J$-$V$ characteristics of OPV cells for PCDTBT samples A to E under AM1.5G illumination with a structure of ITO / MoO$_3$(15 nm) / PCDTBT:PC$_{71}$BM (70 nm) / LiF (1 nm) / Al.
<table>
<thead>
<tr>
<th>Batch</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Average PCE (%) [s.d.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.7</td>
<td>0.91</td>
<td>58.5</td>
<td>5.7</td>
<td>5.6 [0.02]</td>
</tr>
<tr>
<td>B</td>
<td>10.3</td>
<td>0.89</td>
<td>56.9</td>
<td>5.3</td>
<td>5.1 [0.14]</td>
</tr>
<tr>
<td>C</td>
<td>9.5</td>
<td>0.90</td>
<td>51.6</td>
<td>4.4</td>
<td>4.3 [0.11]</td>
</tr>
<tr>
<td>D</td>
<td>9.1</td>
<td>0.91</td>
<td>47.8</td>
<td>4.0</td>
<td>3.9 [0.08]</td>
</tr>
<tr>
<td>E</td>
<td>7.8</td>
<td>0.77</td>
<td>41.1</td>
<td>2.5</td>
<td>2.3 [0.12]</td>
</tr>
</tbody>
</table>

Table 5.2  OPV cells performance of PCDTBT samples A to E. The average $PCE$s and the standard derivations are calculated based on 3 – 4 devices.

There are some reported literatures investigating how molecular weight affects the molecular packing and optical properties of crystalline PV polymers.[5.9, 5.10] In general, polymer films with low molecular weight ($M_n < 10$ kDa) have a weaker optical absorption, and a blue shifted cut-off absorption.[5.9, 5.10] For poly(3-hexylthiophene) (P3HT), reduced intermolecular ordering ($\pi-\pi$ stacking) was found for low molecular weight polymers resulting in poor device performance.[5.9] However, PCDTBT has no clear evidence of $\pi-\pi$ stacking.
Figure 5.7  OPV cell parameters, $J_{\text{SC}}$, $V_{\text{OC}}$, FF, and PCE vs the overall average molecular weight, $\overline{M}_n$. 
We sought to investigate the cause of the reduced $J_{SC}$ and $FF$. First, we consider how molecular packing and optical properties may influence the $J_{SC}$ and the $FF$. As checked by GIXRD measurements shown in Figure 5.3, the difference in molecular weight should not affect the molecular packing of PCDTBT as it is amorphous. As shown in Figure 5.4, all the measured optical absorption spectra and the cut-off of the PCDTBT films are similar. Moreover, all PV devices have the same device structure and similar active layer thicknesses (70 nm). The amount of photon absorption and internal electric field should be comparable. Therefore, molecular packing or optical absorptions cannot be the origin of reduced $J_{SC}$ and $FF$ in the low weight polymers.

### 5.3.3. Charge Carrier Transport Study

Charge carrier transport is known to be affected by the molecular weight of a polymer.[5.9, 5.11 – 5.13] Irrespective of the crystallinity, polymer films fabricated with lower molecular weight polymers have lower carrier mobilities. However, the origin of the reduced mobility is still controversial. Therefore, it is important to understand the charge carrier transport for further development of OPV cells.

Carrier transport properties of different batches of PCDTBT were studied to correlate the $J_{SC}$ and $FF$ of the photovoltaic devices. Hole-only devices were fabricated for current-voltage ($I$-$V$) measurements. The device structure is ITO / MoO$_3$(20 nm) / PCDTBT (250-350 nm) / Au. Carrier mobilities were extracted using the space-charge-limited current (SCLC) equation,[5.14 – 5.16]

$$J_{SCL} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp\left(0.89 \beta \sqrt{F}\right) F^2$$

\[(5.1)\]
where \( J_{\text{SCL}} \) is the space-charged-limited current density, \( d \) is the thickness of polymer thin film, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the relative permittivity of the polymer, \( \mu_0 \) is the zero-field mobility, \( \beta \) is the field-dependent coefficient, and \( F \) is the average electrical field. Figure 5.8 shows the room temperature data. The current densities of the hole-only devices decrease from batch A to E. Batch A has a current four orders of magnitude larger than that of batch E. Moreover, the measured \( J-V \) characteristics of devices are in good agreement with Eq. 5.1. The fitted values of \( \mu_0 \) and \( \beta \) are shown in Table 5.3. So, hole mobilities \( \mu_{\text{jsc}} = \mu_0 \exp(0.89\beta\sqrt{F_{\text{jsc}}}) \) can be readily extracted where \( \mu_{\text{jsc}} \) is the carrier mobility corresponding to the short-circuit condition and \( F_{\text{jsc}} = 0.9 \text{ V} / 70 \text{ nm} = \sim 129 \text{ kV/cm} \) is the electric field at short-circuit condition.

<table>
<thead>
<tr>
<th>PCDTBT</th>
<th>Thickness (nm)</th>
<th>( M_\eta ) (kDa)</th>
<th>( \mu_0 ) (cm²/Vs)</th>
<th>( \beta ) (V/cm)(^{1/2})</th>
<th>( \mu_{\text{jsc}} ) (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>361</td>
<td>27.3</td>
<td>3.13×10⁻⁶</td>
<td>6.78×10⁻³</td>
<td>2.72×10⁻⁵</td>
</tr>
<tr>
<td>B</td>
<td>253</td>
<td>23.6</td>
<td>4.30×10⁻⁷</td>
<td>8.91×10⁻³</td>
<td>7.39×10⁻⁶</td>
</tr>
<tr>
<td>C</td>
<td>370</td>
<td>11.6</td>
<td>7.10×10⁻⁸</td>
<td>1.12×10⁻²</td>
<td>2.53×10⁻⁶</td>
</tr>
<tr>
<td>D</td>
<td>257</td>
<td>6.0</td>
<td>2.08×10⁻⁸</td>
<td>8.93×10⁻³</td>
<td>3.59×10⁻⁷</td>
</tr>
<tr>
<td>E</td>
<td>369</td>
<td>5.0</td>
<td>8.00×10⁻¹⁰</td>
<td>9.36×10⁻³</td>
<td>1.59×10⁻⁸</td>
</tr>
</tbody>
</table>

Table 5.3 Fitted parameters from SCLC fitting (Figure 5.8) on hole-only devices of PCDTBT A to E. \( \mu_{\text{jsc}} \) are calculated based on the average electric field, \( F_{\text{jsc}} \) (0.9 V / 70 nm), the fitted values of the zero-field mobility, \( \mu_0 \), and the field-dependent coefficient, \( \beta \).
Figure 5.8  $J$-$V$ data (open symbols) of PCDTBT A to E with hole-only configuration of ITO / MoO$_3$(20 nm) / PCDTBT(250-350 nm) / Au and the SCLC fittings (solid lines) at room temperature in (a) semi-log plots and (b) log-log plots.
Temperature dependence $J$-$V$ measurements were carried out to extract detailed carrier transport parameters. We employed the Gaussian disorder model (GDM) for analysis.[5.17] The model describes carrier hopping in energetically Gaussian distributed transporting sites. The zero-field mobility can be described by:

$$
\mu_0 = \mu_\infty \exp \left[ - \left( \frac{2\sigma}{3kT} \right)^2 \right]
$$

(5.2)

where $\mu_\infty$ is the high-temperature limit mobility, $\sigma$ is the energetic disorder parameter, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. According to Eq. 5.2, the energetic disorder $\sigma$ plays a key role in determining the carrier mobility. In fact, for a photoactive polymer, $\sigma$ affects not only the mobility, but also the carrier recombination rate.[5.18] Several theoretical models have been proposed to correlate $V_{OC}$ and $FF$ with $\sigma$.[5.19, 5.20] Therefore, it is anticipated that $\sigma$ for different batches of polymers might be significantly different. In order to obtain $\sigma$, we measured $\mu_0$ for each batch of PCDTBT at different temperatures. From a plot of $\mu_0$ vs $1/T^2$, the slope can be used to extract $\sigma$.[5.21, 5.22] Figure 5.9 shows a summary of these plots and the carrier transport parameters are summarized in Table 5.4. Interestingly, the slopes from different batches are very similar, indicating that they have a similar value of $\sigma$. All the $\sigma$ from different batches have almost the same values of $115 \pm 3$ meV. In fact, instead of $\sigma$, the difference in carrier mobility in different batches is due to the difference in $\mu_\infty$ which is indicated at the y-intercept. The $\mu_\infty$ drops from $2.0 \times 10^{-2}$ to $1.2 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ from batch A to E.
<table>
<thead>
<tr>
<th>PCDTBT</th>
<th>$\bar{M}_n$ (kDa)</th>
<th>$\mu_\infty$ (cm$^2$/Vs)</th>
<th>$\sigma$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>27.3</td>
<td>$2.0 \times 10^{-2}$</td>
<td>112</td>
</tr>
<tr>
<td>B</td>
<td>23.6</td>
<td>$2.8 \times 10^{-3}$</td>
<td>112</td>
</tr>
<tr>
<td>C</td>
<td>11.6</td>
<td>$9.8 \times 10^{-4}$</td>
<td>117</td>
</tr>
<tr>
<td>D</td>
<td>6.0</td>
<td>$2.0 \times 10^{-4}$</td>
<td>115</td>
</tr>
<tr>
<td>E</td>
<td>5.0</td>
<td>$1.2 \times 10^{-5}$</td>
<td>118</td>
</tr>
</tbody>
</table>

Table 5.4  Transport parameters extracted from GDM analysis.
Figure 5.9  Zero-field mobility against $1/T^2$ for GDM analysis. Solid symbols are the data extracted from SCLC. Solid lines are the GDM fittings.
5.3.4. Correlation between Photovoltaic Performance and High-Temperature Limit Mobility

Based on the device and the transport data in the previous sections, the device performance can be correlated to the high-temperature mobilities, $\mu_\infty$, as shown in Figure 5.10. Three device parameters, $J_{SC}$, $FF$, and $PCE$, show a linear relation with the $\mu_\infty$ in a semi-log scale. Previously, Blom et al showed that in a semiconducting polymer, the $\mu_\infty$ can be written in the form:[5.23]

$$\mu_\infty = \frac{e v_0 a^2}{\sigma} \exp \left( \frac{-2a}{L} \right)$$  \hspace{1cm} (5.3)

where $e$ is the elementary charge, $v_0$ is the attempt-to-hop frequency, $a$ is the charge hopping distance, and $L$ is the localization radius. Figure 5.11 is a schematic diagram illustrating the various parameters involved in Eq. 5.3. A charge makes an attempt to hop from a site with energy $E_n$ to another site with energy $E_m$. The distance between the two sites is $a$. Within each site, the wavefunction has a localization radius $L$. The random fluctuation in site energies, arising from disorder, is $\sigma$. As $v_0$ and $L$ are primarily determined by the material and molecular structure, it is reasonable to assume that they are constants among batch A to E. As found in the GDM analysis, PCDTBT A to E have similar values of $\sigma$ around 115 ± 3 meV. Therefore, Eq. (5.3) suggests that the variation in $\mu_\infty$ of different batches is primarily due to the difference in hopping distances, $a$. 
Figure 5.10  OPV cell parameters, $J_{SC}$, $FF$, and $PCE$ vs the high-temperature limit mobility, $\mu_\infty$, of PCDTBT A to E.
Figure 5.11  Schematic diagram illustrating the various parameters, \( a \), \( L \), and \( \sigma \), in Eq. 5.3
In the case of a polymer with strong π-π stacking, such as P3HT, higher molecular weight is beneficial to promote intermolecular ordering, and therefore the hopping distance is smaller in higher crystalline thin film. On the other hand, thin film of PCDTBT is amorphous as it lacks notable XRD patterns (Figure 5.3). So, it is not clear on how the additional small molecular weight component can increase the overall hopping distance in PCDTBT. However, compared to P3HT, polymer chain of PCDTBT are non-planar.[5.24] Such a non-planar polymer is unlikely to form closely packed domains, and the rate determining step for carrier transport is the probability of finding the lowest energy adjacent hopping sites. Although the intramolecular charge transfer is efficient along the polymer chain, the small molecular weight component in such non-planar and amorphous structure would hinder the intermolecular charge transfer as illustrated in Figure 5.12. Once a charge is transferred to a small molecular weight polymer chain [Figure 5.12(b)], the probability of finding the nearest neighboring site to another chain is smaller than that of a long chain polymer. This results in increasing the overall hopping distances, and therefore reduced the carrier mobility.

Using Eq. 5.3 with typical values of, $v_0 = 10^{14}$ Hz, $L = 0.3$ nm,[5.25] and $\sigma = 115$ meV, we can simulate the high-temperature limit mobility, $\mu_\infty$, as a function of the hopping distance, $a$, as shown in Figure 5.13. Based on the $\mu_\infty$ of different batches of PCDTBT, the corresponding hopping distances can be extracted from Figure 5.13. For $\mu_\infty$ in the range between $2.0 \times 10^{-2}$ and $1.2 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$, the hopping distances vary between 0.9 and 2.3 nm. These results are in good agreement with other amorphous semiconducting polymers.[5.26]
Figure 5.12  Schematic diagrams illustrating how charge carriers transport through a polymer layer. (a), holes transport through a polymer layer with large fraction of high molecular weight polymer content. (b), holes transport through a polymer layer with large fraction of low molecular weight polymer content.
High temp. limit mobility, $\mu_\infty$ (cm$^2$/Vs)

Hopping distance, $a$ (nm)

Figure 5.13  Simulated high-temperature limit mobility, $\mu_\infty$, as a function of the hopping distance, $a$, using $\mu_\infty = \frac{e\nu_0 a^2}{\sigma} \exp\left(\frac{-2a}{L}\right)$. The horizontal lines are the experimentally extracted $\mu_\infty$ for samples A to E from the GDM analysis. The vertical lines are the graphical solutions to the hopping distances $a$. 
5.3.5. Recombination Study

Besides variations in molecular weights, it is conceivable that impurities may give rise to batch-to-batch variations in device performance. Impurities may arise from trace metal content or organic impurities. Both trace metal and organic impurities can be present in the polymer as traps. These traps may increase the trap-assisted recombination in the OPV cell. As revealed by the both vendors of PCDTBT, the trace metal contents in the PCDTBT are in the range of 0.01 – 0.001%. This range of concentration of trace metal should not influence the device performance as it was shown that at least 0.1% of trace metal (e.g. Pd) is needed to have any detrimental effect to OPV devices.[5.27]

To check if impurities have impacts on the device performances, we investigate how intensity affects $V_{OC}$ for different batches of polymers as discussed in Chapter 2. OPV cells using PCDTBT A, D, E were tested under different incident light intensity.

Figure 5.14 shows the results for sample A, D, and E. If trap-assisted charge recombination is operative, we should see steeper slopes in Figure 5.14 for samples A to E. However, all three samples have a similar slope of $kT/e$ suggesting increase in trap concentration is not the origin of reduced $PCE$ from sample A to E. Furthermore, if the trap recombination is dominant, the trap state will probably broaden the effective density of state resulting in larger energetic disorder, $\sigma$. This result also confirms the GDM analyses that similar $\sigma$ were found for all batches of PCDTBT.
Figure 5.14 $V_{OC}$ vs incident light intensity.
5.4. Summary

We have investigated in details the batch-to-batch variation of photovoltaic device performance and carrier transport properties using an amorphous PV polymer PCDTBT. We discovered that commercially available PCDTBT possesses bimodal molecular weight distribution. The low weight component is undesirable. It significantly reduces both the device efficiency and carrier mobility. The reduction of mobility is not related to the increase of energetic disorder. Instead, the cause of the reduced carrier mobility is due to the larger hopping distances arising from the additional small molecular weight component. The results show that there is a correlation between the topology of polymer chains and the carrier transport properties. This work not only provides a detail analysis of the effect of batch-to-batch variation of photoactive materials on device performance, but also provides a physical origin of the difference in carrier mobility and hence the resulting PV device performance.
References:


Chapter 6
Low Temperature Processable Sol Gel Zinc Oxide as Electron Transporting Layer and Electron Injection Layer in Optoelectronic Devices

6.1. Introduction

Organic solar cells often employ inverted structures for several purposes. Low work-function metals which are susceptible to the degradation by moisture and oxygen are not necessary for inverted solar cells. Instead, high work-function metals can be used as the top anode electrode such as Ag and Au. Moreover, hygroscopic and acidic PEDOT:PSS layer can be avoided to enhance device stability.[6.1 – 6.3]

ZnO is a promising candidate for the n-type interlayer in inverted solar cell. ZnO possesses environmentally stability, high transmittance in visible region, and high electron mobilities. There are many fabrication methods for ZnO thin films including sputtering, spin-coating ZnO nanoparticles, and sol gel method.

In this chapter, we report a method of growing ZnO films by low temperature sol gel annealing. Only 200 °C annealing is required for converting the precursor solution to ZnO. Our method should be contrasted with some older methods which an annealing temperature as high as 500 °C was required.[6.4 – 6.6] Below, we first present basic characterizations of ZnO films prepared by our sol gel method. Second, we employed the ZnO films as an electron transporting layer (ETL) in an inverted solar cell. Third, the ZnO films were used as an electron injection layer (EIL) for electron transport measurements in bulk-heterojunction
(BHJ) blend. Although ZnO is widely used as ETL in inverted organic photovoltaic (OPV) cell, using sol gel ZnO as EIL is rather scarce. Electron mobility of a BHJ blend was probed by charge transport measurement techniques such as space-charge-limit current (SCLC) and admittance spectroscopy (AS).

6.2. Experimental Details

Figure 6.1 shows the schematic diagram of the preparation the ZnO precursor solution. To start, ZnO precursor solution, 100 mg zinc acetate dihydrate, Zn(CH₃COO)₂·2H₂O, (Aldrich, 99.9 %) and 27.7 μl (28 mg) ethanolamine, NH₂CH₂CH₂OH, (Aldrich, 99.5 %) was dissolved in 1 ml 2-methoxyethanol, CH₃OCH₂CH₂OH, (Aldrich, 99.8 %). The precursor solution was heated at 40 °C and stirred vigorously at 1500 rpm for 12 – 18 hours in air. Ethanolamine acted as a stabilizer to prevent aggregation of zinc acetate dihydrate and the molar ratio of zinc acetate dihydrate to ethanolamine was 1:1.

The ZnO precursor solution was first filtered by 0.45 μm filter and then spin-coated on different substrates at 3000 rpm for 60 s resulting. For grazing incident X-ray diffraction (GIXRD), scanning electron microscopy (SEM), and field-effect transistor (FET) samples, p⁺-Si wafers with 300 nm SiO₂ on top were used as substrates. For transmittance measurement, quartz substrates were used. For X-ray photoelectron spectroscopy (XPS) and Ultra-violet photoemission spectroscopy (UPS), 50 nm Au coated ITO substrates were used. Finally, for inverted OPV cell and carrier transport measurement, cleaned ITO substrates were used. Table 1 below summaries the substrate used for different measurements.
<table>
<thead>
<tr>
<th>Measurements</th>
<th>Substrate for ZnO films</th>
</tr>
</thead>
<tbody>
<tr>
<td>GIXRD, SEM, FET</td>
<td>p⁺ Si wafer with 300 nm SiO₂</td>
</tr>
<tr>
<td>Transmittance</td>
<td>Quartz</td>
</tr>
<tr>
<td>XPS, UPS</td>
<td>ITO / Au (50 nm)</td>
</tr>
<tr>
<td>OPV cells, charge transport</td>
<td>ITO</td>
</tr>
</tbody>
</table>

Table 6.1 Substrates used for different measurements.
Figure 6.1 Schematic diagram showing the preparation of the sol gel precursor for ZnO films.
After spin coating, the samples were annealed on a hotplate immediately with different annealing temperatures for 1 hour in air. During thermal annealing in air, Zn(CH$_3$COO)$_2$·2H$_2$O is transformed into ZnO. As measured by a profilometer, the film thicknesses were around 30 nm.

The electrical properties of the ZnO were probed in a FET structure. For the FET samples, Al was thermally evaporated onto the ZnO active layer through a shadow mask under a pressure of 10$^{-6}$ mbar as the source (S) and drain (D) electrodes. The p$^+$-Si wafer acted as the gate electrode (G). The channel length ($L$) and channel width ($W$) of the ZnO FET were 50 $\mu$m and 6 mm, respectively. After fabrication, the FET sample was transferred to an Oxford cryostat with pressure of less than 20 mTorr. The FET sample was heated to 395 K for 1 hour to remove the absorbed moisture and oxygen on ZnO surface before measurement.

We aim to employ ZnO as a meaningful functional layer in organic electronic devices. First, its application as a cathode layer for OPV cells was explored. PCDTBT:PC$_{71}$BM (1:4 in mass) was used as the active layer for both inverted and conventional OPV cells. PCDTBT and PC$_{71}$BM were purchased from 1-Material (batch C in the last chapter) and Nano-C respectively. The preparation of the BHJ blend solution and the fabrication are same as those in the last chapter. For inverted OPV cell, 10 nm of MoO$_3$ was thermally evaporated onto the active layer under 10$^{-6}$ Torr. Then, 100 nm of Al was thermally evaporated under another vacuum with a pressure of 10$^{-6}$ mbar.

Next, we applied the ZnO layer as an electron injection layer for transport study in BHJ sample. PCDTBT:PC$_{71}$BM (1:4 in mass) was used as the active
layer for electron transport measurement with ZnO as EIL and ETL. 40 mg of PCDTBT and 160 mg of PC71BM were dissolved in 1,2-dichlorobenzene (DCB) of 1 ml. The fabrication procedure was similar to an OPV cell except the active layer was spin-coated on Al coated ITO or sol gel ZnO coated substrates at 600 rpm for 5 – 10 s and then naturally dry overnight in N₂ filled plastic glove box. SCLC and AS measurement were carried out in an Oxford cryostat with a pressure less than 20 mTorr.

6.3. Results and Discussion

6.3.1. Characterization of Sol Gel Zinc Oxide

To ensure the formation of ZnO prepared by sol gel method after the annealing the precursor solution, grazing incident X-ray diffraction (GIXRD) were performed to check the crystalline peak of ZnO. Figure 6.2 shows the GIXRD measurement of the sol gel ZnO for annealing temperatures from 100 to 350 °C. From 200 °C onwards, 3 crystalline peaks were observed at 32.0°, 35.5°, and 36.4° which correspond to the (100), (002), and (101) crystalline peaks of ZnO, respectively.[6.7] The intensities of these peaks increase with the annealing temperature. As a result, an annealing temperature of at least 200 °C is required for obtaining ZnO.

Scanning electron microscope (SEM) was used to characterize the morphology of the sol gel ZnO. Figure 6.3 shows the SEM images of the sol gel ZnO at different annealing temperatures. In all of the SEM images, grains densely cover the substrates. In general, the grain size increases with the annealing temperature. Beyond 200 °C, the grain size is about 5 nm.
Figure 6.2 GIXRD spectra of sol gel ZnO with different annealing temperatures.
Figure 6.3 SEM images of sol gel ZnO at different annealing temperatures.
The annealing time is 60 minutes.
Figure 6.4 shows the transmission spectra of the sol gel ZnO at different annealing temperatures. All the sol gel ZnO films behave similarly and exhibit high transmittance with at least 90% transmittance in the visible light region. The absorption cut-offs occur at around 370 nm, which correspond to an energy gap value of 3.35 eV. We note that for ZnO films annealed at 200 °C, the resulting film has a slightly higher transmittance than others. As a result, we adopt an annealing temperature of 200 °C for ZnO films preparation for subsequent device applications.

Figure 6.5 shows the core level X-ray photoelectron spectroscopy (XPS) spectra of Zn 2p and O 1s for the sol gel ZnO film annealed at 200 °C. The binding energy of Zn 2p1/2 and 2p3/2 peaks were at 1045.5 and 1022.3 eV respectively while the binding energy of O 1s peak was at 531.1 eV. The positions of these two peaks confirm the ZnO film is correctly made.[6.8]
Figure 6.4  Transmission spectra of sol gel ZnO films with different annealing temperatures on quartz substrates. The annealing time was about 60 minutes for each case.
Figure 6.5 (a) Zn 2p and (b) O 1s XPS spectra of sol gel ZnO film with 200 °C annealing for 60 minutes.
Ultra-violet photoemission spectroscopy (UPS) was used to determine the valence band maximum (VBM). Figure 6.6 (a) shows the full UPS spectrum of sol gel ZnO with 200 °C annealing. The onset of photoemission, $E_B^{\text{max}}$, and the low energy cut-off of the spectrum, $E_B^{\text{min}}$, extracted from the intersections of the red solid lines in Figure 6.6 (b) and (c) are 16.87 and 3.43 eV, respectively. The photon source used in UPS is a helium discharge lamp which emits He I radiation with a wavelength of 58.4 nm corresponding to 21.2 eV in energy. With the photon energy of the ultra-violet source, the VBM of the sol gel ZnO can be calculated by the following equation:

$$VBM = \hbar \nu - (E_B^{\text{max}} - E_B^{\text{min}})$$  \hspace{1cm} (6.1)

where $\hbar$ is the Planck constant, $\nu$ is the frequency of the ultra-violet source. Therefore, the VBM was found to be 7.76 eV below the vacuum level. This value agrees with other published sol gel ZnO work.[6.8]
Figure 6.6  UPS spectrum of the sol gel ZnO with 200 °C annealing. (a) The full UPS spectrum. (b) The onset of photoemission. (c) The low energy cut-off of the spectrum.
6.3.2. *Transport Study of Sol Gel Zinc Oxide*

Field-effect transistor (FET) was used to probe the n-type characteristics of ZnO film. Figure 6.7 shows the output and transfer characteristics of the sol gel ZnO FET at different temperatures. For the output characteristic at room temperature, well-defined n-channel field-effect behavior was observed with well-defined linear and saturation regions. For lower temperature, the output characteristic behaves similarly to the room temperature data. However, for higher temperature, the saturation current drops with the different between source and drain voltage for all the gate voltages. With the transfer characteristic, the corresponding field-effect mobility can be found by the following equation:[6.9]

\[
I_{DS} = \frac{W}{L} C_{in} \mu_{Sat} (V_G - V_T)^2
\]

where \( I_{DS} \) is the source-to-drain (DS) current, \( W \) is the channel width, \( L \) is the channel length, \( C_{in} \) is the capacitance of the insulator per unit area, \( \mu_{Sat} \) is the saturation mobility, \( V_G \) is the gate voltage, and \( V_T \) is the threshold voltage of the device. The \( \mu_{Sat} \) at room temperature was found to be \( 2.2 \times 10^{-3} \) cm²/Vs and the corresponding \( V_T \) is 12 V.
Figure 6.7  FET output characteristics of sol gel ZnO with 200 °C annealing. The FET data was taken at different sample temperatures: at (a) 290 K, (c) 201 K, and (d) 420 K. (b) Transfer characteristic of the FET at $V_{DS} = 60$ V at 290 K.
Figure 6.8 shows the $\mu_{\text{Sat}}$ extracted from different temperatures. Generally, $\mu_{\text{Sat}}$ follows Arrhenius dependence. For temperature larger than $\sim 340$ K, $\mu_{\text{Sat}}$ starts to drop when the temperature further increases. This may be due to the lattice vibrations of the ZnO at high temperatures. At high temperature and above $\sim 340$ K, many phonons are present to scatter transporting electrons. Increasing the temperature increases the number of phonons and therefore reduces $\mu_{\text{Sat}}$. On the other hand, at lower temperatures, transport of electrons is limited by grain boundaries. (Figure 6.3) Raising temperature tends to increase $\mu_{\text{Sat}}$. The activation energy, $E_A$, can be evaluated from the data in Figure 6.8 by fitting $\mu_{\text{Sat}}$ with the Arrhenius equation:[6.10]

$$\mu(T) = \mu_\infty \exp \left( -\frac{E_A}{kT} \right)$$  \hspace{1cm} (6.3)

where $\mu_\infty$ is the high temperature limit mobility, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. $\mu_\infty$ and $E_A$ are found to be 0.18 cm$^2$/Vs and 110 meV from the y-intercept and slope, respectively.
Figure 6.8 Arrhenius plot of the $\mu_{\text{Sat}}$ of sol gel ZnO with 200 °C annealing. The solid line represents the best linear fit to the data. The two points at low temperatures were not fitted.
6.3.3. Applications of Sol Gel Zinc Oxide in Organic Electronics

6.3.3.1. Organic Photovoltaic Cells

The sol gel ZnO with 200 °C annealing was integrated in an OPV cell as the ETL for the inverted structure. PCDTBT:PC71BM (Batch C PCDTBT in Chapter 5) was picked as the active layer for the PV device. The \( J-V \) characteristic of the sol gel ZnO inverted PV cells under AM1.5G illumination was shown in Figure 6.9. For comparison, OPV cell using a conventional structure with the same active layer and anode buffer layer, MoO3, was also plotted in the same graph. Their performances are listed in Table 6.2. Similar \( V_{OC} \) and \( FF \) of around 0.90 V and 50 % are obtained, respectively, for both inverted and conventional structures. Since the \( V_{OC} \) of 0.91 V for the inverted structure can be obtained which is almost the maximum value that can be obtained in the PCDTBT:PC71BM BHJ system,[6.11] this indicates the conduction band edge is located close to the LUMO of PC71BM for efficient electrons extraction from the BHJ blend.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>( J_{SC} ) (mA/cm²)</th>
<th>( V_{OC} ) (V)</th>
<th>( FF ) (%)</th>
<th>( PCE ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inverted</td>
<td>10.6</td>
<td>0.91</td>
<td>50.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Conventional</td>
<td>9.5</td>
<td>0.90</td>
<td>51.6</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 6.2  OPV cells performance of the inverted and conventional device structures with PCDTBT:PC71BM as active layers.
Figure 6.9  \( J-V \) characteristics of OPV cells for the inverted and conventional structure under AM1.5G illumination. Device structure for the inverted cell is ITO / ZnO / PCDTBT:PC71BM / MoO3 / Al; device structure for the conventional cell is ITO / MoO3 / PCDTBT:PC71BM / ZnO / Al.
Furthermore, although the thicknesses of the active layer for both structures are similar, about 70 nm, the inverted OPV cell exhibits a higher $J_{SC}$ of 10.6 mA/cm$^2$ than the conventional OPV cell of 9.5 mA/cm$^2$. The origin of the increase in $J_{SC}$ is not yet clear. One possibility is that the sol gel ZnO has a relatively rough surface compared to MoO$_3$, leading to more scattering of the incident light.[6.12] Figure 6.10 shows the atomic force microscopy (AFM) images of the sol gel ZnO and MoO$_3$ on the ITO substrates.(AFM images of ITO are also shown for comparison) The root-mean-square roughness, $R_a$ of the sol gel ZnO is 0.9 nm which is slightly larger than that of MoO$_3$ of 0.8 nm. As a result, the sol gel ZnO inverted OPV cell has a higher PCE of 4.9 %.
Figure 6.10  AFM images (2 μm × 2 μm) of ITO, sol gel ZnO, and MoO₃. Left column shows the height profiles with scale bar from 0 to 50 nm. Right column shows the phase profiles with scale bar from 0 to 60°.
6.3.3.2. Electron Transport Measurement on a BHJ Blend

The sol gel ZnO with 200 °C annealing was further applied as EIL for electron transport measurements of a BHJ blend. PCDTBT:PC$_{71}$BM with 1:4 mass ratio was picked as the BHJ blend. Electron-only devices were fabricated with the sol gel ZnO with device structure of ITO / ZnO (30 nm) / PCDTBT:PC$_{71}$BM (2.01 μm) / LiF / Al.

Figure 6.11 shows the $J$-$V$ measurements of an electron-only device at different temperatures. Carrier mobilities were extracted using the SCLC equation,[6.13]

$$J_{SCL}d = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp\left(0.89 \beta \sqrt{F}\right) F^2$$  \hspace{1cm} (6.4)

where $J_{SCL}$ is the space-charged-limited current density, $d$ is the thickness of BHJ blend, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the relative permittivity of the BHJ blend, $\mu_0$ is the zero-field mobility, $\beta$ is the field-dependent coefficient, and $F$ is the average electric field. In general, the $J$-$V$ data fits well with the SCLC model indicating the electrons can inject efficiently from the sol gel ZnO to the BHJ blend. The extracted $\mu_0$, $\beta$, and the calculated mobilities at short-circuit condition, $\mu_{sc}$ [$\mu_{sc} = \mu_0 \exp\left(0.89 \beta \sqrt{F_{sc}}\right)$ where $F_{sc} = 0.9 \text{ V} / 70 \text{ nm}$] for all the temperatures are listed in Table 6.3 and plotted in Figure 6.12.

$\mu_0$ increases with temperature and varies from $6.22 \times 10^{-8} \text{ cm}^2/\text{Vs}$ at 245 K to $4.69 \times 10^{-5} \text{ cm}^2/\text{Vs}$ at 302 K. At room temperature, PCDTBT:PC$_{71}$BM BHJ blend has electron mobility between $2.41 \times 10^{-5}$ and $1.50 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for open-circuit and short-circuit condition respectively. For the $\beta$, it decreases
slightly with the temperature from $9.95 \times 10^{-3} \text{(V/cm)}^{1/2}$ at 245 K to $5.29 \times 10^{-3} \text{(V/cm)}^{1/2}$ at 302 K.
Figure 6.11 $J$-$V$ data (open symbols) of PCDTBT:PC$_{71}$BM with sol gel ZnO as EIL and the SCLC fittings (solid lines) at different temperatures in (a) semi-log plots and (b) log-log plots.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\mu_0$ (cm$^2$/Vs)</th>
<th>$\beta$ (V/cm)$^{1/2}$</th>
<th>$\mu_{\text{fsc}}$ (cm$^2$/Vs)</th>
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<tr>
<td>245</td>
<td>$6.22 \times 10^{-8}$</td>
<td>$9.95 \times 10^{-3}$</td>
<td>$1.49 \times 10^{-6}$</td>
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<tr>
<td>252</td>
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<td>$9.14 \times 10^{-3}$</td>
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<tr>
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<td>$8.15 \times 10^{-3}$</td>
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<td>$3.00 \times 10^{-6}$</td>
<td>$7.11 \times 10^{-3}$</td>
<td>$2.90 \times 10^{-5}$</td>
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<td>$6.38 \times 10^{-3}$</td>
<td>$6.47 \times 10^{-5}$</td>
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<td>$5.74 \times 10^{-3}$</td>
<td>$1.50 \times 10^{-4}$</td>
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<td>302</td>
<td>$4.69 \times 10^{-5}$</td>
<td>$5.29 \times 10^{-3}$</td>
<td>$2.54 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 6.3  Fitted parameters from SCLC fitting (Figure 6.11) on electron-only device of PCDTBT:PC$_{71}$BM. $\mu_{\text{fsc}}$ are calculated based on the average electric field, $F_{\text{fsc}}$ (0.9 V / 70 nm), the fitted values of the zero-field mobility, $\mu_0$, and the field-dependent coefficient, $\beta$.

The same sample was also probed by admittance spectroscopy (AS).[6.14, 6.15] Different biases were applied to the sample. Figure 6.13(a) shows the frequency dependent capacitances of PCDTBT:PC$_{71}$BM with sol gel ZnO as EIL and the corresponding negative differential susceptances, $-\Delta B$. Standard AS features were observed indicating the Ohmic injection from the sol gel ZnO. The frequencies corresponding to the maximum points, $f_r$, in the $-\Delta B$ plots can be used to calculate the mobilities for different biases with the following equation:

$$\mu_{\text{AS}} = \frac{d^2 f_r}{0.56 V}$$

(6.5)

where $d$ is the thickness of the active layer and $V$ is the applied bias. The extracted field dependent mobilities were shown in Figure 6.14. The electron mobilities of PCDTBT:PC$_{71}$BM at room temperature are ranged from $2 \times 10^{-5}$ to $1 \times 10^{-4}$ cm$^2$/Vs.
Figure 6.12  Fitted parameters from Table 6.3. (a) $\mu_0$, $\mu_{JSC}$ vs $1/T^2$. (b) $\beta$ vs $1/T^2$. 

Field-dependent coefficient (cm/V)$^{1/2}$

Mobility (cm$^2$/Vs) vs $(1000/T)^2$ (K$^{-2}$)
Figure 6.13 (a) Capacitance vs frequency plots of PCDTBT:PC$_{71}$BM at different applied biases with sol gel ZnO as EIL. (b) The corresponding negative differential susceptances.
Figure 6.14 Extracted field dependent mobilities of PCDTBT:PC$_{71}$BM (1:4) at different temperatures with sol gel ZnO as EIL. The solid lines represent the best linear fits to the data.
6.4. Summary

Low temperature annealing sol gel method for ZnO has been investigated. Only 200 °C is required to convert ZnO precursor solution to ZnO. The properties of the sol gel ZnO were characterized by several techniques. From GIXRD, crystalline peaks are observed if the annealing temperature larger than 200 °C. Furthermore, as revealed by SEM, the grain size increases with the annealing temperature. Transmittance measurement shows that at least 90 % of transmittance is in the visible region. In XPS spectrum, Zn 2p and O 1s peaks are found. The VBM of the sol gel ZnO is found to be -7.76 eV from the UPS. With the energy gap found from the transmittance measurement, 3.35 eV, the CBM is found to be 4.41 eV.

The electrical property of the sol gel ZnO is tested by FET. The electron field effect mobility at room temperature is \(2.2 \times 10^{-3} \text{ cm}^2/\text{Vs}\). In the temperature dependent measurement, the mobilities of the sol gel ZnO is found to be Arrhenius type with an activation energy, \(E_A\), of 110 meV.

The application of low temperature process sol gel ZnO to inverted OPV cell and electron transport measurement on BHJ blend are demonstrated. Sol gel ZnO with 200 °C annealing is integrated to inverted OPV cell as ETL. \(PCE\) of 4.9 % is achieved which is slightly higher than the \(PCE\) of conventional device structure with the same hole transporting layer. The improvement is from the increased \(J_{SC}\) which can be attributed to a rougher surface of the sol gel ZnO.
Electron mobility of PCDTBT:PC$_{71}$BM is probed by SCLC fitting and AS with the sol gel ZnO as EIL. The injection from the sol gel ZnO to PCDTBT:PC$_{71}$BM is found to be Ohmic. The extracted electron mobilities of PCDTBT:PC$_{71}$BM (1:4) by SCLC and AS are between $2 \times 10^{-5}$ and $1 \times 10^{-4}$ cm$^2$/Vs.
References:


Chapter 7
Conclusion and Outlook

This thesis looks into the transport properties of OPV materials and how these properties affect OPV cell performance.

Electron leakage is found in a nominally hole-only device of P3HT with a structure of ITO / PEDOT:PSS / polymer or BHJ blend / Au resulting in ill-defined transport measurement signals such as DI-SCLC and AS which require unipolar transport. Three kinds of interlayer of 10 nm are inserted between P3HT and Au to suppress the electron leakage. Among these interlayers, electron blocking and trapping (EBT) interlayer, especially, Spiro-TPD:CuPc, is the most efficient design to suppress the electron leakage. This phenomenon also happens in polymer:fullerene BHJ blends, P3HT:PCBM and PCDTBT:PC71BM. With the EBT interlayer, classic transport measurement signals, conformed to space-charge-limited conduction theory, can be captured and therefore reliable transport properties of the OPV materials can be obtained.

Mobilities at different temperatures are extracted and GDM is applied for further analysis. For P3HT containing samples, the mobilities are insensitive to the presence of fullerene in the tested region (D:A ratio from 1:0 to 1:1). At room temperature, the mobilities of P3HT containing samples range between $2 \times 10^{-4}$ cm$^2$/Vs and $4 \times 10^{-4}$ cm$^2$/Vs at electric field less than 360 kV/cm. However, for PCDTBT containing samples, the mobilities are sensitive to the presence of fullerene in the tested region (D:A ratio from 1:0 to 1:4). At room temperature, the mobilities of PCDTBT containing samples at electric field of around 130 kV/cm
are $4 \times 10^{-5} \text{cm}^2/\text{Vs}$, $7 \times 10^{-6} \text{cm}^2/\text{Vs}$, and $3 \times 10^{-6} \text{cm}^2/\text{Vs}$ for D:A ratio of 1:0, 1:2, and 1:4, respectively. This result can be attributed to the structural property of the polymer. From GIXRD measurement, P3HT is polycrystalline while PCDTBT is amorphous. Therefore, P3HT polymer chains are well-connected even there is presence of fullerene while PCDTBT are not.

In GDM analysis, similar $\sigma$ are found within the same donor material with different BHJ blend ratios. For P3HT:PCBM, the $\sigma$ is around 80 – 90 meV. For PCDTBT:PC71BM, the $\sigma$ is around 115 – 125 meV. It indicates that the disorder of the energetic sites is mainly contributed from the donor material since holes mainly transport via the donor material. Furthermore, the $\sigma$ extracted from these two systems are quite different. It is known that large $\sigma$ will suppress the $V_{OC}$ in OPV cell. Due to the difference between $\sigma$, around 40 meV, it causes 0.2 V extra loss in PCDTBT OPV cell compared with P3HT OPV cell.

Based on the experience in measuring the transport properties of OPV materials, we further look into a puzzling problem in OPV cell which is the batch-to-batch variation of device performance from a charge carrier transport perspective. An amorphous PV polymer PCDTBT is selected in this study. As revealed by GPC, two molecular weight peaks are generally observed in all 5 batches of PCDTBT. The small molecular weight component of the polymer significantly reduced both the device efficiency and carrier mobility. The $\sigma$ for all batches are unexpectedly similar of 115 ± 3 meV. This implies the energetic environment for transporting sites is basically the same. However, the main differences in the transport properties are the $\mu_\infty$ which vary from $2.0 \times 10^{-2}$ to $1.2 \times 10^{-5} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The huge reduction in $\mu_\infty$ is attributed to the difference in
hopping distances which is lengthened by the presence of the small molecular weight component. From a simple estimation, the hopping distances are between 0.8 and 2.3 nm for batch A to E. The findings bring insight into the correlation between the topology of polymer chains and the carrier transport properties.

Low temperature annealing of 200 °C sol gel method for ZnO has been investigated. ZnO crystalline peaks are observed in GIXRD. Transmittance of the ZnO is larger than 90 % in the visible region. The CBM for ZnO is found to be 4.41 eV. From FET measurement, the mobility of ZnO at room temperature is 2.2 \times 10^{-3} \text{ cm}^2/\text{Vs}. Based on the processing, optical, energetic, and charge transport properties, sol gel ZnO is found to be useful in organic electronic device.

The applications of the sol gel ZnO to inverted OPV cell and electron transport measurement are demonstrated. The PCE for the inverted OPV cell with ZnO as ETL is 4.9 % which is slightly larger than that for the conventional device structure. The improvement is mainly from the higher roughness on ZnO surface. Electron mobility of PCDTBT:PC_{71}BM is probed by SCLC fitting and AS with the sol gel ZnO as EIL. The injection from the ZnO to the BHJ blend is found to be Ohmic. The extracted electron mobilities of PCDTBT:PC_{71}BM (1:4) by SCLC and AS vary from 2 \times 10^{-5} to 1 \times 10^{-4} \text{ cm}^2/\text{Vs}

In the course of this thesis work, efficiencies of OPV cells have been increasing gradually to beyond 10 %.\cite{7.1} Recently, some research groups discovered that organolead halide perovskite materials can be used as the active layer in solar cells.\cite{7.2 – 7.7} The efficiencies can be as high as 17 – 19 %.\cite{7.8, 7.9, also see Figure 1.4, Chapter 1} Perovskite materials started to draw huge
attention in the late 2012. Kim et al integrated the perovskite materials into the dye-sensitized solar cell structure which requires a mesoporous TiO$_2$ layer leading to 9.7 % efficiency.[7.2] Later in 2013, perovskite materials were applied to an OPV cell structure (planer structure) so that the mesoporous TiO$_2$ layer is no longer necessary.[7.7, 7.10, 7.11] Now, perovskite solar cell can adopt both dye-sensitized cell and organic photovoltaic cell structures. Generally, a hole extraction layer is needed in these cells. 2,2',7,7'-Tetrakis(N,N -di-p -methoxyphenylamino)-9,9'-spirobifluorene (Spiro-MeOTAD) is employed as the material in the hole extracting layer. Based on the experience and knowledge on organic hole transporters in our group, we realize that Spiro-MeOTAD is a rather poor organic hole transporter, with a hole mobility $\sim 10^{-6} - 10^{-5}$ cm$^2$/V·s$^1$.\[7.12\] There ought to be alternatives. A polymer hole transporter, possessing good infiltration capabilities into mesoporous TiO$_2$ and high hole mobilities should be good candidates for replacement of Spiro-MeOTAD. In collaboration with Prof. S Yang’s group in The Hong Kong University of Science and Technology, we identify three polyfluorene derivatives as replacements for Spiro-MeOTAD.\[7.13\] Among these three compounds, one of the polyfluorene derivatives, poly[(9,9-diocetylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine)] (TFB), outperforms the commonly used hole transporting materials spiro-MeOTAD with efficiency of 10.9 % for TFB device and 9.7 % for spiro-MeOTAD device. Details of this work have been reported in Ref. 7.13.

Perovskite solar cells enjoys a rapid growth but require a lot of efforts on the fundamental studies.(see Figure 1.4, Chapter 1) Although the efficiencies of the best perovskite solar cells are much higher the best OPV cells, OPV cells still have the potential for further growth. Also, the knowledge learned from the
extensive research of organic electronics can be applied to the perovskite systems and vice versa. We anticipate abundant, new opportunities in organic photovoltaic cells, and imminent commercialization of these cells may be sooner than expected.
References:


Appendix

Introduction to Vigor glove box

Vigor glove box is an isolated environment used in Chapter 5. Very high purity of nitrogen (99.999 %) is filled to the box. The glove box consists of one main box connecting with gloves, two antechambers, two purifiers, and one blower as shown in Figure A1. Besides, there are two sensors to monitor the oxygen and moisture levels inside the box. Although it is an enclosed system with slightly higher pressure (0 – 5 mbar) than the atmosphere, air leakage still exists via seals. Also, oxygen or moisture can be introduced after transferring something to the box from air. Therefore, to provide a low oxygen and moisture environment, purification is needed as illustrating in Figure A2. For Vigor glove box, both oxygen and moisture levels can be reduced to less than 0.1 ppm if the purification system keeps running. However, usually, we maintain both oxygen and moisture levels between 0.2 and 1 ppm.

To operate the Vigor glove box correctly, please follow the notes and procedures below. For details, please read the manual of the glove box.

Pressure Setting

The working pressure of the glove box is controlled in a pressure range. To enter the pressure setting, press “Settings” on the main screen as shown in Figure A3. Usually, the upper limit and the lower limit of the box pressures are 5 and 0 mbar.
Figure A1  Appearance of the Vigor glove box.
Figure A2  Schematic diagram of the purification of the Vigor glove box.
Figure A3    Main control panel screen shown on the glove box.
Circulation

The gas inside the glove box is circulated through the purifiers by the blower for absorbing oxygen, moisture, and solvent as shown in Figure A2. During circulation, no fresh nitrogen is required. On the main screen, press “Circ.” to enter Circulation as shown in Figure A3. There are two modes in Circulation:

I. “On Demand” mode

Usually, this mode will be used. Using this mode, the system will automatically decide whether Circulation is on or not based on the pre-set oxygen and moisture levels. Normally, Circulation will be started when either oxygen or moisture levels are larger than the 1 ppm. Circulation will be stopped when both oxygen and moisture levels are smaller than the 0.2 ppm.

II. “Manual” mode

In this mode, users can manually turn on or turn off Circulation.

Purge

Fresh nitrogen is flowed to the glove box to purge large amount of impurities such as oxygen, moisture, or solvent from the glove box. When there is any leakage of air (oxygen or moisture > 100 ppm) or after using solvent such as spin-coating, Purge is used to remove the large amount of impurities rather than Circulation. To enter Purge, press “Purge” under “Tasks” on the top of the main screen. Depending on how much impurity inside, different duration will be set, for example, 10, 20, or 30 mins.
Antechambers

Antechambers are used to transfer things between glove box and air. There are a large and a small antechambers as shown in Figure A1. For each antechamber, there are two doors separating from the nitrogen filled box (inner door) and air (outer door). There are some important notes for using the antechambers:

1. Always keep antechambers in vacuum.
2. Two doors must not be opened at the same time.
3. Before opening the inner door or after closing the outer door, users must evacuate the antechamber and then fill nitrogen to the antechamber for at least three times.

Regeneration

The active materials inside the purifiers for removing oxygen and moisture should be regenerated after using few months (It depends on the usage, usually 2 – 3 months for using almost every day). This procedure takes 1203 minutes (~20 hours). During regeneration, oxygen and moisture levels will raise. Besides, please pay extra attention to the following points:

Before Regeneration:

1. Make sure the glove box is connected to a nitrogen:hydrogen (5%) mixed gas with at least half a bottle for each regeneration.
2. Set the pressure of the regulator for the mixed gas to 1 bar.
During Regeneration:

1. During the first 3 mins, adjust the flow rate of the mixed gas to 4 units. (At lift side of the glove box)

2. From 4th to 183rd mins (3 hrs), the purifiers are heated up. (Feeling warm with hands)

3. From 184th to 363rd mins (3 hrs), the mixed gas is mainly consumed in this period. Make sure the mixed gas is enough for Regeneration by checking the usage of the mixed gas every half an hour. In case of overuse (not enough for the remaining Regeneration), adjust the pressure of the regulator for the mixed gas to slightly less than 1 bar. (Please try your best to avoid this situation happened)

4. From 364th to 1203rd mins (14 hrs), the mixed gas is still required but the amount is much less. Set the Circulation mode to “On Demand” so that Circulation will be turned on automatically after Regeneration.

Maintenance

1. Store an extra pair of gloves for replacement.

2. Run Regeneration every 2 to 3 months.

3. Refill the mechanical pump oil every year.

4. Replace the core of the oxygen sensor every 2 years.

5. Replace the oxygen and moisture purifiers every 5 years.

6. Replace the activated carbon if necessary.
Curriculum Vitae

Academic qualifications of the thesis author, Mr. LEE Ka Hin, Harrison:

1. Received the degree of Bachelor of Science (Honors) in Physics (First Class) from Hong Kong Baptist University, June 2010.

Publications


**Conference Presentations**

   - Oral and poster presentations

   - Poster presentation
3. 16th International Workshop on Inorganic and Organic Electroluminescence & 2012 International Conference on the Science and Technology of Emissive Displays, Hong Kong, China (10 – 14 Dec 2012)
   - Poster presentation

4. SPIE Photonics Europe 2012, Brussels, Belgium (16 – 19 Apr 2012)
   - Poster presentation

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