NANOSTRUCTURED THIN FILMS FOR ORGANIC PHOTOVOLTAIC CELLS AND ORGANIC LIGHT-EMITTING DIODES

By

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To my family and friends
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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By

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Achieving efficient organic optoelectronic devices, such as organic photovoltaic (OPV) cells and organic light-emitting diodes (OLEDs), relies on the understanding of the formation of various organic nanostructures as well as the fundamental of physical processes in device operation. The research presented in this thesis systematically investigates the controlled growth of organic nanostructure through different approaches and their relationship to OPV cell performance. Moreover, new materials and device structure are explored to achieve efficient OLEDs, which also provide further insight of the physical processes governing the performance of these devices.

We first investigated the phase separation process in a molecular mixed donor-acceptor (D–A) bulk heterojunction (BHJ) composed of pentacene and C60 using a combination of experimental and computational approaches. Both experiment characterization and the MD simulation reveals that strong aggregation of pentacene exists in the pentacene:C60 mixtures due to the strong \(\pi-\pi\) interaction among pentacene molecules. By controlling the processing conditions to suppress the pentacene aggregation to nanoscale leads to higher device efficiency as the more photogenerated excitons are able to reach the D–A interface and contribute to the photocurrent. To circumvent the limits on phase separated D–A mixed heterojunction, an
interdigitated D–A BHJ is synthesized through the oblique angle deposition (OAD) of copper phthalocyanine (CuPc). The morphology of CuPc nanorod arrays grown under the OAD process can be controlled by careful selection of the processing conditions, and we have achieved a high density, vertically aligned, polycrystalline CuPc nanorod array with nanorod size as small as 20-30 nm. Successful infiltration of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) into the optimized CuPc nanorod arrays has resulted in doubling of the power conversion efficiency of the OPV cell over planar heterojunction device based on the same D–A materials.

We also show that the efficiency of a deep-blue phosphorescent OLED (PHOLED) can be significantly enhanced by improving the exciton and charge confinement in the multilayer organic stack. A peak external quantum efficiency of (20 ± 1) % is achieved, which approaches the theoretical maximum of PHOLED without specific out-coupling mechanisms. We further demonstrate PHOLEDs with enhanced power efficiency by using the p-i-n device structures to reduce driving voltage and achieved a maximum of (14 ± 1) lm/W and (12 ± 1) lm/W at a luminance of 100 cd/m². Moreover, an ultra low turn-on voltage of ~1.3 V is observed in an orange-emitting polymer light-emitting diode (PLED) using ZnO nanoparticles as the electron injection layer. An Auger-assisted electron injection mechanism is proposed to explain the low turn-on voltage. The novel ZnO nanoparticles electron injection layer opens a new way to reduce driving voltage in PLED.
CHAPTER 1
INTRODUCTION TO ORGANIC SEMICONDUCTORS

Introduction

Research on organic semiconductors has made significant breakthroughs in the past two decades due to increasing knowledge of material synthesis, device physics and nanostructured thin films. Fruitful advances have been made, especially on organic photovoltaic cells and organic light-emitting diodes.\textsuperscript{1-10} The future decrease in supply of fossil fuels coupled with the rapid growth of global demand on energy will boost the commercialization of energy related organic semiconductor products. The purpose of this chapter is to provide a brief overview of the knowledge related to science and technology on organic semiconductors. The contents do not intend to cover every aspect of organic semiconductors but what is needed to help interpret the works achieved in this thesis.

This review will be broken down several sections. The electronic structure of isolated organic molecule and their solid-state aggregates will be presented in the first section, where intramolecular and intermolecular interactions and their effect on the energy transfer, exciton and charge carrier transport are briefly reviewed. The following section will talk about the growth of organic thin films and different types of structure that can be achieved inside the organic thin film. The next two sections will discuss two of the most actively studied organic optoelectronic devices: organic photovoltaic (OPV) cells and organic light-emitting diodes (OLEDs). Here, the operation principles along with typical optical and electrical characteristics of these two types of device are introduced. Moreover, the existing challenges in achieving efficient OPV cells and OLEDs will also be summarized. The outline of each chapter is presented in last section, which serves as a reading guide for this thesis.
Electronic Structures of Organic Semiconductors

Organic semiconductors are a class of semiconductor materials that exhibit different properties from the conventional inorganic semiconductors, such as Si and Ge.\textsuperscript{11-13} The unique properties of organic materials have enabled fascinating applications that are very difficult to achieve by conventional inorganic semiconductors, such as large-area, flexible lighting and displays, low-cost plastic solar cells and ink-jet printing of integrated circuits (see Figure 1-1). All these revolutionary products could not have been realized without understanding the peculiar electronic properties of organic semiconductors.

Figure 1-1. A flexible small molecule OLED display made by Universal Display Corporation (left), and plastic solar cells developed by Konarka (right). Images courtesy of Universal Display Corporation and Konarka Technologies, Inc.

Electronic State of Isolated Molecule

Most organic semiconductors can be divided into two major categories: small molecular weight materials and polymers. Figure 1-2 lists a number of typical organic molecules that are used in organic semiconductor devices. Note that all of these organic compounds are composed of conjugated $\pi$-electron systems, which corresponds to by the alternative appearance of C – C and C = C in their molecular structure. Increased conjugated length within a molecular structure
generally leads to stronger delocalization of electrons within the molecule and produces high charge mobility.

The simplest and most representative conjugated molecule is ethene, which is composed of two carbon atoms and four hydrogen atoms. The $sp^2$ hybridization of each carbon atom gives rise of three identical $sp^2$ orbitals, leaving one $p_z$ orbital intact. The six $sp^2$ orbitals of two carbon atoms will allow the formation of five $\sigma$-bonds, four C – H bonds and one C – C bond. The two remaining $p_z$ orbitals will form $\pi$-bond between two carbon atoms in addition to the C – C $\sigma$-bond. Figure 1-3 shows the relative energy level of atomic orbitals of $sp^2$ hybridized carbon atom and the molecular orbitals (MO) of $\pi$-conjugated molecule of ethene. Compared with the $\sigma$-bonding formed as the backbone of the molecules, the $\pi$-bonding is much weaker due to less overlap of the two parallel $p_z$ atomic orbitals compared with two $sp^2$ orbitals forming C – C $\sigma$-
Figure 1-3. The energy levels of π-conjugated ethene molecule with sp2 hybridized carbon and formation of bonding molecular orbitals (MOs), σ and π, and antibonding MOs, σ* and π*.

bonding. Therefore, the energy level of the bonding σ MO is lower than that of bonding π MO, while the antibonding π* MO is lower than antibonding σ*. The energy for π-π* transition corresponds to the lowest energy needed to generate electronic excitation in conjugated molecules. In most cases, π-bonding MO and π* antibonding MO are the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), respectively.

The energy difference between HOMO and LUMO strongly depends on the level of conjugation in a molecule. Table 1-1 summarizes the wavelength of absorption and emission maximum for the family of polyacenes. It can be seen that as the degree of conjugation increases (more benzene rings) the absorption and emission maxima red-shift accordingly, indicating a smaller energy gap between HOMO and LUMO. Thus, the optoelectronic properties of molecules can be tuned by adding different functional group to modify the conjugation level, reflecting the versatility of organic materials.
Table 1-1. Molecular structure of the family of polyacene molecules, together with the wavelength of the main absorption and emission peak.

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<th>Structure</th>
<th>Absorption maximum</th>
<th>Emission Maximum</th>
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<td>Benzene</td>
<td><img src="image" alt="Benzene structure" /></td>
<td>205 nm</td>
<td>278 nm</td>
</tr>
<tr>
<td>Naphthalene</td>
<td><img src="image" alt="Naphthalene structure" /></td>
<td>286 nm</td>
<td>321 nm</td>
</tr>
<tr>
<td>Anthracene</td>
<td><img src="image" alt="Anthracene structure" /></td>
<td>365 nm</td>
<td>400 nm</td>
</tr>
<tr>
<td>Tetracene</td>
<td><img src="image" alt="Tetracene structure" /></td>
<td>390 nm</td>
<td>480 nm</td>
</tr>
<tr>
<td>Pentacene</td>
<td><img src="image" alt="Pentacene structure" /></td>
<td>580 nm</td>
<td>640 nm</td>
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</tbody>
</table>

Energy Level and Charge Carriers Transport

The macroscopic optical and electrical properties of organic semiconductors are not only determined by the electronic structure of isolated molecules but also by their solid-state aggregates, whereas inorganic semiconductors are entirely formed by covalent bonding. There are two types of bonding present in molecular solids. The strong covalent-type interaction with typical interaction energy of 2 – 4 eV is present in the intramolecular interaction, while much weaker Van der Waals type of interaction with interaction energy of $10^{-3} – 10^{-2}$ eV dominates the intermolecular interaction.\(^\text{11}\) Generally, the total Van der Waals interaction energy $U_{vdW}$ between molecules can be expressed as:

$$U_{vdW} = U_{dis} + U_{ind} + U_{d-d}$$
where $U_{\text{dis}}$ is energy from dispersion interaction, $U_{\text{ind}}$ from inductive interaction and $U_{d-d}$ from dipole-dipole interaction. In the case of non-polar molecules, to which most of the organic semiconductor materials belong, the inductive and dipole-dipole interaction is negligible. Therefore, the total intermolecular interaction energy mainly depends on the attractive dispersion interaction $U_{\text{dis}}$ and repulsive interaction $U_{\text{rep}}$. The Lennard-Jones equation is an empirical formula that describes the potential energy of intermolecular interaction:\textsuperscript{15}

$$U(r) = U_{\text{dis}}(r) + U_{\text{rep}}(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

where $r$ is the distance between the molecules, and $A$ and $B$ are empirically derived constants. Potential energy of the system is minimized at certain distance of $r_0$, at which point attractive and repulsive interactions equals. The weak intermolecular interaction produces only slight changes in the electronic structure of molecules on formation of the solid phase, and as a result, molecules retain their identity.

Due to the molecular nature of the solid the band structure and charge carrier transport in organic semiconductors behave differently from inorganic semiconductors. Figure 1-4 indicates the difference between LUMO and HOMO levels of isolated molecule and the valence and conduction band in molecular crystals and amorphous solids. It can be seen that the energy level of conduction and valence band in molecular crystals are slightly shifted compared with the LUMO and HOMO level of the isolated molecule, indicating lower hole and electron (charged molecules) energy in the solid. This is because the charged molecules are stabilized by the surrounding polarized molecules in the solid. When moving from crystals to amorphous molecular solids, the highly localized molecular environments lead to a Gaussian distribution of density of state for the electron and hole transport levels.
Based on the above two different types of energy level present in organic solid, the charge carrier transport characteristics can be divided into two categories: band or hopping transport. The band transport is only observed in highly purified molecular crystal and the charge carrier mobility can usually reach as high as 1 to 10 cm²/Vs. However, most of organic semiconductors exhibit hopping transport characteristics due to the difficulty to obtain molecular crystals. In the hopping transport, the charge carrier has to hop from one molecule to the next. Because of the weak coupling of adjacent molecules, the hopping barrier is sometimes so high that it induces very low mobility ranging from 10⁻⁶ to 10⁻³ cm²/Vs. Because of the activated nature of the hopping transport, the mobility $\mu$ is temperature and electric field dependent:

$$\mu(F, T) \propto \exp\left(-\frac{\Delta E}{kT}\right) \cdot \exp\left(-\frac{\beta \sqrt{F}}{kT}\right)$$

with $T$ as the temperature, $F$ as the electric field, $k$ as the Boltzmann constant, $\Delta E$ as the activation energy for intermolecular hopping and $\beta$ as constant.
Excitons

The exciton, a bound electron-hole pair, can be created in organic semiconductors through optical excitation or electrical injection of holes and electrons. In the optical excitation, a photon is absorbed by the molecule, followed by excitation of one electron from HOMO level on to LUMO level, leaving one hole in the HOMO level. In electrical injection, holes and electrons are injected into the HOMO and LUMO level from anode and cathode and move towards opposite electrodes under an applied electric field. As they meet each other, a portion of electrons and holes bound to each other and form excitons due to Coulombic interaction.

Based on strength and distance between the bounded electron and hole, excitons in organic semiconductors can fall into two extreme categories: Frenkel exciton and Wannier-Mott exciton. As shown in Figure 1-5, a Frenkel exciton is strongly bounded electron and hole pair being confined within one molecule, with exciton binding energy of 0.5-2 eV.\textsuperscript{12,21,22} The Frenkel exciton can diffuse around in the organic semiconductors through hopping between neighbor molecules. However, the mobility of exciton could be very low due to weak intermolecular interaction. In Wannier-Mott exciton, however, electron and hole are weakly bounded (a binding energy of a few meV) and reside on two separated molecules.\textsuperscript{13} The distance between the electron and hole in Wannier excitons could be ten times of the intermolecular distance, making them unstable and easily dissociated. The third type of exciton, charge-transfer (CT) exciton, has a binding energy between Frenkel and Wannier exciton. In a CT exciton, the electron and hole also reside on separated molecules, but the separation distance is only a few times of the intermolecular distance. Thus, the CT exciton is stable and can diffuse around in very similar way to Frenkel exciton.
Figure 1-5. Schematic of three different types of exciton in molecular solid: a Frenkel exciton with tightly bounded electron-hole pair resides on one molecule (left); a Wannier-Mott exciton with loosely bounded electron-hole pair, which is delocalized over a distance longer than lattice distance (middle); a charge-transfer exciton, which is in between the previous two types of exciton (right).

**Energy Transfer**

Once excitons are created in the organic semiconductors, the excitons will diffuse around inside organic solid before their energy released in radiative (emit photon) or non-radiative (generate phonon) ways if they are not dissociated into free charges within their lifetime. However, the diffusion of an exciton is accompanied by an energy transfer between molecules, which is an essential process during the operation of OPV cells and phosphorescent OLEDs.

There are two types of energy transfer mechanisms in organic semiconductors: Föster and Dexter energy transfer. In Föster energy transfer, a photon is emitted through the exciton recombination on a donor molecule. The photon is then absorbed by an acceptor molecule and simultaneously creates an exciton. The efficiency of Föster energy is proportional to the overlap between the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule. However, instead of two individual emission and absorption process observed conventional, the recombination and excitation during Föster energy transfer occur
simultaneously and no real photon is emitted. The dipole-dipole interaction and the distance
between the donor and acceptor molecules play an important role in determining the energy
transfer rate. Efficient Föster energy transfer can occur over a distance of tens of Angstroms. The
Dexter energy transfer, on the other hand, is realized through direct charge exchange between
neighboring molecules. An electron or hole on a donor can transfer to an acceptor when there is
strong overlap between the orbitals of the two molecules. Therefore, Dexter energy transfer can
only occur in a range of a few Angstroms.

**Growth and Structure of Organic Thin Film**

Currently, the active layer of most organic semiconductor devices composed of thin film
with thickness ranging from 10 to a few hundred nanometer. Therefore, growth of high quality
organic thin film with desired structure is the key to achieve certain electrical and optical
properties in the devices.

**Vacuum Thermal Evaporation and Spin-Coating**

There are many ways of growing organic thin films, such as molecular beam epitaxy,
organic vapor phase deposition, etc.24 Two of the most widely used methods to grow organic thin
film are vacuum thermal deposition and spin-coating. Generally, vacuum thermal evaporation is
used to grow small molecular weight based organic thin films, while spin-coating is used to
deposit polymer based thin films.

Figure 1-6a shows the schematic of vacuum thermal evaporation (VTE). In VTE, the
substrate and shadow mask are placed above the source boats at a distance of tens of centimeters.
During the deposition the boats (usually made of Tungsten or Tantalum) are heated by applying
sufficient electrical current and the organic materials inside sublime under high vacuum. The
evaporated organic molecules travel ballistically and finally deposit on the cold substrate above
as well as on chamber walls. A quartz crystal monitor (QCM) and a shutter are combined to
accurately control the film thickness. During the whole deposition process, the chamber pressure is kept at $10^{-7} - 10^{-6}$ Torr.

Polymer thin films, however, are mostly prepared through solution processes, where spin-coating prevails. Figure 1-6b shows the schematic of the spin-coating method. Here, the solution containing polymer materials is dispensed on a spinning substrate. The centrifugal force spreads the solution evenly over the surface. After the solvents are driven away by baking, polymer films with various thicknesses can be achieved. Spin rate and solution viscosity are two important parameters that determine the film thickness.

The VTE method has advantages over solution spin-coating, such as high vacuum clean environment, ability to fabricate of multilayers as well as doped organic thin films. However, the low-cost spin-coating method is suitable for large area deposition and has much higher material use efficiency. Other methods of organic thin film deposition, such as ink-jet printing, organic vapor phase deposition (OVPD), laser induced thermal imaging (LITI), are also widely use to

Figure 1-6. Schematic of vacuum thermal evaporation (VTE) and spin-coating.
deposit organic thin film with desired structure and morphology.\textsuperscript{24-26} Therefore, careful selection and combination of different thin film deposition techniques should provide versatile ways to achieve organic thin films with various structures.

**Amorphous and Crystalline Thin Films**

In general, the structure of organic thin films can be either amorphous or crystalline, which show different electrical and optical properties. As a matter fact, early studies on organic semiconductors started with applying very high voltage across anthracene crystals and light emitting behavior of the materials was observed.\textsuperscript{27,28} Due to the conjugation nature for most of the organic semiconductor materials, polycrystalline organic thin films is commonly observed. Figure 1-7 shows the unit cell of anthracene crystals. The anthracene crystals are monoclinic (a ≠ b ≠ c, \(\alpha = \gamma = 90^\circ, \beta \neq 90^\circ\)) with two molecules in each unit cell. Molecule I is located at the position (0,0,0) of the unit cell is transformed into molecule II at (1/2,1/2,0) by a glide operation.

![Figure 1-7. Schematic structure of unit cell of an anthracene crystal. [Ref 29,30]](image-url)
Table 1-2. Crystallographic data on anthracene, teteracene and pentacene crystals. [Ref 11]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Anthracene</th>
<th>Teteracene</th>
<th>Pentacene</th>
</tr>
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<td>Triclinic</td>
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<tr>
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<td><strong>a (Å)</strong></td>
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<td><strong>b (Å)</strong></td>
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<td>6.03</td>
<td>6.04</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
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<td>13.53</td>
<td>16.01</td>
</tr>
<tr>
<td><strong>α (degree)</strong></td>
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<td>101.9</td>
</tr>
<tr>
<td><strong>β (degree)</strong></td>
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<td>112.6</td>
</tr>
<tr>
<td><strong>γ (degree)</strong></td>
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<td>86.3</td>
<td>85.8</td>
</tr>
<tr>
<td><strong>z</strong></td>
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<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>1.25</td>
<td>1.29</td>
<td>1.32</td>
</tr>
</tbody>
</table>

$z$: number of molecules in unit cell

Table 1-2 lists the crystallographic data on crystals from polyacenes family. It can be seen that all polyacenes show very similar crystal structure and increased unit cell volume with larger molecular size. The similar crystal structure results in very similar electrical and optical properties of the polyacene molecules.

Amorphous thin films, on the other hand, also play an important role in organic semiconductor devices. Compared with polycrystalline thin films, the amorphous structure may lead to much lower carrier mobility. However, the highly localized electronic states present in the amorphous film could be good for charge trapping and exciton confinements, which is beneficial for efficient light-emitting devices. For instance, in phosphorescent OLEDs, which adopts a host and dopant mixture as the emitting layer, the amorphous structure of the active layer can secure good dispersion of dopants in the host and reduce quenching from aggregates.

Whether the organic molecule will form crystalline or amorphous state depends on the molecular structure. Planar molecules with delocalized π-electron orbitals tend to stack on each
other in their aggregates, which forms polycrystalline thin films.\textsuperscript{31-33} Polyacenes and phthalocyanine molecules are two of the representative materials that have a strong tendency to form polycrystalline thin film. Non-planar molecules with large steric hindrance, such as Alq\textsubscript{3} and C\textsubscript{60} for instance, tend to form amorphous structure due to difficulty to closely pack with each other.

**Heterojunctions**

Heterojunctions, which are the junctions between two different semiconductor materials, are of great importance for the optoelectronic properties of organic and inorganic semiconductors. C. W. Tang first reported the usage of organic heterojunctions on organic light-emitting diodes (OLEDs) and organic photovoltaic (OPV) cells in the 1980’s.\textsuperscript{1,2} Since then the research on understanding the properties of organic heterojunctions has brought forward significant enhancement on device performance.

In OLEDs, heterojunctions play an important role in confining or blocking charge carriers due to the energy offset between the HOMO and LUMO levels of the two materials. The charge confinement effect, due to energy offset at the heterojunction, can enhance the quantum efficiency of the device significantly. Moreover, in phosphorescent OLEDs, the emitting layer can form a heterojunction with materials with high triplet exciton energy. This confines the exciton within the emitting layer, which increases quantum efficiency remarkably.

Heterojunctions formed between donor and acceptor materials, on the other hand, is the key component of the OPV cells due to its capability to dissociate the photo-generated excitons. In a donor-acceptor heterojunction, if the energy offset of between LUMO or HOMO level of the two materials is higher than the exciton binding energy, a charge transfer process will take place at the junctions, leaving separated holes on the donor and electrons on the acceptor.
**Organic Photovoltaic Cells**

One of the most widely studied optoelectronic organic semiconductor devices is the organic photovoltaic cells due to potential to provide low-cost solar energy, which is an important technology to resolve the global warming issue and increasing energy demand.

**Progress of Organic Photovoltaic Cells**

The study on organic photovoltaics has spurred significantly since C. W. Tang first introduced a bilayer heterojunction solar cell composed of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) in 1986. The introduction of the bulk heterojunction and successful realization of the tandem structure in the last two decades have further boosted the efficiency of OPV cells. Figure 1-8 compares OPV cells with other types of solar cells; it can be seen that the current state-of-the-art efficiency of organic solar cells is only around 5%, which is much lower than other inorganic and dye-sensitized solar cells.

Even though the efficiency of OPV cells is low, the fabrication cost of OPV cells could also be

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**Figure 1-8.** Energy conversion efficiency progress of state-of-the-art research on different photovoltaic devices. [Ref.38]
very low. That makes OPV cells a very competitive candidate for the third generation solar cells, whose average cost for generating 1 watt electrical power falls in the $0.2 ~ 0.5/watt category.39

However, there are still plenty of challenges to overcome in the OPV cell, which hinder its commercialization. One big challenge is efficient collection of excitons generated in the active layer. The exciton diffusion length in organic materials is only tens of nanometers, preventing most of the excitons from reaching the donor-acceptor interface. To overcome this shortcoming, bulk heterojunctions composed of nanostructured donor-acceptor phase is highly desired and a number of research groups have demonstrated how such structure can be generated. For instance, people have shown that bulk heterojunctions composed of nanoscale percolated donor and acceptor phase can be achieved by controlling the phase separation in donor-acceptor mixtures.4,6,40-47 This method applies to both the small molecular weight based OPV cells composed of CuPc/PTCBI and polymer based OPV cells composed of P3HT/PCBM. Other challenges in OPV cells include low open circuit voltage, short lifetime, etc.48-51 More fundamental understanding of the material properties and physical process of the OPV cells is important to further enhance the device performance.

**Principles of Organic Photovoltaic Cells**

The typical structure of OPV cells, as shown in Figure 1-9a, is composed of an organic active layer sandwiched between a layer of transparent conductive oxide (TCO) as anode and a metal layer as cathode. The light enters the device from the glass/TCO side and gets absorbed by the organic layer. In addition to working as cathode, the metal layer can reflect the transmitted light, increasing the optical path and absorption. The active layer of OPV cells usually uses organic donor-acceptor heterojunctions to generate free holes and electrons after absorbing
Figure 1-9. (a) Typical structure of organic photovoltaic (OPV) cells and (b) equivalent circuit for an organic heterojunction to describe the current-density voltage ($J - V$) model of OPV cells. The series and parallel resistances are $R_s$ and $R_p$, respectively, and $J_{dark}$ and $J_{ph}$ the dark and photocurrent density, respectively.

Photons. The holes and electrons are collected by the anode and cathode respectively to produce photocurrent. The photovoltaic behavior of organic PV cells can be characterized in the same way as inorganic PV by short-circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$), and fill factor (FF). The equivalent circuit of OPV cells is shown in Figure 1-9b, where the $J_{dark}$ is the dark current density and $J_{ph}$ as photocurrent density. After taking the series ($R_s$) and shunt resistances ($R_p$) into consideration, the current-density–voltage ($J - V$) characteristic of OPV cells can be expressed in the form of the Schockley equation:

$$J = \frac{R_p}{R_s + R_p} \left\{ J_s \left[ \exp \left( \frac{q(V - V_{RS})}{nk_B T} \right) - 1 \right] + \frac{V}{R_p} \right\} - J_{ph}(V)$$

where $n$ is the ideality factor of the diode, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $J_s$ is the reverse saturation current of the diode. The $V_{OC}$ is obtained when $J = 0$. Thus,

$$V_{OC} = \frac{n k_B T}{q} \ln \left[ \frac{J_{ph}(V_{OC})}{J_s} + 1 - \frac{V_{OC}}{J_s R_p} \right]$$

It can be seen that $V_{OC}$ depends on $J_{ph}(V)$ when the temperature is kept constant. Since $J_{ph}(V)$ is proportional to the incident power density $P_0$, (i.e., $J_{ph}(V) \propto P_0$), the $V_{OC}$ shows dependence on $P_0$ as $V_{OC} \propto \ln(P_0)$. This rule applies in OPV cells until the product $J_s R_p$ becomes
comparable with $V_{OC}$ due to $R_p \propto P_0^{-1}$. The maximum $V_{OC}$ is achieved when the quasi-Fermi levels of donor and acceptor are pinned at high photocurrent density.

**Photocurrent Generation**

The process of photocurrent generation in OPV cells is quite different from conventional inorganic photovoltaic cells, where a free electron and hole are generated in the depletion region after absorbing a photon. The photocurrent generation process in OPV cells can be generally divided into four consecutive steps (see Figure 1-10), which includes generation of an exciton after absorbing a photon (step 1), exciton diffusion (step 2), exciton dissociation at the D-A interface through charge transfer (step 3), and charge collection by electrodes (step 4). Therefore, the external quantum efficiency ($\eta_{EQE}$) of the OPV cell is determined by the above four steps, viz.:

$$\eta_{EQE} = \eta_A \times \eta_{ED} \times \eta_{CT} \times \eta_{CC}$$

where $\eta_A$, $\eta_{ED}$, $\eta_{CT}$ and $\eta_{CC}$ are the efficiency of absorption, exciton diffusion, charge transfer and charge collection respectively. In most of the cases, $\eta_{CT}$ is unity due to the extremely high charge transfer rate. Therefore, the $\eta_{EQE}$ of OPV cells is mainly limited by $\eta_A$, $\eta_{ED}$, and $\eta_{CC}$.

The absorption of a photon and generation of exciton is accompanied by the electronic transition of organic molecules from the ground state to the excited state. The presence of various vibronic levels in the molecular excited state leads to several narrow bands in the absorption spectrum of organic materials. This is different from inorganic materials, where the high density of states results in a continuous absorption spectrum with a clear band-edge absorption cut-off. The organic semiconductor materials have a typical absorption coefficient of $\alpha \sim 10^5 \text{ cm}^{-1}$. Since most photons are absorbed over a distance of $1/\alpha$, the thickness needed to efficiently absorb light is generally on the order of 100 nm.
Figure 1-10. Four steps in the photocurrent generation process in OPV cells, namely 1) light absorption and exciton generation, 2) exciton diffusion, 3) exciton dissociation and 4) charge collection. The efficiencies of above four steps are labeled as $\eta_A$, $\eta_{ED}$, $\eta_{CC}$ and $\eta_{CT}$, respectively. The black circles represent electrons, while the open circles are holes. Excitons are indicated by a dash line between electrons and holes. The dip of the electron and hole energy level at the vicinity of the exciton reflects the lower energy state of the exciton compared to an unbounded electron-hole pair, which corresponds to a exciton binding energy of 0.5 – 1 eV.

Even though $\eta_A$ can be enhanced by simply increasing the film thickness, the dependence of exciton diffusion and charge collection efficiency on the morphology and thickness has put another restriction on achieving high $\eta_{EQE}$. Because of the short exciton diffusion length ($\sim 10$ nm) in organic materials,9,56 only excitons generated at the vicinity of the donor-acceptor heterojunction can reach the interface and dissociate into free charge carriers. Therefore, the exciton diffusion efficiency in bilayer donor-acceptor heterojunction can be very low. In order to circumvent this limitation a bulk heterojunction composed of donor-acceptor mixture can be
used. However, even if the exciton diffusion efficiency can reach nearly 100% in this structure, the charge collection efficiency can be very low due to poor charge transport. Xue et al. have studied the electron and hole mobility in CuPc and C₆₀ mixtures, in which they found that higher charge carrier mobility is observed in neat films, while the presence of traps and defects in mixed films lead to lower mobility. In order to secure both efficient exciton diffusion and charge collection, a bulk heterojunction with percolated donor-acceptor phase shown in Figure 1-11 is preferred. The width of the percolated donor-acceptor network phases should be on the order of tens of nanometers so that all the excitons, regardless of their generation location, can be collected. This structure also allows efficient charge transport due to the existence of pure donor and acceptor phases. However, creation of such an ideal nanostructured bulk heterojunction is challenging. Chapter 3 and Chapter 4 of this thesis mainly focus on addressing this issue through controlling the phase separation in donor-acceptor mixed heterojunctions and controlled growth of one-dimensional organic nanorods using oblique angle deposition.

Figure 1-11. Schematic of bulk heterojunction with percolated donor-acceptor phase.
Organic Light-Emitting Diodes

Organic light-emitting diodes (OLEDs) are very promising for next generation lighting and display applications and have attracted a lot of research attention over the past decade. In this part, we will mainly discuss the knowledge regarding OLEDs.

Progress of Organic Light-Emitting Diodes

The first electroluminescence (EL) effect from organic materials dates back to 1963, when Pope et. al. applied 400 V across 20 μm thick anthracene single crystal. It was not until 1987 when C. W. Tang from Kodak reported an OLED with a heterojunction composed of Alq3 as the emitting layer and NPD as the hole transport layer that low driving voltage and high EL efficiency were achieved. This has led to the prosperous development of OLEDs with a lot of new observation and technologies. Among the most important findings was the work by Förrest et. al., in which OLED phosphorescence was first observed. Phosphorescence OLEDs are able to break the theoretical limit of 25 % on internal quantum efficiency of fluorescent OLEDs.

Even though OLEDs have significant advantages over conventional displays and lighting technologies, there are still some challenges that must be overcome before large scale commercialization of OLEDs. For instance, the current efficiency and power efficiency are still low compared with florescent lighting. In order to improve the current efficiency, better confinement of charge carriers and excitons in the emitting layer using charge transport layers with appropriate LUMO/HOMO level is suggested. High power efficiency, on the other hand, requires efficient electron and hole injection layer to reduce driving voltage. Therefore, new materials and device architectures based on better understanding of molecular properties and device physics are essential for realizing high efficiency OLEDs. Furthermore, there exist still more challenges, such as device lifetime, packaging, etc, before large scale commercial development.
**Principles of Organic Light-Emitting Diodes**

The photon energy emitted by organic materials strongly depends on the energy difference between the ground state and excited state of the molecule. Therefore, various color emission from organic materials can be tuned by changing the bandgap of molecules. Thompson, *et. al.* show that the emission spectra of platinum-based organic compounds, which cover nearly the whole visible region, can be varied through replacing the functional groups. This indicates the versatility in using an organic chromophore as the emitter.

The operation principle of OLEDs is illustrated in Figure 1-12, where a simple three layer device composed of electron and hole transporting layers (ETL and HTL) and emitting layer (EML) is shown. Under an applied bias, holes and electrons are injected into the HTL and ETL from the anode and cathode, respectively. Holes will transport through the HOMO level of the HTL, while electrons through the LUMO level of the ETL. If injection of charge carriers is balanced, most of the electrons and holes will form excitons inside the EML and emit light. In order to further improve OLED performance, additional layers such as charge injection layers...
and blocking layers could also be used. The external quantum efficiency ($\eta_{EQE}$) of an OLED, which is defined as the ratio of photons emitted to charges flowing in the circuit, can be expressed as:

$$\eta_{EQE} = \gamma r_{st} q \eta_{EXT}$$

where $\gamma$ is the ratio of excitons created to charges injected, $r_{st}$ is the fraction of excitons which can radiatively decay, $q$ is the efficiency of radiative decay of singlet excitons, and $\eta_{EXT}$ is the optical outcoupling efficiency. For fluorescent emission, $r_{st}$ is limited to 25%, while $r_{st}$ can potentially reach 100% for phosphorescent emission.

**Phosphorescent Organic Light-Emitting Diodes**

Light emission in OLEDs originates from radiative decay of excited molecules. Since the two electrons in excited molecule occupy two different MOs, i.e. LUMO and HOMO, respectively, the net spin value of the excited molecule can be either $S = 0$ or $1$ depending on the spin angular momentum of the two electrons. An excited state with net spin value $S = 0$ is called a singlet excited state, while $S = 1$ corresponds to a triplet excited state. Any radiative decay process of a singlet excited state is called fluorescence, whereas radiative decay of a triplet state is called phosphorescence. Figure 1-13 shows the Jablonski diagram of the fluorescence and phosphorescence process. In general, the rate of fluorescent decay is much faster than phosphorescent decay, in which the spin angular momentum needs to change in order to generate a singlet ground state. Typical lifetimes of the singlet excited state are in the range of $1 – 10$ ns, whereas the lifetimes of triplet excited states can be in the millisecond range for pure aromatic hydrocarbons. Therefore, most of the light-emitting process in organic molecule originates from fluorescence rather than phosphorescence. Since the number of singlet to triplet excited states
Figure 1-13. Jablonski diagram for the fluorescence and phosphorescence of organic molecules with $S_0$ as the ground state and $S_1$, $T_1$ as the singlet and triplet excited state, respectively. The rate of fluorescence, phosphorescence and intersystem crossing is $k_F$, $k_P$ and $k_{ISC}$, respectively.

created during electrical injection is 1:3, any OLED whose emission completely relies on fluorescence can have a maximum of 25 % internal quantum efficiency. However, Forrest et. al. found that by introducing a heavy metal atom onto the organic molecule, the rate of intersystem crossing between singlet and triplet states is significantly enhanced, while the lifetime of the triplet excited state is also shortened. All these lead to efficient phosphorescent OLEDs (PHOLEDs) with a maximum 100 % internal quantum efficiency.

PHOLEDs are usually composed of a guest-host type emitting layer with phosphorescent molecules doped into a host matrix. The host matrix plays a couple important roles to help obtain efficient phosphorescent emission from dopants. During operation, electrons and holes are injected into the host material, on which the excitons are formed and transferred to phosphorescent dopants through Dexter or Foster energy transfer. In some cases, the excitons are directly formed on the dopants through direct trapping.

Due to a cascade energy transfer process in the EML of PHOLED, the host molecules should have higher exciton energy than phosphorescent dopants in order to secure efficient energy transfer. However, excitons may recombine non-radiatively due to transferring to the
adjacent HTL or ETL layer through Forster and Dexter process if the HTL or ETL materials have lower exciton energy. This will significantly reduce quantum efficiency of the device. Therefore, HTLs and ETLs will high exciton energy are desired to prevent such exciton loss.

**Overview of This Thesis**

The works presented in this thesis can be divided into two major parts with focuses on organic photovoltaic (OPV) cells and organic light-emitting diodes (OLEDs), respectively. First, accurate measurement of efficiencies of OPV cells and OLEDs are introduced in Chapter 2. Here, we describe the method to measure the external quantum efficiency of the OPV cells and to use the spectrum mismatch factor to correctly characterize an OPV cell efficiency. At the same time, the method of measuring OLED efficiency using a Si photodiode and a luminance meter is presented by assuming a Lambertian source.

Next, Chapter 3 and 4 focus on improving the power conversion efficiency of the OPV cells through creation of nanostructured bulk heterojunctions. Specifically, Chapter 3 investigates the phase separation process in donor-acceptor molecular mixtures composed of pentacene and C\textsubscript{60}. Here, a molecular dynamic (MD) simulation is used to monitor the nanoscale structural evolution in the pentacene:C\textsubscript{60} mixture computationally, while the structure and morphology of the mixed films are studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results reveal that the performance of the OPV cells relates to the degree of phase separation inside the donor-acceptor mixture. Chapter 4 demonstrates a facile way to fabricate one-dimensional organic nanorods using oblique angle deposition. The morphology of the nanorods grown under different conditions is investigated. By changing the substrate rotation mode, CuPc nanorods with different diameter and packing density can be obtained. The power conversion efficiency of a bulk heterojunction
utilized the organic nanorods show two times enhancement over the planar heterojunction device.

Chapter 5 and 6 of this thesis cover studies on organic light-emitting diodes. In Chapter 5, new ETL and HTL materials are applied to blue PHOLEDs. The charge carrier and exciton confinement properties from different charge transport layers are compared and their effects on improving the PHOLED efficiency are summarized. Moreover, p- and n-type doping of the charge injection layer are investigated to further reduce the overall driving voltage of PHOLEDs. Chapter 6 discusses a novel electron injection layer comprising ZnO nanoparticles applied to polymer light-emitting diodes (PLEDs). It is found that the turn-on voltage of the PLED is significantly reduced due to an electron injection process through interfacial Auger recombination.

Finally, Chapter 7 of the thesis consists of conclusions and future outlook. Conclusions are drawn based on the results from studies on OPV cells and OLEDs, and the limitations that remain for these two types of optoelectronic device are discussed. Future research works that could further enhance the performance of OPV cells and OLEDs are also suggested.
CHAPTER 2
MEASUREMENT OF ORGANIC PHOTOVOLTAIC CELLS AND ORGANIC LIGHT-EMITTING DIODES

Introduction

Organic photovoltaic (OPV) cells and organic light-emitting diodes (OLEDs) have attracted substantial research attention in the past a few years due to their potential to meet future needs for clean and efficient energy devices. However, since various device areas and patterns are used, the measurement procedures for OPV cells and OLED are inconsistent between different research groups. Therefore, it is critical to accurately measure the efficiency of these two types of devices so that direct comparisons can be made between different groups. In this chapter, setups for efficiency measurements of OPV cells and OLEDs are presented. We also provide details of our methods to calibrate the measurement systems so that accurate measurements can be achieved.

The first section of this chapter will focus on the measurement of OPV cells, where the spectrum mismatch factor is considered based on our measurement system. The measurement of OLED efficiency using a planar geometry by assuming a Lambertian emission pattern is given in the second section. Finally, the conclusions are provided in the last section.

Measurement of Organic Photovoltaic Cells

In the past two decades, the power conversion efficiency (PCE) of OPV cells has gradually progressed from less than 1% to nearly 6% today. The highest PCE reported so far for the polymer bulk heterojunction (BHJ) OPV cells is around 6%. For small-molecular-based OPV cells, PCE up to 5.7% has been reported for device based on tandem cells using copper phthalocyanine (CuPc). Since the PCE is now approaching the threshold for commercial applications of OPV cells, it is of great importance to accurately determine the efficiency values so that fair comparisons of results from different research groups can be achieved.
Power Conversion Efficiency Measurement with Spectrum Mismatch Factor

Generally, the efficiency measurement of OPV cells concerns two parts of information, which includes the power conversion efficiency (PCE) and the external quantum efficiency (EQE) as function of the wavelength. To obtain an accurate PCE value, $I-V$ characteristics of OPV cells under standard reporting conditions (SRC) suggested by the American Society for Testing and Materials (ASTM) are required. And the SRC recommended by ASTM for rating the performance of terrestrial PV cells include: 1000 W/m$^2$ irradiance, AM 1.5 (AM: air mass) global reference spectrum, and 25 °C cell temperature.$^{62,63}$ In reality, a solar simulator is widely used to conveniently generate a simulated AM 1.5G spectrum with various irradiance. Figure 2-1 shows the diagram of $I-V$ characteristics measurement under simulated AM 1.5G illumination for OPV cells. Here, an Oriel solar simulator equipped with a Xenon lamp with spectral coverage from 250 nm to 1100 nm is used as the light source. In front of the lamp, an AM 1.5G filter is used to adjust the raw spectrum into a simulated AM 1.5G solar spectrum. The beam then goes through a set of irises and neutral density (ND) filters to achieve a uniform light spot with desired irradiance. At the end, the OPV cells or a silicon reference cell are mounted on a three-dimensional manipulator to give a relatively fixed position. With certain irradiance, the $I-V$

![Figure 2-1. Diagram of power conversion efficiency (PCE) measurement for OPV cells.](image-url)
measurements of OPV cells are taken by a semiconductor analyzer. Therefore, the PCE of the OPV cell is given as:

\[
PCE = 100 \times \frac{P_{\text{max}}}{E_{\text{tot}} A} = 100 \times \frac{I_{SC} V_{OC} FF}{E_{\text{tot}} A}
\]

here, \(P_{\text{max}}\) is the measured maximum power output reading from the \(I - V\) curve of test cell, \(A\) is the device active area, \(E_{\text{tot}}\) is the incident irradiance, \(I_{SC}\) is the short-circuit current, \(V_{OC}\) is the open-circuit voltage, and \(FF\) is the fill factor.

In order to obtain the real PCE value of the solar cell, it is crucial to accurately secure the right \(E_{\text{tot}}\) based on the reference AM 1.5G spectrum provided by ASTM standard G159. The \(E_{\text{tot}}\) incident on the PV cell is typically measured with a calibrated Si reference cell, which is suggested by ASTM standard E948. However, for \(I - V\) measurements of OPV cells under the simulated AM 1.5G spectrum, a spectral error could exist in the measured \(I - V\), which leads to inaccurate \(V_{OC}, FF\) and especially, \(I_{SC}\). Such spectral error could originate from the spectrum difference between the simulated spectrum and the reference spectrum, and the spectral response difference between the Si reference cell and our OPV cell. To correct this spectral error on \(I_{SC}\), the spectrum mismatch factor \((M)\) is introduced by ASTM standard E973, which is expressed as:

\[
M = \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{Ref}}(\lambda) S_R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{Ref}}(\lambda) S_T(\lambda) d\lambda} \times \frac{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda} = \frac{I_{R,R}}{I_{R,T}} \times \frac{I_{S,T}}{I_{S,R}}
\]

where \(E_{\text{Ref}}(\lambda)\) is the reference spectral irradiance, \(E_S(\lambda)\) is the simulated spectral irradiance, \(S_R(\lambda)\) is the spectral responsivity of the reference cell, and \(S_T(\lambda)\) is the spectral responsivity of the test cell. All of them are as a function of the wavelength (\(\lambda\)). The wavelength integration limits \(\lambda_1\) and \(\lambda_2\) should encompass the spectral responsivity limits of the OPV cells and Si
reference cell. It can be seen that the real $I_{SC}$ of test cell under the reference spectrum can be expressed as:

$$I_{R,T}^{R} = \frac{I_{R}^{R}}{M} \times \frac{I_{S,T}^{S}}{I_{S,R}^{S}}$$

therefore, by adjusting the simulator spectral irradiance so that $I_{S,R}^{S}$ is equal to $I_{R,T}^{R}$, $I_{R,T}^{R}$ can be directly obtained by dividing the measured $I_{S,T}^{S}$ by the mismatch factor $M$. In the real measurement setup, it is more convenient to adjust the simulator spectrum and responsivity of the reference cell so that $M$ is close to unity. In this case, the measured $I_{S,T}^{S}$ closely equals $I_{R,T}^{R}$. 

Here, we showed the calculation value of the spectrum mismatch factor $M$ for a bilayer OPV cell of ITO/CuPc (20 nm)/C$_{60}$ (40 nm)/bathocuporine (BCP) (8 nm)/Al with a Si reference cell. Figure 2-2a compares the standard AM 1.5G reference spectrum and the simulated AM 1.5G spectrum from Oriel solar simulator. And Figure 2-2b shows the responsivity of the silicon reference cell with and without the KG1 color filter. It can be seen that $M = 0.80$ with the unfiltered Si reference cell, which originates from the large difference in the spectral responsivity between the OPV cells and the reference cells. The unfiltered Si reference cell has a spectral response over a range of 400 – 1100 nm, whereas the CuPc/C$_{60}$ cell only shows response from 300 to 800nm (see Figure 2-4). Therefore, in order to obtain $M$ close to unity, it is important to choose a reference cell whose spectral response closely matching that of the OPV cell. Therefore, a KG1 color filter with a cut-off at around 800 nm is used to correct the responsivity of the Si reference cell. It can be seen from Figure 2-2b, the KG1 filtered Si reference cell shows much narrower spectral response of 400 – 800nm, which is very close to that of the CuPc/C$_{60}$ cell. This leads to an almost unity mismatch factor of $M = 0.99$. Clearly, the KG1-filtered Si reference cell is more suitable for use as a reference cell in measuring the spectral irradiance from the solar simulator.
Figure 2.2. Calculation of spectrum mismatch factor with specific solar spectrum and reference cell (a) Comparison of reference AM 1.5G solar spectrum and simulated AM 1.5 spectrum. (b) Responsivity of Si reference cell with and without KG-1 filter. Inset: the transmission of KG-1 filter.

**External Quantum Efficiency Measurement**

By using a KG1-filtered Si reference cell, a spectrum mismatch factor close to unity can be obtained. The PCE of the OPV cell under standard reference spectrum can be directly inferred from the $M$ value for particular simulated spectrum and an OPV cell/reference cell combination. It is also important to obtain the external quantum efficiency (EQE) of the OPV cell so that 1) the spectral responsivity of the OPV cell can be calculated from the EQE curve by $S(\lambda) =$
EQE(\(\lambda\)) q\(\lambda/hc\), and 2) the short circuit current under reference spectral irradiance \(I^{R,T}\) can be calculated to compare with \(I^{S,T}\) to confirm the solar simulator system is correctly set up.

Moreover, the EQE curve provides useful information about the physical processes inside the OPV cell, such as exciton diffusion, charge collection, etc.

Figure 2-3 shows our setup for EQE measurement based on the guidelines from ASTM E1021,\(^{65}\) where a monochromatic, chopped beam of light is incident at normal direction onto the OPV cell. At the same time, a continuous white bias light is used to illuminate the entire device at an irradiance approximately identical to normal operating conditions intended for the OPV cell (1000 W/m\(^2\) irradiance in most cases). The spectral dependence of the AC (chopped) component of the short circuit current is picked up by the lock-in amplifier as the wavelength of the monochromatic light varies over the response band of the cell. The power of the incident monochromatic light is determined by Newport 818-UV Si detector with known spectral responsivity. In the current setup, two condensing lenses combined with slits on the monochromator are used to adjust the beam size to an appropriate level so that all

---

Figure 2-3. Diagram of external quantum efficiency (EQE) measurement for OPV cells.
monochromatic light is incident on the device’s active area. With this information, the $EQE(\lambda)$ of the OPV cell can be obtained through:

$$
EQE(\lambda) = \frac{hc}{q\lambda} \cdot \frac{I_{cell}(\lambda)}{I_{det}(\lambda)/S_{det}(\lambda)}
$$

Here, $I_{cell}(\lambda)$ and $I_{det}(\lambda)$ are the short circuit currents generated by the monochromatic beam for the OPV cell or detector, respectively. $S_{det}(\lambda)$ is the spectral responsivity of the detector. With $EQE$ information, the short circuit current under reference spectral irradiance can be calculated through the equation:

$$
I_{SC} = \frac{hc}{q\lambda} \cdot \int_{\lambda_1}^{\lambda_2} EQE(\lambda) E_{Ref}(\lambda) d\lambda
$$

Figure 2-4 shows the measured EQE curve of a bilayer CuPc/C60 OPV cell along with the current density-voltage ($J-V$) characteristics of the same device at 1000 W/cm$^2$ simulated AM 1.5 G irradiances.

![Figure 2-4](image_url)

**Figure 2-4.** External quantum efficiency as a function of the wavelength for ITO/CuPc (20 nm)/C$_{60}$ (40 nm)/BCP (8 nm)/Al OPV cell. Inset: current density-voltage ($J-V$) characteristics of same device under calibrated AM 1.5G 1000 W/cm$^2$ irradiance.

$J_{SC(direct)} = 3.70 \pm 0.09$ mA/cm$^2$

$J_{SC(cal)} = 3.46 \pm 0.03$ mA/cm$^2$
1.5G irradiance measured through the KG1 filter Si reference cell mentioned above. It can be seen that the direct measurement gives a short circuit current density of \( J_{SC(\text{direct})} = 3.70 \pm 0.09 \) mA/cm\(^2\) based on 0.04 cm\(^2\) device area, whereas the calculated \( J_{SC(\text{cal})} = 3.46 \pm 0.03 \) mA/cm\(^2\) based on EQE curve. The difference between the two values is around 5%, which suggests good consistency between two measurement systems.

**Measurement of Organic Light-Emitting Diodes**

OLED technology has made significant advances in the last decade, and different commercial products have recently been available on the market. However, the efficiency measurement setup adopted by different research groups varies significantly, which makes valid comparison between different laboratories difficult. Here, we present our simple yet accurate way to measure the efficiency of OLEDs.

**Measurement Setup for Organic Light-Emitting Diodes**

For OLEDs targeted for display and lighting applications, it is of key importance to accurately measure the luminance from the OLEDs so that accurate values for the different types of efficacy can be realized. One important assumption we make in our OLED measurements is that the emission pattern of the devices resembles that from an ideal Lambertian emitter.\(^{66}\) Basically, a Lambertian emitter is isotropic, emitting with equal luminance into any solid angle within the forward viewing hemisphere. Nevertheless, such assumption becomes violated when microcavity, out-coupling or other structures are applied to the OLEDs, which can significantly change the emission pattern from Lambertian type.\(^{67-69}\)

The luminance of OLEDs with Lambertian emission patterns can be easily measured using a commercial luminance meter. With the recorded luminance value \( L \) (cd/m\(^2\)), the current efficiency of the device \( \eta_L \) (cd/A) can be simply calculated by dividing \( L \) by the drive current density of the device \( J_{OLED} \). The power efficiency \( \eta_P \) and external quantum efficiency \( \eta_{EQE} \) can be
also be calculated based on $\eta_L$ with knowledge of the driving voltage, emission spectrum and photopic response of the human eye. In practical measurements, the current-density-luminance-voltage ($J – L – V$) characteristics of the OLEDs are desired, which is obtained by sweeping the OLEDs across a certain voltage range and recording $J_{\text{OLED}}$ and $L$ at each corresponding voltage. Using a luminance meter to measure the luminance over the whole scan range can take substantial amount of time due to integration time needed for each measurement. One accurate yet convenient way for measuring the luminance is shown in Figure 2-5a, which employs a photodetector to collect the emitting light. Here, only a fraction of light $f$ is being collected by

![Diagram of luminance measurement setup](image_url)

**Figure 2-5. Luminance measurement of OLEDs.** (a) Diagram of the luminance measurement setup for organic light-emitting diodes (OLEDs) with Si photodetector collected $f$ fraction of forward emitting light. (b) Linear dependence of the luminance (measured by luminance meter) and photocurrent (measured by Si photodetector) using the above measurement diagram.
the photodetector, and the corresponding luminance is related to the photocurrent $I_{\text{det}}$ through $L = \alpha \cdot I_{\text{det}}$. The conversion factor $\alpha$ is determined by $f$ as well as the spectral responsivity of the photodetector $R(\lambda)$. The value of $\alpha$ can be obtained by curve fitting $L$ and $I_{\text{det}}$ over a certain range of luminance. As shown in Figure 2-5b, $I_{\text{det}}$ exhibits linear dependence vs. luminance over the range of 25 – 55 cd/m$^2$ for a deep-blue phosphorescent OLED, with $\alpha = 0.391$ cd/m$^2$·A from curve fitting.

Generally, $f$ is a parameter that only depends on the geometric arrangement of the photodetector and the OLEDs by assuming the emission pattern does not change at different driving voltage nor with different OLED emission spectra. Therefore, by fixing the relative position of the photodetector to the OLEDs, $f$ should be a constant. With knowledge of the emission spectrum of an OLED $S(\lambda)$ and its conversion factor $\alpha$, $f$ can be expressed as:

$$f = \frac{\Phi_0 \int g(\lambda)S(\lambda)d\lambda}{A\pi \alpha \int S(\lambda)R(\lambda)d\lambda}$$

where $\Phi_0$ is the peak value of the photopic response curve, i.e., 683 lm/W, $g(\lambda)$ is the normalized photopic response curve and $A$ is the device area. Since $f$ is only determined by the geometry of the measurement setup, the $\eta_L$ of any OLEDs with such geometry can be obtained by simply measuring the photocurrent and the corresponding emission spectrum:

$$\eta_L = \frac{Al_{\text{det}}\Phi_0 \int g(\lambda)S(\lambda)d\lambda}{\pi f I_{\text{OLED}} \int S(\lambda)R(\lambda)d\lambda}$$

while $\eta_P$ and $\eta_{\text{EQE}}$ can be related to $\eta_L$ through the equations:

$$\eta_P = \frac{\pi}{\sqrt{V}} \times \eta_L$$

$$\eta_{\text{EQE}} = \frac{qI_{\text{det}} \int \lambda S(\lambda)d\lambda}{\hbar c f I_{\text{OLED}} \int S(\lambda)R(\lambda)d\lambda}$$
One should be cautious since all of the above equations are spectrum sensitive. Therefore, if the emission spectrum changes with respect to the driving voltage, it is required that the right spectrum be plugged in to get the corresponding efficiency at certain driving conditions. The efficiency measured using the current method only accounts for the forward direction, so any photons emitted from the substrate edge and backward direction are missed. The forward efficiency is widely used in display applications.\textsuperscript{60} The total external quantum efficiency, which accounts for the photons emitted from the device in all directions, can be measured by placing the OLEDs into an integrating sphere.\textsuperscript{60}

**Conclusions**

In this chapter, we provided accurate ways to measure the efficiency of OPV cells and OLEDs. For OPV cells, it is important to select a reference cell with similar spectral response compared to the OPV cells being tested. By using a KG1-filtered Si reference cell, the spectral mismatch factor reaches 0.99, which suggests the efficiency measured by such a solar simulator system accurately reflects the performance of the device under reference spectral irradiance. The short circuit current calculated by integration of the product of external quantum efficiency and reference spectral irradiance is also a reference for the measured short circuit current, and the difference should be less than 10\% to indicate good agreement between the two setups. In the measurement of OLEDs efficiency, a simple method involving a calibrated photodetector is suggested. By fixing the geometry-determined $f$ parameter and measuring the emission spectrum, the current, power and external quantum efficiencies in the forward direction can be readily obtained through existing equations by assuming a Lambertian emission pattern of.

All the OPV and OLED efficiencies provided in this thesis are obtained through the methods outlined in this chapter, which should serve as a good reference base for understanding the physical processes in the devices.
CHAPTER 3
PHASE SEPARATION IN MOLECULAR DONOR-ACCEPTOR MIXTURE

Introduction

Organic photovoltaic (OPV) cells commonly employ a donor-acceptor (D-A) heterojunction structure to provide the driving force for the dissociation of photogenerated excitons due to an appropriate energy level offset at the D-A interface. However, the exciton diffusion length for most organic materials is on the order of a few nanometers.\textsuperscript{9,72-74} Thus, only excitons generated in the vicinity of the D-A interface can be collected, which limits the efficiency of OPV cells that employ a bilayer heterojunction structure. Therefore, it is crucial to properly design the morphological structure of the active layer to maximize the amount of the photogenerated excitons reaching the D-A interface and contribute to the photovoltaic process.

It has been shown that a bulk heterojunction (BHJ) composed of a mixture of donor and acceptor molecules with percolated D-A phase can enhance the exciton diffusion efficiency and hence the OPV efficiency.\textsuperscript{3,4,6,80-82,75-78} In an optimized BHJ structure, nanoscale three-dimensional percolated networks of the donor and acceptor phase lead to both good exciton diffusion and charge collection. Various approaches have been reported to realize the BHJ structure. Two of the most common methods include deposition of a thin film by spin-casting a blended solution with a polymer donor and small molecular acceptors\textsuperscript{3,4,41,43} or by co-evaporation of two molecular species in vacuum.\textsuperscript{6,45} It has been found that the morphology of the D-A networks strongly depends on the donor-to-acceptor mixing ratio and various processing conditions during film deposition as well as the molecular properties.\textsuperscript{6,47,58,79} The film morphology may even be further optimized by employing thermal or solvent post-annealing processes.\textsuperscript{80,81} One important parameter for determining the film morphology, the degree of phase separation in a D-A mixture, strongly depends on both the intrinsic molecular properties
Figure 3-1. Different morphological structure in molecular donor-acceptor mixtures and the charge transport within. (a) complete mixing of two molecular species with discontinued conducting path; (b) molecular level conducting paths are formed with weak phase separation in the mixture; (c) ideal bulk heterojunction with nanoscale phase separation in D-A mixtures. [Ref 45]

and the thermodynamic and kinetic processes involved during the mixing of the two molecular species. 

Figure 3-1 illustrates three different morphological structure of the molecular D-A mixtures. It can be seen that a very weak phase separation results in a high degree of intermixing between molecular species (Figure 3-1a). Although efficient exciton diffusion is obtained in this case, the discontinuous conducting pathways for electrons and holes result in poor charge collection. A medium level of phase separation could produce morphology like Figure 3-1b, where continuous conducting path basedways on molecular-level interconnections are formed. Ideally, the degree of phase separation should be neither too weak nor too strong so that a pure donor and acceptor phase with structural dimension of tens of nanometers can be obtained as shown in Figure 3-1c. The nanoscale phase separation could secure both good exciton diffusion and charge collection.

Although there have been intensive research efforts to correlate the degree of phase separation with experimental observations, it is still challenging to understand the phase
separation process and how it determines the resulting morphology within the mixture, such as the domain size and degree of percolation. In this chapter, the morphological behavior between donor and acceptor molecules at the atomic scale is explored using computational methods. Specifically, the results obtained from molecular dynamics simulations indicate how the molecules behave with a given concentration and how their initial neighbors affect the final outcome. At the same time, experimental studies of the structure and morphology of the donor-acceptor mixed films are conducted. The combined computational and experimental results give a profile of the phase separation behavior between pentacene and C_{60}.

It is therefore the purpose of this work to combine experimental and computational methods to understand the phase separation process in organic D – A mixtures. The pentacene:C_{60} molecular system was chosen for this study due to the simplicity in dealing with small hydrocarbon molecules computationally. Efficient OPV devices based on bilayer pentacene:C_{60} heterojunctions have also been demonstrated previously. Here, we use classical molecular dynamics (MD) simulations to examine morphology evolution in various pentacene:C_{60} mixtures. A quantitative way to describe the phase separation between pentacene and C_{60} in equilibrated mixtures was suggested. Experimentally, X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were employed to characterize the crystal structure and surface morphology of mixed films prepared with various processing parameters. Photovoltaic (PV) devices using pentacene:C_{60} BHJs were fabricated based on the information obtained from simulation and morphology characterization. We found that devices constructed with D-A mixed films in which nanoscale phase separation was successfully controlled exhibit the highest efficiency amongst all BHJ devices considered in the work.
This chapter is organized as follows. A general introduction of the thermodynamics and kinetics involved in phase separation process is given first, followed by the molecular dynamic simulation and discusses the computational results of structural evolution of pentacene:C\textsubscript{60} mixtures. With the simulation results, the experimental study of phase separation degree in pentacene:C\textsubscript{60} mixed films are conducted, followed by the PV performance comparison of devices based different pentacene:C\textsubscript{60} mixed film. The last two sections summarize the contents in this chapter and draw a conclusion based on the results.

**Thermodynamics and Kinetics of Phase Separation**

**Behavior of Regular Solution**

In general, whether phase separation can happen in a mixture is determined by the energy level of each thermodynamic state adopted by the mixture. The lowest thermodynamic energy state corresponds to the most stable structure, which the mixture will finally adopt if there is no kinetic limitation during the structure evolution. One of the most widely used parameters to describe the energy change during the mixing and phase separation of various components is the Gibbs free energy. The Gibbs free energy change ($\Delta G^M$) due to the mixing of different components can be expressed as:\textsuperscript{86}

$$\Delta G^M = \Delta H^M - T \Delta S^M$$

where $\Delta H^M$ and $\Delta S^M$ are the enthalpy and entropy change due to mixing, respectively. And $T$ is the temperature. In a regular solution model consisting of only two components, the enthalpy and entropy change of the mixing can be obtained statistically by considering the interaction energy between some species as well as between different species. For instance, in a binary system composed of donor and acceptor molecule with concentration of $X_D$ amd $X_A$, the $\Delta H^M$ and $\Delta S^M$ can be expressed as:
\[ \Delta H^M = zN_0 \left[ E_{DA} - \frac{1}{2}(E_{AA} + E_{DD}) \right] X_A X_D \]

\[ \Delta S^M = -N_0 k (X_A \ln X_A + X_D \ln X_D) \]

where \( N_0 \) is Avogadro’s constant, \( k \) is the Boltzmann’s constant, \( z \) is coordinates, and \( E_{DA}, E_{AA} \) and \( E_{DD} \) are the energies of donor-acceptor interactions, acceptor-acceptor interaction and donor-donor interactions, respectively. Figure 3-2 shows the plots of \( \Delta G^M \) as a function of mixing ratio, where three different scenarios can be recognized in terms of phase separation level. As indicated by the blue curve, \( \Delta G^M \) is negative with only one global minimum when \( 2E_{DA} > E_{AA} + E_{DD} \), suggesting complete intermixing of the mixture and no phase separation will be observed. On the other hand, if \( 2E_{DA} < E_{AA} + E_{DD} \) and the temperature is not very high, two

**Figure 3-2.** The variation, with composition, of the molar Gibbs free energy of the formation of a binary regular solution. The three scenarios suggest the thermodynamic stable states of the solution with (green curve) and without (blue and red curve) phase separation in the solution.
saddle points corresponding to two different stable phases with different mixing ratios can be observed along the $\Delta G^M$ plot (see green curve). In this case, if a mixture with a 1:1 mixing ratio of donor and acceptor is created, the system is unstable due to a relatively high Gibbs free energy. Therefore, the mixture tends to have phase separation so that two phases, one donor-rich and the other acceptor-rich, will form in the mixture. Although phase separation could happen under this condition, increasing the temperature will cause the two species to mix with each other again, which results in no phase separation (see red curve).

Therefore, a complete and stable mixing of donor and acceptor molecules happens when the donor-acceptor interaction is stronger than the donor-donor and acceptor-acceptor interactions ($2E_{DA} > E_{AA} + E_{DD}$). To realize phase separation in a D-A mixture, the donor-donor and acceptor-acceptor interactions should be stronger than the donor-acceptor interaction ($2E_{DA} < E_{AA} + E_{DD}$), and at the same time the system temperature should not be very high. In the current pentacene:C$_{60}$ mixture, the pentacene-pentacene interaction is expected to be stronger than the pentacene:C$_{60}$ interaction due to stronger $\pi-\pi$ interaction between pentacene molecules. Therefore, phase separation is expected to be seen in the pentacene:C$_{60}$ mixtures. Further computational study to calculate the interaction energy between the molecular species involved will provide a more profound understanding of the phase separation in the pentacene:C$_{60}$ mixtures.

**Spinodal Decomposition and Nucleation**

The Gibbs free energy curve of the mixture provides an insight of whether a phase separated structure is thermodynamic favorable state of the mixture. Nevertheless, how the molecules evolve in the mixture during the phase separation process is of great importance in determining the microstructure in the final phase separated mixture. Basically, there are two
distinct mechanisms for phase separation; namely, spinodal decomposition and nucleation plus growth. Although the final thermodynamic state could be the same, different routes took by the mixture during the phase separation could result in different structure and morphology.

The spinodal decomposition happens at a part of the Gibbs free energy curve where the curvature is negative, which means $\frac{\partial^2 \Delta G}{\partial X_A^2} < 0$. Figure 3-3a shows a part of the Gibbs free energy curve with negative curvature. It can be seen that a small deviation away from the initial concentration point can lower the free energy of the system, i.e. $\Delta G_{\text{unmixing}} < 0$. Therefore, one part of the system gets more concentrated of one species at the expense of another. The spatial composition change of the system with respect to the time is illustrated in Figure 3-3b. It can be noticed that one part of the system become more concentrated with one species, while another part gets less concentrated as time proceeds. Finally, two different phases with concentrations corresponding to the saddle points on the free energy curve are reached.

The nucleation and growth mechanism is quite different from spinodal decomposition. As shown in Figure 3-4a, the nucleation and growth takes place when a part of the free energy curve has positive curvature, i.e., $\frac{\partial^2 \Delta G}{\partial X_A^2} > 0$. As a result, a small fluctuation of the concentration will increase the system energy instead of lower the system energy as spinodal
Figure 3-4. Phase separation through nucleation (a) The nucleation process, (b) spatial composition variation during the nucleation process.

decomposition did, i.e. $\Delta G_{\text{unmixing}} > 0$. Therefore, the phase separation in this case requires large composition fluctuations to decrease energy, which means the new phase must start with a composition far from the parent phase. This suggests a nucleation process of a new phase within an existing phase, followed by crystal growth of the new phase. Figure 3-4b illustrates the spatial composition change during the nucleation process, where a tiny part of the system become highly concentrated with concentration of other part nearly unchanged.

Generally, nucleation is a phase transition that is large in degree in terms of composition change but small in extent, whereas spinodal decomposition is small in degree but large in extent. Therefore, in order to achieve morphology in the D-A mixture that is favorable for OPV application, phase separation through nucleation and growth is highly desired due to the capability to generate smaller domains in the mixture. However, whether phase separation will take the route of spinodal decomposition or nucleation and growth depends on the Gibbs free energy curve of the mixture, which is again determined by the temperature and interaction energy between the molecular species.

**Structural and Morphological Control of Pentacene:C₆₀ Mixtures**

**Effect of Mixing Ratio on Structure and Morphology**

To understand the phase separation in the pentacene:C₆₀ mixtures, the structure and morphology of different pentacene:C₆₀ mixed films are first investigated using X-ray diffraction...
and atomic force microscope. Pentacene:C$_{60}$ films with various mixing ratios were deposited via vacuum thermal evaporation in a custom-made vacuum chamber with a background pressure of $\sim 2 \times 10^{-7}$ Torr. For structural and morphological studies, all films were deposited on Si (100) substrates, which is obtained by immersion in diluted hydrofluoric acid (HF:H$_2$O = 1:50) to etch away the native oxide layer.

To investigate the structure of pentacene:C$_{60}$ mixtures, X-ray diffraction (XRD) is first used to characterize films with different mixing ratios. Figure 3-5 shows diffraction patterns of 30 nm thick films of pentacene, C$_{60}$ and pentacene:C$_{60}$ deposited on an Si substrate. The XRD patterns were obtained using a Philips X’pert MRD diffractometer in the $\theta$-2$\theta$ geometry with a 45 kV Cu K$\alpha$ radiation source. It can be seen that the neat pentacene film shows diffraction peaks from the thin film (00$n'$) and bulk (00$n$) ($n = 1,2,3$) phases of pentacene. And the peaks for the

![X-ray diffraction patterns for 30 nm thick pentacene and pentacene:C$_{60}$ mixed films with various mixing ratios, taken in the $\theta$-2$\theta$ geometry.](image)

Figure 3-5. X-ray diffraction patterns for 30 nm thick pentacene and pentacene:C$_{60}$ mixed films with various mixing ratios, taken in the $\theta$-2$\theta$ geometry.
thin film phase are more prominent due to the small thickness of the film.\textsuperscript{16,87} The presence of higher order diffraction peaks indicate the good crystalline order in the neat pentacene film. The pentacene (001') and (001) peaks, located at $2\theta = 5.7^\circ$ and $6.1^\circ$, respectively, correspond to the interplanar spacing ($d$) of 15.5 Å and 14.5 Å, which agrees well with the values reported in the literature.\textsuperscript{87,88} When pentacene and $C_{60}$ are mixed with a weight ratio of 3:1, the less prominent pentacene (001) peak disappears, and the intensity for the (001') peak reduces significantly. Additionally, all higher-order diffraction peaks, except the (002') peak, cannot be discerned anymore, an indication of the increased disorder among pentacene stacks. As the concentration of $C_{60}$ continues increasing in the mixture, the (001') peak intensity further decreases and it eventually disappears in the XRD pattern for the 1:2 mixed film. These data suggest that the pentacene aggregates in the form of crystalline domains exist in pentacene-rich films, although the disorder increases with the $C_{60}$ concentration. It is noted that the general trend observed in the XRD patterns here is similar to that for CuPc:$C_{60}$ mixtures.\textsuperscript{58} However, the CuPc aggregation can only be found when the CuPc concentration is high enough, i.e., a CuPc to $C_{60}$ mixing ratio of 6:1 or higher. All these suggest that pentacene molecules have a stronger tendency to aggregate than CuPc.

To gain an insight of the nanostructure inside the phase separated pentacene:$C_{60}$ mixtures, AFM is used to investigate 3 nm thick neat or mixed films grown on Si. The AFM images are obtained using a Veeco Dimension 3100 AFM working in tapping mode with Si probe tips. As shown in Figure 3-6, the layer-plus-island growth mode can be observed in neat pentacene films, which is consistent with previous reports.\textsuperscript{89-92} The first monolayer covers most of the area with µm-sized domains, on top of which islands of second and subsequent monolayers are grown. The neat $C_{60}$ film, on the other hand, shows a smooth and featureless surface under AFM. The
pentacene:C₆₀ mixed films (as shown in Figure 3-6), however, show remarkably different morphologies from those of the two neat films. As the mixing ratio changes from pentacene:C₆₀ (4:1) to pentacene:C₆₀ (1:2), the morphologies change accordingly. The root-mean-square
roughness ($R_{rms}$) increases from 2.0 nm for pentacene:C$_{60}$ (4:1) to the maximum value of 2.9 nm for pentacene:C$_{60}$ (1:2). The $R_{rms}$ value of all mixed films is higher than that of either neat film (1.4 nm for pentacene and 1.5 nm for C$_{60}$). Furthermore, two different types of features can be identified in the AFM image for pentacene:C$_{60}$ (4:1): “islands” with a typical size of 200 nm and an average height of a few nanometers as well as relatively flat domains in between islands. As the C$_{60}$ concentration increased, the island features become more prominent with increased height. The flat domains, on the other hand, gradually diminish and become almost nonexistent in the mixed films with more than 50% C$_{60}$. Based on the XRD patterns from the 30nm films shown above, we believe that the flat domains correspond to the crystalline pentacene aggregates which contribute to the characteristic pentacene diffraction peaks, whereas the islands could be an amorphous pentacene-rich phase.

**Effect of Deposition Rate on Structure and Morphology**

The AFM study of ultrathin films (3 nm thick) indicates the existence of two different features in the pentacene:C$_{60}$ mixtures, which leads to a rough surface morphology. We have found that these two typical features can evolve into significantly different structures in much thicker films. Moreover, the phase separation can be further affected by the deposition rate, which provides a route to control the degree of phase separation. Figure 3-7 shows the SEM and AFM images of three 50 nm thick mixed films with mixing ratio of 1:1 (a, b), 1:2 (c, d), and 1:4 (e, f), deposited at a total rate of 0.6 Å/s. Here, the thickness of 50 nm is chosen as it is very close to the typical thickness used in PV devices. Numerous ridgelike structures on the surface are found on these films. The height of the ridges reaches nearly 200 nm in pentacene:C$_{60}$ (1:1), substantially higher than the nominal thickness of 50 nm. The density and height of the ridges decrease as the pentacene concentration is decreased from 50% to 20%, and the ridge height
Figure 3-7. [(a), (c), and (e)] Tapping mode atomic force microscope (AFM), and [(b), (d), and (f)] scanning electron microscope (SEM) images of 50 nm thick pentacene:C$_{60}$ = 1:1 [(a) and (b)], 1:2 [(c) and (d)] and 1:4 [(e) and (f)] deposited at 0.6 Å/s (total rate) on Si substrate. The scale bar in the SEM images is 1 μm, and the scanning area in the AFM images is $5\times5\mu m^2$ while the height scale is 300 nm.
reaches around 50 nm in pentacene:C_{60} (1:4). This leads to a reduction of $R_{rms}$ from 50 nm in pentacene:C_{60} (1:1) to 20 nm in pentacene:C_{60} (1:4). Besides the ridgelike structures, many “bumps” with size of about 200 nm between the ridges can be identified in the SEM image for the 1:1 mixed film (Figure 3-7a), although similar features become indiscernible in the films with higher C_{60} concentration. By comparing the morphologies observed in the ultrathin film and considering the dependencies of these features on the mixing ratio, we believe that the ridgelike structures found in the thicker film are evolved from the coalescing of the pentacene-rich islands observed in the ultrathin films, whereas the “bumps” between ridges correspond to the flat crystalline domains from the ultrathin film. Similar ridgelike structures also appear in neat pentacene films grown under certain extreme condition where the growth of crystalline pentacene domains is disturbed.\textsuperscript{93} The presence of C_{60} molecules in the mixtures certainly represents one of the scenarios that the crystalline growth of pentacene is disturbed.

The very rough surfaces of pentacene:C_{60} mixed films observed in Figure 3-7 could be practically undesired for OPV device as they could result in poor metal/organic contact and low device yield. One way to obtain smoother morphology is to utilize the non-equilibrium nature of the vacuum deposition processes and push the growth of thin film into the kinetic regime. Here, we increase the deposition rate so that the molecules arrived at the substrate surface have less time to diffuse on the surface before being buried the later arriving molecules. Figure 3-8 shows the SEM and AFM images of three mixed films deposited at a much higher rate of 6 Å/s, with a mixing ratio of 1:1 (a, b), 1:4 (c, d), and 1:5.5 (e, f). It can be seen that those long ridges observed in films deposited at low rate (see Figure 3-7) break down into much shorter and smaller ones and no “bumps” can be identified in areas between the ridges. For the 1:1 mixed
Figure 3-8. [(a), (c), and (e)] Tapping mode atomic force microscope (AFM), and [(b), (d), and (f)] Scanning electron microscope (SEM) images of 50 nm thick pentacene:C_{60} = 1:1 [(a) and (b)], 1:4 [(c) and (d)], and 1:5.5 [(e) and (f)] deposited at 6 Å/s (total rate) on a Si substrate. The scale bar in the SEM images is 1μm, and the scanning area in the AFM images is 5×5μm² while the height scale is 300 nm.
film, the surface roughness is significantly reduced from $R_{\text{rms}} = 50$ nm for the film deposited at 0.6 Å/s to 26 nm for the film with a 6 Å/s deposition rate.

To further confirm that the high deposition rate can suppress the stacking of pentacene molecules in the mixed film, XRD measurement of 1:1 mixed films fabricated at 0.6 Å/s and 6 Å/s is carried out. As shown in Figure 3-9, a small diffraction peak corresponds to the crystalline phase pentacene can be identified in the diffraction pattern of pentacene:$C_{60}$ (1:1) deposited at 0.6 Å/s, whereas no peak is observed in 1:1 mixed film grown with 6 Å/s. All these suggest that the mixed films are more uniform and that the formation of both crystalline pentacene domains and pentacene-rich structures is significantly suppressed. In the 1:5.5 mixed film (Figure 3-8e and f), almost no ridgelike features can be recognized under SEM or AFM, resulting in a low $R_{\text{rms}} = 6$ nm.

![X-ray diffraction patterns for 50 nm pentacene:$C_{60}$ (1:1) mixed films fabricated under 0.6 Å/s (red curve) and 6 Å/s (blue curve). Inset: the corresponding SEM image of the mixed films with scale bare size of 1 μm.](image)

Figure 3-9. X-ray diffraction patterns for 50 nm pentacene:$C_{60}$ (1:1) mixed films fabricated under 0.6 Å/s (red curve) and 6 Å/s (blue curve). Inset: the corresponding SEM image of the mixed films with scale bare size of 1 μm.
Molecular Dynamics Simulation of Pentacene:C\textsubscript{60} Mixtures

In this section, Molecular Dynamics (MD) simulation is used to investigate the structural evolution within the pentacene:C\textsubscript{60} mixtures. The MD simulation works presented here is conducted by Sharon Pregler, Jason Myers, and Dr. Susan Sinnott.

Method of Molecular Dynamics Simulation

Molecular dynamics (MD) simulation is a technique that widely used to compute the equilibrium and transport properties of classical many-body systems.\textsuperscript{84,85} In MD simulations, a model system composed of \(N\) particles is first built and initialized. The MD process then numerically integrates Newton’s equations of motion to predict particle responses to applied forces until their properties no longer change with time, which is also known as equilibrating the system. After equilibration, atom displacements, bond lengths, crystal structure, or other macroscopic properties of interest can be calculated.

In the current MD simulations of structural evolution in pentacene:C\textsubscript{60} mixtures empirical many-body potentials are employed because it can allow the MD simulations to model the relaxation of thousands of atoms in a relatively short time. Here, the adaptive intermolecular reactive empirical bond order (AIREBO) potential is used.\textsuperscript{84,94} Compared with the second-generation reactive empirical bond-order (REBO) potential, which was designed to model short range interactions of carbon and silicon including hybridization and bond breaking and reformation, AIREBO can account for the nonbonding interactions via an adaptive method, hence overcoming the limitations that REBO has on long-ranged interactions. A 6-12 Lennard Jones (LJ) potential (\(E_{\text{LJ}}\)) and torsion potential (\(E_{\text{tors}}\)) are used to described the nonbonded interactions through the equation:

\[
E = E_{b}^{\text{REBO}} + E_{\text{LJ}} + E_{\text{tors}}
\]

where
\[ E_{b}^{REBO} = \sum_{i} \sum_{j (> i)} \left[ V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right] \]

The functions \( V^R(r) \) and \( V^A(r) \) describe pair additive interactions for core-core repulsive and attractive interactions, respectively, \( b_{ij} \) accounts for the bonding between atoms \( i \) and \( j \), while \( r_{ij} \) is the distance between these atoms. A screening function that smoothly transitions between the REBO and LJ potentials is used in AIREBO. The molecular forces depend on the local chemical environment of the atoms, making the AIREBO potential well suited for modeling liquid hydrocarbons, thin films, and hydrocarbon molecules and mixtures.

In order to check the validity of the computational method we first used AIREBO to calculate the cohesive energies for bulk \( C_{60} \) and bulk pentacene. As summarized in Table 3-1, the experimental cohesive energy determined from heats of sublimation of bulk \( C_{60} \) and pentacene is 1.74 eV and 1.30 eV, respectively.\(^95,96\) These two experiment values match very well with the cohesive energy obtained through AIREBO, which is 1.70 eV for \( C_{60} \) and 1.38 eV for pentacene. This suggests that AIREBO is an adequate tool for studying the short-range and long-range evolution of the molecular systems investigated here.

To simulate the structural evolution of pentacene:\( C_{60} \) mixtures, relaxation of the molecules were carried out in a \( 5 \times 5 \times 7 \) nm supercell with periodic boundary conditions due to the complexity in handling a larger system computationally. To accelerate the molecular relaxation,

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{60} )</td>
<td>1.70</td>
<td>1.74(^a)</td>
</tr>
<tr>
<td>Pentacene</td>
<td>1.38</td>
<td>1.30(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 96 \(^b\) Ref. 95.
the system was placed at an elevated Langevin thermostat temperature of 600 K, which allows
the molecules to shift out of their initial positions faster. After that, all the atoms in the system
were set to 300 K. When the desired temperature was reached within the system, the thermostat
was lifted, setting all the atoms to active. The molecules were then allowed to evolve in time
according to Newton’s law of motion. The mixtures were set to relax for 100 ps until the energy
of the system reached a constant level. We believe that such a simulation method is appropriate
to predict the final thermodynamic stable structure of the selected pentacene:C_{60} mixtures.

Structural Evolution in Pentacene:C_{60} Mixtures

The computational studies begin with a virtual mixed film of pentacene and C_{60} built from
an ordered structure approach. A low density structure was built with a starting unit cell and a
given mixing ratio, and was then duplicated in three dimensions to create a supercell. The
pentacene:C_{60} mixture with a weight mixing ratio of 2.3:1, or 6:1 by molar ratio, was first chosen
to simulate the morphology evolution. For consistency, all mixing ratios referred to in this
chapter will be by weight unless otherwise noted. In the pentacene:C_{60} (2.3:1) structure, the unit
cells were arranged in a simple cubic (SC) structure with a density of 1.0 g/cm^{3}.

Figure 3-10a shows a snapshot of the SC structure pentacene:C_{60} (2.3:1) mixture before
relaxation, where each fullerene molecule is surrounded by six pentacene molecules. It can been
seen from Figure 3-10b that after 100 ps of equilibration the structure of the mixture changed
significantly, where molecules of the same type clump together but are not completely phase
separated. Extending equilibration time up to 300 ps does not lead to complete phase separation.
The potential energy curve as a function of molecular position is considered as a flat potential
energy surface. Nevertheless, varying the initial structures of the molecules could lead to
numerous local minima. We found that in different initial structures, face-centered cubic (FCC)
or body-centered cubic (BCC) for example, the pentacene and C_{60} equilibrate in the same
manner as mentioned above. The planar pentacene molecules have a tendency to stack on each other to maximize their $\pi-\pi$ interaction.\textsuperscript{32} Due to the presence of much more pentacene than C\textsubscript{60} molecules (6 to 1 in numbers) in the mixture, it is clear from Figure 3-10b that some of the pentacene molecules form stacks in addition to simple agglomerating.

Figure 3-10. Molecular model of pentacene:C\textsubscript{60} (2.3:1) (by weight) (a) before and (b) after 100 ps equilibration. Periodic boundaries are applied in three dimensions. The unit cell dimension is $5\times5\times7$ nm with a density of 1.0 g/cm$^3$. (Courtesy of S. Pregler)
In order to quantitatively describe the stacking nature of the pentacene molecules from the simulation, we use a combination of pair-wise distance calculation and molecular vector agreement. In this method, each pentacene molecule is assigned a longitudinal and transverse vector, along the benzene rings and across them, respectively, and the corresponding vectors for all molecules in a stack should be the same. Here, pentacene molecules are considered as forming stacks if their corresponding vectors are aligned within an angle of 10°. Additionally, intermolecular center-to-center distances are also checked to make sure that molecules with aligned vectors are indeed stacked closely, not just coincidentally aligned. We choose a cutoff interplanar distance of 4.1 Å, which is 0.5 Å greater than the closest interplanar stacking distance between neighboring molecules in a pentacene crystal.

The histogram shown in Figure 3-11a indicates that 22% of the pentacene molecules in the equilibrated (2.3:1) mixture form pairs, and approximately another 8% of the pentacene molecules form either three- or four-molecule stacks. The inset of Figure 3-11b shows all the

![Figure 3-11. Pentacene stacks in the equilibrated pentacene:C60 (2.3:1) structure (left) Percentage of pentacene molecules forming stacks versus number of molecules in each stack, (right) isolated pentacene stacks in the film. (Calculation done by J. Myers)](image-url)
pentacene molecules that form stacks inside the mixture. This suggests that the pentacene molecules tend to form aggregates in the mixture after equilibration. The aggregation nature of C₆₀ molecules, however, can be quantified using the pair distribution functions (PDFs). Figure 3-12a compares the PDFs of the C₆₀ molecules in the pentacene:C₆₀ (2.3:1) mixture before and after relaxation as well as that of a pristine C₆₀ crystal, which adopts a FCC lattice structure. It is found that the center-to-center nearest neighbor distance of C₆₀ molecules is reduced from approximately 1.5 nm to 1 nm after system is equilibrated. This nearest neighbor distance after relaxation is very close to that in an FCC lattice of C₆₀ crystal, which indicates the presence of short range order in the relaxed mixed film. The oscillation in the PDF of the equilibrated structure becomes relatively small at distance > 1.5 nm, suggesting the lack of long-range ordering of C₆₀ molecule in the equilibrated mixed film.

![Graph comparing PDFs of C₆₀ molecules](image)

Figure 3-12. C₆₀ aggregation in pentacene:C₆₀ (2.3:1) before and after 100 ps equilibration. (left) Pair distribution functions (PDFs), g(r), of the C₆₀ molecules as a function of the pair distance, r. The PDF of the face-centered-cubic C₆₀ crystal is also shown as comparison. (right) isolated C₆₀ molecules in the equilibrated film. (Courtesy of S. Pregler)
Effect of Mixing Ratio and Deposition Rate

In the above structural evolution simulation of the penacene:C\textsubscript{60} (2.3:1) mixture, we found that both pentacene and C\textsubscript{60} molecules have certain degree of tendency to agglomerate with themselves. Here, the simulation is conducted by first building the bulk mixture, which is then allowed to relax. Such simulation resembles the annealing process in the real case and helps to understand the thermodynamic stable structure of the mixture. However, consideration of kinetic process involved during the mixture formation, deposition process for instance, is missing in this simulation. Moreover, the simulated structure is a pentacene-rich mixture, which is biased to claim general aggregation nature of pentacene or C\textsubscript{60} molecules under other mixing ratio.

Therefore, we investigated the effect of mixing ratio and deposition rate on the morphology of pentacene:C\textsubscript{60} mixed films computationally. A Monte Carlo\textsuperscript{101} random film builder (RFB) program is employed to simulate the experimental film deposition process. In the RFB program, pentacene and C\textsubscript{60} molecules, at a predetermined ratio but with a random order, appear on random locations on a virtual flat surface with in a supercell area. The program also randomizes the translation and rotation of the molecules. Once a layer of molecules is created by the RFB, the films were then relaxed suing MD simulations.

Here, films with two different mixing ratios of pentacene:C\textsubscript{60} = 1:2.6 and 1:5.5 deposited under low and high deposition rate were simulated. The condition of low deposition rates is mimicked by first building one layer using RFB, followed by equilibrating the layer at 300 K. This process is repeated for two more layers, i.e. another RFB layer is “deposited” on top of the previous equilibrated one and is equilibrated together with the underlying layer(s) before next layer is “deposited”. The high deposition rate condition in experiment, however, is approximated by generating three different layers with the RFB consecutively and equilibrating the entire structure altogether. Depending on how the randomization of molecules affects the interface of
the layer underneath, the distance between the centers of each layer range from 11 Å to 13 Å. Similar to simulation in low density structures, the whole system was set to thermostat at 300 K, which was then lifted after system reached the desired temperature.

Figure 3-13 shows the simulation results of the pentacene stacks formed in the pentacene:C₆₀ (1:2.6) and (1:5.5) mixed films deposited at the low rate (LR) condition. Because of the higher C₆₀ concentration in these films, only two-molecule stacks, i.e. pairs, are found after 100 ps relaxation. It can be seen that with 10° as the upper limit for the angle offset of the molecular vector only one stack is observed for the (1:2.6, LR) film. However, relaxing the stack detection criterion by increasing the angle offset results in more pentacene stacks being detected, and six stacks are observed when the angle offset is set to 30°. An even higher C₆₀ concentration in the (1:5.5, LR) mixed film leads to substantially less stacks, with only one stack at 30°.

![Figure 3-13](image_url)

Figure 3-13. Number of two-molecule pentacene stacks versus the maximum allowed angle offset to qualify as stacks for the pentacene:C₆₀ (1:2.6) and (1:5.5) deposited at low and high deposition rates (LR and HR, respectively) from simulation.
Figure 3-13 also reflects the pentacene stacking condition in two mixed films deposited at high rate (HR). Similar to the situation in low deposition rate case, significantly fewer stacks are found in the (1:5.5 HR) film than in the (1:2.6 HR) film. However, no stacks is observed in either film if the angle offset is set to 15° or lower, while two stacks are found in the (1:2.6 LR) film. For either (1:2.6) or (1:5.5) mixing ratio, the variation in the number of detected pentacene stacks in the LR and HR films is no more than one when the maximum allowed angle offset is 20° or higher. We believe this is due to the limitations of the computational system where only three layers of molecules are involved. If more molecular layers were considered in the simulation, it is expected to see a more remarkable difference between the two cases, i.e., the movement of underlying molecules would be suppressed by the overlayers more significantly under high deposition rate condition. Nevertheless, the computational results from different mixing ratio and deposition rate scenario indicate that both higher C₆₀ concentration and higher deposition rate lead to a lower degree of pentacene aggregation. However, approximately five pair-stacks out of a total 51 pentacene molecules in one supercell still exist in the (1:2.6) mixed film, indicating the strong aggregation nature of the pentacene.

**Photovoltaic Performance of Pentacene:C₆₀ Mixtures**

To correlate the photovoltaic performance of pentacene:C₆₀ mixtures to the degree of phase separation in the mixture, OPV cells with a device structure of ITO/pentacene:C₆₀ (50 nm)/BCP (8 nm)/Al were fabricated. All OPV devices were fabricated on glass substrates pre-coated with an indium tin oxide (ITO) anode with a sheet resistance of 15 Ω/sq. Performance of OPV cells was tested in air without encapsulation. An Agilent 4155C semiconductor parameter analyzer was used to measure the current density-voltage (J – V) characteristics of devices in the dark and under simulated AM 1.5 solar illumination.
Here, the 50 nm pentacene:C\textsubscript{60} active layers with three different mixing ratios (1:1, 1:2 and 1:5.5 by weight) deposited at \(\sim\) 6 Å/s were used to fabricate the OPV cells. The \(J - V\) characteristics of these three devices in dark are shown in Figure 3-14. The device with a 1:5.5 mixing ratio shows a rectification ratio of more than \(10^4\) (at \(\pm 1\) V), while the 1:1 and 1:2 devices do not show any rectification. The \(J - V\) characteristics of the three devices under illumination intensity of 120 mW/cm\(^2\) are shown in Figure 3-14 as well. It can be seen that the short-circuit current \(J_{SC}\) and fill factor (FF) for the 1:5.5 device are 1.48 mA/cm\(^2\) and 0.29, respectively. Both the 1:1 and 1:2 devices show much lower \(J_{SC}\) and FF, especially for \(J_{SC}\) which is reduced by factor of approximately 150 compared with the 1:5.5 device. The open circuit voltage \((V_{OC})\), on
Table 3-2. Comparison of the short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and power conversion efficiency (PCE) of two bulk heterojunction devices based on pentacene:C$_{60}$ = 1:1, 1:2 and 1:5.5 (by weight) under 120 mW/cm$^2$ simulated AM 1.5G solar illumination.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentacene:C$_{60}$ (1:1)</td>
<td>9.7 × 10$^{-3}$</td>
<td>0.45</td>
<td>0.14</td>
<td>5.1 × 10$^{-4}$</td>
</tr>
<tr>
<td>Pentacene:C$_{60}$ (1:2)</td>
<td>1.7 × 10$^{-2}$</td>
<td>0.56</td>
<td>0.12</td>
<td>9.5 × 10$^{-4}$</td>
</tr>
<tr>
<td>Pentacene:C$_{60}$ (1:5.5)</td>
<td>1.48</td>
<td>0.60</td>
<td>0.29</td>
<td>0.21</td>
</tr>
</tbody>
</table>

On the other hand, gradually decreases from 0.6 V in the 1:5.5 device to 0.56 V in the 1:2 device and 0.45 in the 1:1 device. The substantial change of $V_{OC}$ with respect to the mixing could possibly be due to the increase of photocurrent in devices with higher C$_{60}$ concentration. This can be associated with our previous understanding that reduced domain size can be achieved by increasing the C$_{60}$ concentration in the mixed film, leading to improved exciton dissociation. Also, the $V_{OC}$ of current pentacene:C$_{60}$ bulk heterojunction devices is higher than the typical bilayer heterojunction device ($V_{OC} \sim 0.4$ V),$^{82,83}$ which can be attributed to the much lower dark current observed in the bulk devices than that in bilayer devices. The 1:5.5 device shows significant improvement of $J_{SC}$, $V_{OC}$ and FF over 1:1 and 1:2 devices, which results in 0.21 % power conversion efficiency (PCE). Table 3-2 compares a few important PV parameters of the three devices under illumination. The PCE of the 1:5.5 device is approximately 400 times higher than the other two mixing ratio devices. Since the 1:5.5 mixing ratio provides a working PV device, we also compared the effect of deposition rate on the pentacene:C$_{60}$ (1:5.5) devices. Figure 3-15 shows the $J - V$ characteristics of two pentacene:C$_{60}$ (1:5.5) devices with the mixed layer fabricated at ~ 0.6 Å/s and ~ 6Å/s. It can be seen that $J_{SC} = 0.65$ mA/cm$^2$ in the ~0.6 Å/s device, which is less than half of the ~ 6 Å/s device. The $V_{OC} = 0.64$ V, however, which
is higher in the ~ 0.6 Å/s device due to suppressed dark current. The resulting PCE is only 0.10 % in the ~ 0.6 Å/s device, which is approximately 50 % lower than the ~ 6 Å/s device.

Figure 3-15. Current density versus voltage ($J – V$) characteristics for pentacene:C$_{60}$ = 1:5.5 devices with the mixed layer deposited at ~ 0.6 Å/s and ~ 6 Å/s under 120 mW/cm$^2$ of simulated AM 1.5 illumination.

Discussion

In the current MD simulation, the 5×5×7 nm supercell is relatively too small to simulate the formation of ridgelike structures (which are a few hundred nanometer is size), but we still gain useful insights into the phase separation process between the pentacene and C$_{60}$ in the mixture. The XRD patterns have confirmed the existence of crystalline pentacene domains in mixtures with more than 50 % pentacene. This is somehow consistent with the MD simulation results, which show that nearly 30 % of the pentacene molecules form stacks in the (2.3:1) mixed film after relaxation. Moreover, both computational and experimental studies indicate that the portion of pentacene molecules forming stacks decreases as the pentacene concentration in the
mixed film decreases. Although the XRD pattern indicates crystalline pentacene domains do not
exist in when the pentacene concentration is lower than 50 %, the stacked pentacene molecular
pairs may still be present even in the 1:5.5 mixed films as from the simulation results. Here,
simulation serves as a powerful complement to experimental study. Previous studies on
CuPc:C\(_{60}\) mixtures also suggest the presence of CuPc aggregates in the mixture. However, the
aggregation of CuPc can be strongly suppressed by introducing even a small amount of C\(_{60}\) (25
% by weight) into the mixture.\(^{58}\) Compared to CuPc, the pentacene molecules exhibit a stronger
tendency to aggregate which could be attributed to the strong intermolecular interaction between
pentacene molecules.\(^ {102}\) In addition, the energy barrier for pentacene molecules to rearrange and
form stacks in the mixtures is much lower than that of CuPc due their smaller size.

The aggregation of C\(_{60}\) molecules is difficult to characterize experimentally due to their
amorphous nature. However, the PDFs from MD simulation do show that the first nearest
neighbor distance of C\(_{60}\) in the mixtures reduces after relaxation, approaching the value in a FCC
C\(_{60}\) crystal. Such short range order (but no long range order) of C\(_{60}\) molecules in the mixture
could be viewed as indicative of aggregation to some extent.

Even though a certain level of phase separation in a D – A bulk heterojunction is
considered to be beneficial to enhancing PV performance, too strong phase separation could also
be problematic.\(^ {79,103}\) Strong phase separation, for instance, may produce pure domains with sizes
significantly larger than the exciton diffusion length. This will lead to lower exciton diffusion
efficiency with a large portion of excitons unable to reach the D – A interface and dissociate into
free charge carrier. In other cases, the phase separated large domains may contain a tiny amount
of the other molecular species because of the spinodal decomposition process, forming donor- or
acceptor rich domains. In this scenario, the exciton diffusion efficiency could be still be high
initially due to the presence of minority molecules with the domains, but the dissociated charge
carriers will be trapped on these isolated molecules, which prevents the further dissociation of
excitons at the D – A heterojunction.

Too strong phase separation in the mixed film will also lead to significantly increased
surface roughness, causing poor contact between the top electrode and organic layer as well as a
greater chance of electrode shorting between the electrodes. In the current pentacene:C_{60}
mixtures, the pentacene has such strong aggregation that crystalline pentacene domains with
sizes between 100 and 200 nm can be readily observed in the mixed films with pentacene
concentrations higher than 50 %. Moreover, ridgelike μm-long features can also be found in
pentacene:C_{60} (1:2) and (1:4) films due to the strong aggregation of pentacene. XRD pattern
without any characteristic diffraction peak suggests these ridgelike structures are amorphous.
Since the prevalence of ridgelike structures decreases with pentacene concentration, it is believed
that the ridges are composed of amorphous pentacene-rich clusters. Amorphous pentacene
clusters were previously found in neat pentacene films as well, where the pentacene molecules
are lying flat in the clusters instead standing on their edges as in the crystalline phases.\textsuperscript{93} \(R_{rms}\) of
50 nm pentacene:C_{60} (1:1) film reaches 56 nm with 300 nm peak to valley distance of the surface
features. Depositing 100 nm thick Al on such rough surface could still produce incomplete
coverage, causing poor contact and erratic \(J – V\) curves of the device. The CuPc:C_{60} films with
similar mixing ratio, however, show very smooth (\(R_{rms} < 1\) nm) and featureless surface under
SEM or AFM is observed.\textsuperscript{58} This again suggests stronger tendency of aggregation of pentacene
than CuPc. Because of the too strong phase separation in pentacene:C_{60} mixed, it is necessary to
suppress the phase separation to nanoscale in the mixture to obtain better PV performance. It has
been demonstrated in the above studies that higher C_{60} concentration could hinder the stacking of
pentacene, hence suppressing the phase separation. With more than 50 % $C_{60}$ in the mixture, the crystalline phase pentacene become almost nonexistent, while amorphous pentacene-rich domains could still exist in the mixture. In order to fully suppress the pentacene aggregation, $C_{60}$ concentration as high as 80 % is required. Another way to manipulate the degree of phase separation is through varying the deposition rate. Basically, the low deposition rate allows molecules to diffuse longer distance over the surface and reconfigure themselves into a lower energy state, which promotes the growth of a structure closer to a thermodynamically stable state. A high deposition rate, on the other hand, will hinder the diffusion or rearrangement of molecules on the surface, leading to weaker phase separation.

Therefore, strong suppression of phase separation in pentacene:$C_{60}$ mixed films is achieved with a 1:5.5 mixing ratio and high deposition rate. With such mixed film, the bulk heterojunction OPV device shows a PCE of 0.21 %, which is a 400-fold increase of efficiency compared to a pentacene:$C_{60}$ (1:1) device. Such significant improvement in PV performance is related to better morphology in the pentacene:$C_{60}$ (1:5.5) film. The 1:1 mixed film shows a rough surface with large domain (100 to 200 nm). The 1:5.5 film, in contrast, is much smoother and shows very rare large domains. All this indicates the successful suppression of phase separation in the 1:5.5 mixed film, whose morphology is more favorable for efficient exciton diffusion and charge collection.

Nevertheless, the PCE of the pentacene:$C_{60}$ (1:5.5) BHJ device is still low compared with a bilayer pentacene/$C_{60}$ device, which is between 1.1 and 1.6 %. This is due to the fact that only a small amount of pentacene molecules are allowed in the mixture (only ~ 15 % by weight) to successfully suppress the formation of large pentacene aggregates. As a result, the absorption of incident photons in the region of 500 to 700 nm will become very weak. Moreover, the low
pentacene concentration will also lead to poor hole transport across the film, which is reflected by the low fill factor in the OPV device (FF = 0.29).

Conclusions

In this chapter, the phase separation process in pentacene:C₆₀ molecular donor-acceptor mixtures is investigated using both computational and experimental methods. Also, results from simulation and different experimental characterization suggest that there is pentacene aggregation in the mixtures. The strong aggregation of pentacene molecules in the mixture results in an extremely rough surface and poor photovoltaic performance. Such observation is quite different from previous studies on CuPc:PTCBI and CuPc:C₆₀ mixtures, where the phase separation is very weak in the as-deposited films and the mixed films present smooth and featureless surfaces. Moreover, phase separation in CuPc:PTCBI mixtures is enhanced through thermal annealing. In the current pentacene:C₆₀ mixture, however, the phase separation can be controlled by tuning the pentacene to C₆₀ mixing ratio and the deposition rate. By adopting a 1:5.5 mixing ratio and high deposition rate, we can successful suppress the phase separation in the pentacene:C₆₀ mixed film and obtain a smooth surface. The efficiency of the device with an optimized level of phase separation is 400 times higher than that of a device based on a 1:1 mixed ratio, in which the scale of phase separated domains reaches ~100 nm. Further investigation of the relation between phase separation degree and other process parameters, such as substrate temperature, molecular properties, etc., is of great importance in engineering the nanoscale morphology of the bulk heterojunction for more efficient energy conversion.
CHAPTER 4
ORGANIC PHOTOVOLTAIC CELLS WITH ALIGNED CRYSTALLINE MOLECULAR NANORODS

Introduction

The research on organic photovoltaic (OPV) cells has made significant progress in the past two decades since the first report of organic bilayer donor-acceptor (D – A) heterojunction photovoltaic (PV) cells. However, the power conversion efficiency of OPV cells is still much lower compared with their inorganic counterpart. One of the limiting factors in achieving high efficiency OPV cells is the short exciton diffusion length in most organic materials, typically a few nanometers. Currently, bulk D-A heterojunction, which is achieved by well controlling phase separation in a D-A mixture, is widely used to circumvent the exciton diffusion bottleneck. However, the random interpenetrating D-A network obtained from phase separation could lead to poor charge transport due to charge trapping at the bottlenecks or cul-de-sacs along the conducting path. This could lead to low charge collection efficiency. Another drawback of relying on phase separated D-A bulk heterojunction (BHJ) for efficient exciton diffusion and charge collection is the lack of control over morphology inside BHJ. As what we learned in Chapter 3, the degree of phase separation in D-A mixture strongly depends on the strength of the interaction between the molecules as well as the processing conditions during the formation of BHJ. For instance, the aggregation of pentacene molecules in pentacene:C₆₀ BHJ is so strong that large domains (a few hundred nanometers) are formed, which results in low exciton diffusion efficiency. Moreover, the increased surface roughness induced by the strong aggregation also leads to poor contact between the electrode and the organic layer. On the other hand, very weak phase separation is observed in CuPc:C₆₀ BHJ, where highly intermixing between two species is observed. Although the exciton can all be dissociated in this case, the charge collection efficiency can be very low due to discontinued conducting paths. Therefore, the degree of phase
Figure 4-1. Schematic of ideal interdigitated bulk heterojunction, where the lateral dimension of the donor and acceptor phase is close to the exciton diffusion length. The presence of straight conducting path for both electrons and holes secure efficient charge collection.

Separation is mostly determined by the nature of the organic molecules, which puts a heavy burden on the synthesis of molecules with desired properties. Even though phase separation can be controlled through varying the processing conditions, the level of controllability is limited.

One way to overcome the above limitations in D-A mixed BHJ is to use a bulk heterojunction composed of nanoscale interdigitated D-A phase, which is indicated in Figure 4-1. Here, the lateral dimension of the interdigitated structure may be composed of pure phase donor or acceptor materials. Such structure can secure both efficient exciton diffusion and charge collection, if the lateral dimensions are small enough. Since the charge transport within a pure phase is improved compared with mixed BHJ, thicker films can be used to increase absorption.

Even though such interdigitated D-A BHJ is ideal for efficient OPV cells, fabrication of such nanostructure is challenging. The interdigitated BHJ is usually formed by infiltrating the second phase into the existing one-dimensional nanostructure template composed of another phase of material. Recently, extensive research has focused on growing one-dimensional organic or inorganic nanostructure, followed by infiltration of acceptor or donor phase into the
nanostructure to achieve OPV device.\textsuperscript{77,106-109} For instance, Yang et. al. use organic vapor phase deposition (OVPD) to grow copper phthalocyanine (CuPc) nanorods, which then infiltrate with PTCBI.\textsuperscript{77} The BHJ achieved using this method showed a nearly two-fold enhancement over the planar heterojunction device. Hsu, et. al. also showed growth of ZnO nanorod arrays through a hydrothermal approach, followed by loading P3HT into the ZnO nanorods to achieve a hybrid PV device.\textsuperscript{108}

However, the efficiency of devices using interdigitated BHJ is still relatively low compared with the best mixed BHJ devices. One reason for this is the lateral size of one-dimensional nanostructures is still too big for efficient exciton diffusion. Another reason may be poor infiltration of the second phase into the nanostructure so that excitons are not dissociated in the unfilled region. In this chapter, we demonstrate that one-dimensional nanorod arrays composed of CuPc can be easily fabricated on different substrates using oblique angle deposition. The process of CuPc nanorod growth is studied and the dependence of nanorod morphology under different deposition conditions is compared. By controlling the processing conditions, the [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) is successfully infiltrated into the nanorod arrays to achieve an interdigitated BHJ OPV cell. The optimized nanorod CuPc/PCBM device achieves a maximum power conversion efficiency (PCE) of $\eta_p = (1.8 \pm 1) \%$, which is approximately twice that of the bilayer CuPc/PCBM device.

The contents in this chapter are organized as follows: the first section introduces oblique angle deposition (OAD); the second section is the structure and morphology study of the OAD grown CuPc nanorod arrays under different condition, followed by CuPc nanorod/PCBM device study; the third section discusses the advantages and existing problems in the current approach.
and points out possible solution to further enhance device efficiency; the last section summarize
the conclusions.

**Oblique Angle Deposition**

Oblique angle deposition (OAD), which is also known as glancing angle deposition, has
been widely used to grow inorganic one-dimensional nanostructures with potential applications
in memory, photovoltaic, and sensor devices.\(^{110-114}\) Figure 4-2 illustrates the schematic of the
OAD process. Unlike conventional high vacuum deposition processes use the ballistic
molecular/atomic beams that arrive at the substrate surface from near-normal directions, an OAD
process, the molecular/atomic beams that arrive at the surface with a large angle, \(\alpha\), from the
substrate normal. Due to the shadowing effect by the deposited molecules and the limited
diffusion of absorbed molecule on the surface, nanorod arrays with various morphologies can be
obtained by controlling the incident angle of the molecular flux as well as the surface diffusivity
of the molecules. The formation of nanorod structure under OAD can be divided into two major
steps, which include (1) nucleation and initial growth and (2) nanorod growth and evolution
under ballistic shadowing effect.

![Figure 4-2. Schematic of oblique angle deposition](image)

- a) Nuclei distributed across the surface lead
to ballistic shadowing of the surrounding regions during oblique angle deposition.
The incident angle is \(\alpha\). b) Restricted growth on tops of the nuclei induces formation
of one-dimensional nanostructure. The nanorods will grow oriented toward the
source, forming an angle \(\beta\) with the substrate normal with \(\beta < \alpha\).
The nucleation and initial growth of thin film under OAD process is in fact similar to the deposition in normal direction, especially on planar and featureless surfaces. An absorbed molecule will diffuse around on the surface until it meets another molecule to form a nucleus, or attach to existing nuclei, or reevaporate from the surface. The nucleus become stable once it reaches the critical size; only after this point does nanorod growth occur. The critical size of the nucleus plays an important role in determining the nanorod morphology under OAD process and it depends strongly on the intrinsic characteristics of the molecule as well as the surface properties. Depending on the surface and interfacial energy between the substrate surface and absorbed molecules, three different modes for nucleation layer growth can be observed.\textsuperscript{115} When the interaction between the surface and the absorbed molecules is stronger than that between the molecules, two-dimensional growth of monolayer with only one molecule in height will occur. This is known as Frank-van de Merwe or layer growth. On the other hand, if the absorbed molecules have a stronger tendency to bind to each other than to the surface, separated three-dimensional nuclei will form. This is known as Volmer-Weber or island growth. The third type of growth mode falls in the regime between the previous two modes, where absorbed molecules initially cover the surface in a monolayer and then form islands formation on top of the monolayer. This growth mode is called Stranski-Krastanov or layer-plus-island growth. For organic molecules, layer-plus-island growth is observed in those with planar structure, such as sexithiophene, pentacene, etc.\textsuperscript{31,47,91} For practical OAD application, the Volmer-Weber growth mode is preferred due to formation of microscopic topologies which lead to ballistic shadowing.

Once a nucleation layer as shown in Figure 4-2a is formed, the nuclei distributed on the surface will lead to a ballistic shadowing effect of their peripheral area, promoting nanorod growth on top of the nuclei. Since the molecules only deposit on top of the nuclei, they will
develop into nanorods which are tilted toward the direction of the incoming flux. The nanorod tilt angle $\beta$ is less than the incident angle $\alpha$, and one simple empirical equation proposed to correlate $\alpha$ and $\beta$ is:\textsuperscript{110}

$$\tan \alpha = 2 \tan \beta$$

Although the ballistic shadowing effect promotes the growth of nanorod structure, there are other processes that may alter the morphology of the nanorod. One important consideration is the diffusion of the absorbed molecule on the surface of existing nanorod structure.\textsuperscript{116 117} The surface diffusion of molecules strongly depends on the substrate temperature and deposition rate. Low substrate temperature and fast deposition rate will reduce the surface diffusivity of an absorbed molecule; therefore these conditions will facilitate the nanorod growth along the elongated direction. In contrast, elevated substrate temperature and slow deposition allow the molecule diffuse longer distance over the surface so that a structure resembled that deposited at normal incident angle is obtained. As shown in Figure 4-2b, nanorod growth under OAD process is a competitive growth process, meaning that shorter nanorods will be shadowed by longer nanorods and cease growth. Such extinction is accompanied by an increase in the diameter of the surviving nanorods to maintain constant planar density. Therefore, thicker nanorod films will necessarily have thicker nanorods. In fact, there are different ways to control the nanorod morphology in OAD process. For instance, instead of using an intrinsic nucleation layer as seed for nanorod growth, a substrate with regular pre-patterned feature can be used to tailor the distribution of nanorods on the surface. Moreover, by rotating the substrate in a controlled fashion, diversified nanorod morphology can be achieved, which is shown in Figure 4-3. It can be seen that OAD is a versatile and convenient way to fabricate one-dimensional nanorod, and
such nanorod structure has potential to generate efficient interdigitated BHJ in OPV cell application.

Figure 4-3. Different nanorod structure achieved under OAD process. [Ref 110]

**Structure and Morphology Study of CuPc Nanorods**

From the previous Section, we know that in order to grow nanorod structure suitable for OPV cell application, a few criteria have to be met. First, nucleation layer grown with Volmer-Weber mode and nuclei with 10 to 20 nm size are preferred for forming seeds for nanorod growth. Second, the absorbed molecule should have limited surface diffusivity to promote one-dimension growth. Third, the nanorod arrays should have optimal packing density so that both good infiltration of the second phase and maximized D-A interface area can be secured. Finally, crystalline nanorod is desired for high charge mobility, hence efficient charge collection. In this section, we investigate the OAD growth of organic nanorod arrays composed of CuPc, which is a donor material widely used in small-molecular-weight based OPV devices. The morphologies of CuPc nanorods grown under different OAD conditions are compared to provide an insight on how to control the morphology to suit OPV applications.
Structure and Morphology Evolution of Nanorod Films

In order to study the growth of CuPc nanorods under OAD condition, we monitored the morphologies of the nanorod film at different stages of the growth. In this study, the CuPc nanorod films were deposited on glass substrates pre-coated with a layer of indium tin oxide (ITO) with sheet resistance of ~ 20 Ω/sq. The substrates were cleaned with de-ionized water, acetone, and isopropanol consecutively for 45 minutes before loading into a custom-made high vacuum deposition chamber with OAD setup (base pressure ~ 1 × 10^{-7} Torr). The molecular beam incident angle from the substrate normal was α ≈ 75° during the nanorod growth. The morphology of the nanorod film was investigated using a JOEL 6335F field-emission gun scanning electron microscope (SEM) and a Veeco Dimension 3100 atomic force microscope (AFM).

Figure 4-4 shows a series of SEM images indicating the surface morphologies for different stages of CuPc nanorod growth on ITO. As can be seen in Figure 4-4a, the bare ITO surface is almost featureless under SEM with vaguely seen large domains with size more than 100 nm. A scrutiny of the ITO surface using AFM reveals the existence of smaller domains on the larger domains (see inset of Figure 4-4a). The small domains have size ranging from a few nanometers to tens of nanometers, and the root mean square roughness ($R_{rms}$) considering both type of features is only $R_{rms} = 2.0$ nm. Figure 4-4b shows that after deposition of a thin layer of CuPc under OAD condition, CuPc domains with sizes from 10 to 30 nm can be observed, which is similar to planar film deposited at normal incident. Such observation is consistent with the layer-plus-island film growth mode observed in a variety of organic films deposited by vacuum thermal evaporation (VTE).\textsuperscript{25,46} The lattice mismatch between the polycrystalline ITO and the
Figure 4-4. Scanning electron microscope (SEM) images of approximately 150 nm thick CuPc nanorod film at different stages of growth. (a) Bare indium tin oxide (ITO) surface. Inset: atomic force microscope (AFM) image of same substrate. (b) – (e) Nanorod films at different stage of the growth. The scale bars are 100 nm in all images.

CuPc crystals puts strains in the continuous organic layer, resulting in island formation. With continued oblique angle deposition upon such structure, the CuPc domains develop into protrusions with maximum diameter of ~ 50 nm (see Figure 4-4c), indicating the onset of shadowing effect from CuPc domains. The increased diameter during the transition from Figure 4-4b to Figure 4-4c is due to the diffusion of molecules deposited on top of the domains, promoting three-dimensional growth rather than two-dimensional. Moreover, such increased CuPc domain size suggests the surface diffusivity of molecules on the existing CuPc surface is higher than that on the ITO surface. As shown in Figure 4-4d and e, further deposition leads to even rougher surface and short tilted nanorods 50 nm in length can be observed, indicating an
enhanced ballistic shadowing effect. One-dimensional growth under OAD finally results in the morphologies shown in Figure 4-4f, where elongated nanorods with more than 100 nm in length and 20 to 50 nm in diameter can be observed. Note that existence of smaller and shorter nanorods versus larger and longer nanorods confirms the competitive growth characteristic of the OAD process, where the survived nanorods become larger and longer to compensate the extinction of smaller nanorods falling in their shadows. The growth of CuPc nanorod arrays on ITO substrates was accompanied by the significantly increase of surface roughness, which increased from a few nanometers in bare ITO to tens of nanometers in the final nanorod film.

Effect of Incident Angle

Based on the previous explanation of morphology evolution during the growth of CuPc nanorods, we conducted another study regarding the morphology dependence on the incident angle, \( \alpha \). Here we compared the morphology of CuPc nanorod arrays deposited at \( \alpha \approx 45^\circ, 55^\circ, 65^\circ \) and \( 80^\circ \). In order to make meaningful comparison between different nanorod films, the nominal thickness of the film was fixed to be 100 nm for all four samples.

Figure 4-5 shows the SEM images of 100 nm CuPc nanorod films fabricated with four different incident angles. It can be observed in Figure 4-5a that the bumps rather than nanorods are formed with \( \alpha = 45^\circ \). The diameter of CuPc bumps ranges from 20 to 50 nm, and no observable gap existed in between the bumps due to the weak shadowing effect at this incident angle. The film shows a roughness of \( R_{\text{rms}} = 9.5 \) nm obtained from AFM, which is not much greater than reported roughness of planar CuPc films (\( R_{\text{rms}} = 4.8 \) nm).

As the incident angle increased to \( \alpha = 55^\circ \), both bumps and short nanorods with similar diameter can be seen on the surface (see Figure 4-5b). Also, visible gaps can be observed across the film, indicating the presence of more prominent shadowing effect. Such a corrugated surface leads to a significant
Figure 4-5. Scanning electron microscope (SEM) and atomic force microscope (AFM) images of 100 nm thick CuPc nanorod film fabricated with different incident angle of $\alpha = 45^\circ$ [(a) and (b)], $55^\circ$ [(c) and (d)], $65^\circ$ [(e) and (f)] and $80^\circ$ [(g) and (h)]. The scale bar is 100 nm for all SEM images. The scanning area of the AFM images is $2\times2\mu m^2$, and the height is 300 nm.
increase of the roughness to $R_{rms} = 14$ nm, which is twice than that of the 45° film. Further increase of incident angle to $\alpha = 65^\circ$ results in complete disappearance of bumps and a larger prominence of nanorods, as shown in Figure 4-5c. Nanorods with less than 100 nm in length and 20 to 50 nm in diameter can be seen. Larger gaps are observed in 65° film compared with 55° one, with maximum gap size of ~ 60 nm. All these contribute to a continued increase of roughness to $R_{rms} = 17$ nm. Finally, CuPc nanorod arrays with nearly 200 nm long and 20 to 50 nm wide nanorods are observed when $\alpha = 80^\circ$ (see Figure 4-5d). It can be seen that all nanorods are tilted toward the direction of incoming flux, and the maximum separation distance between the nanorod is as high as 100 nm. These are evidence of a strong shadowing effect as $\alpha$ goes to 80°. The 80° film shows a roughness of $R_{rms} = 73$ nm, which is the highest among the four angles. Note that such high $R_{rms}$ values obtained through AFM may underestimate the actual $R_{rms}$ due to detection limit of AFM technique for such fine nanorod arrays; nevertheless, it yields a semiquantitative comparison between different nanorod films. It is also worth noticing that since the four nanorod films have the same nominal thickness, increased porosity from 45° to 80° films suggest lower optical density in the high angle sample.

**Effect of Substrate Rotation**

In this study, we studied the effect of substrate rotation on the morphology of CuPc nanorod arrays. Compared with OAD with stationary substrate, the rotational substrate allows the top of the nanorod to receive the oblique angle molecular flux from all directions. Therefore, instead of creating a shadowing effect along one direction in stationary substrate mode, the shadowing effect can be created in all orientations. Here, CuPc nanorods are grown on top of ITO substrate with the substrate either stationary or rotated at a speed of $\omega = 5$ rpm. The incident angle is $\alpha = 75^\circ$ for both growth modes.
Figure 4-6. Topographic [(a) and (b)] and cross-sectional [(c) and (d)] scanning electron microscope (SEM) images of CuPc nanorods grown on a stationary [(a) and (c)] or rotational [(b) and (d)] substrate with speed of ~ 5 rpm. The scale bar is 100 nm for all four images.

Figure 4-6a and b show the topographic SEM images of CuPc nanorod arrays grown with a stationary or rotational substrate, respectively, whereas Figure 4-6c and d are the corresponding cross-sectional images. As we have learned in the previous two parts, the stationary substrate mode generates slanted nanorods with 20 – 50 nm in diameter, tilting towards the direction of the incoming molecular flux (see Figure 4-6a and c). On the other hand, the CuPc nanorods grown with rotational substrates have larger diameters, typically 40 to 70 nm but in some cases up to 100 nm (see Figure 4-6b and d). Moreover, the nanorods are mostly in the up-right orientation instead of tilting in the rotational substrate mode, which is due to the constantly changing flux
direction. Closer observation of the up-right nanorod reveals that the larger nanorods are in fact composed of several smaller nanorods with diameter around 20 nm clumping together. This is consistent with the proposed morphology evolution model of OAD growth on rotational substrate. Another significant difference between the two growth methods is the packing density of nanorods. It can be seen from the cross-sectional SEM images that the nanorods are close packing with gap size of around 30 nm with stationary substrate, whereas the nanorods are further separated and gaps as large as 100 nm can be observed using rotational substrate mode.

**Effect of Surface Property and Deposition Rate**

Two steps that significantly influence the nanorod morphology include the formation of nucleation layer and nanorod formation on the existing nucleation layer, both of which strongly depend on the surface diffusivity of absorbed molecules. It is known that the surface diffusivity are mainly affected be the surface properties, substrate temperature and deposition rate. Therefore, the effects of different surface properties and deposition rates on the morphology of CuPc nanorod are investigated in this part.

Figure 4-7a and b show the SEM images of CuPc nanorod arrays grown on top of stationary Si and SiO2 substrate with α = 75°. Surprisingly, both nanorod films display very similar morphology with 20 – 50 nm in diameter and around 100 nm in length, seemingly not affected by different substrate properties. To better understand why such a phenomenon is present, the morphologies of thin CuPc films deposited on Si and SiO2 substrates under the same OAD condition are compared. As shown in Figure 4-7c and d, the SEM images indicate that the CuPc film grown on SiO2 show larger average grain size than that grown on Si. The grain size ranging from 40 to 100 nm can be observed in film deposited on SiO2 substrate, whereas the film on Si substrate shows grain size of 10 – 50 nm. This suggests there are different wetting conditions for CuPc on hydrophobic (Si) and hydrophilic (SiO2) substrates, which has been
observed in many vacuum deposited organic films.\textsuperscript{118,119} However, such difference becomes hard to distinguish after nanorod arrays are fully developed. This can be explained by different surface diffusivity of CuPc on Si and SiO\textsubscript{2}, which leads to different nucleation morphology. However, as the nanorod start forming, molecules will only deposit on the top of CuPc nanorod, where the surface diffusivity are identical, ignoring the different substrate properties. Therefore, the size of nanorod becomes solely dependent on the surface diffusion distance of CuPc on their own domains. Since the temperature and deposition rate are the same for OAD on Si and SiO\textsubscript{2} substrate, the identical CuPc surface diffusion distance leads to similar nanorod size.

Based on the above study, it is more practical to control the CuPc nanorod morphology through manipulating the surface diffusivity of the molecule. It is known that fast deposition rate will result in short surface diffusion length because the absorbed molecule has less time to
rearrange their position before being buried by the incoming molecules. Here, we compare the effect of deposition rate on the nanorod morphology, where nanorod films deposited at ~ 0.5 Å/s and at ~ 10 Å/s are fabricated on ITO substrate with α = 75°. Figure 4-8a and b show the SEM images of CuPc nanorod films deposited at two different rates but with the same target thickness (determined by quartz crystal monitor). It can be seen that the shorter nanorod with lower packing density is observed in films deposited at ~ 0.5 Å/s, whereas dense nanorod arrays with longer nanorod is obtained using deposition rate of ~ 10 Å/s. Nevertheless, the diameters of nanorods obtained under two conditions are very similar, ranging from 20 to 50 nm. Such observation is consistent with the proposed morphology evolution under OAD condition, where a longer surface diffusion distance promotes the growth of morphology close to that deposited at normal incidence. In the current study, this is indicated by the shorter and sparse CuPc nanorod using a low deposition rate. In some extreme cases, the surface diffusivity of the molecule is so strong that no nanorod structure is formed under OAD process.
Structure of CuPc Nanorods

So far, only the morphologies of CuPc nanorods grown under different OAD conditions have been investigated. However, the application of such nanorod fabrication on efficient interdigitated BHJ OPV cells also requires good charge transport across these nanorods. Here, x-ray diffraction (XRD) patterns of the CuPc nanorod and planar films were investigated using a Philips X’pert MRD diffractometer in the θ-2θ geometry with a Cu Kα radiation source. The XRD pattern of a CuPc nanorod film grown with a rotational substrate is shown in Figure 4-9 along with that for a CuPc flat film deposited at normal incidence. The XRD patterns are very similar, showing diffraction peaks at 2θ = 6.9°, which suggest the existence of polycrystalline α-CuPc phase in the nanorods as well as in the flat film. The polycrystalline structure of CuPc nanorods is important to ensure high mobility for hole transport through the donor material, leading to high collection efficiency for photogenerated holes in the PV devices.

Figure 4-9. X-ray diffraction (XRD) pattern of a CuPc nanorod film with 300 nm long nanorods (blue) and a 100 nm thick flat CuPc film (red).
Organic Photovoltaic Cells Based on CuPc Nanorods and PCBM

With the obtained CuPc nanorod arrays from OAD process, an interdigitated bulk heterojunction can be achieved by infiltrating the acceptor materials into the nanorod arrays. CuPc and C₆₀ have been demonstrated to be one of the most efficient small-molecule-based D–A heterojunction for OPV application, and a maximum PCE of 4.2 % have been achieved by Xue et. al. Nevertheless, infiltrating of C₆₀ into the current CuPc nanorod arrays through vacuum thermal evaporation method is problematic due to the ballistic transport of molecules in high vacuum. Therefore, solution processing with PCBM, which is soluble fullerene derivative, was selected to achieve better infiltration into the nanorod film. Here, performance of OPV cells based on the resulting CuPc/PCBM interdigitated BHJ is investigated.

Infiltration of PCBM into Nanorod Arrays

Before preparing OPV devices based on CuPc nanorod/PCBM BHJ, it is first important to ensure good infiltration of PCBM into the nanorod arrays. Here, the interdigitated BHJ was achieved by spin-coating a chlorobenzene solution of PCBM onto the nanorod arrays. Figure 4-10a and b show two cross-sectional SEM images of CuPc nanorods/PCBM composite films with PCBM concentration of (a) 15 mg/mL and (b) 30 mg/mL in the chlorobenzene solution. The scale bar is 100 nm.
with different PCBM loading. The length of the CuPc nanorods grown with a stationary substrate and $\alpha = 75^\circ$ was approximately 100 nm in both cases. No obvious voids or pin-holes are observed in either film, indicating good infiltration of PCBM into the spacing between CuPc nanorods. With a high PCBM loading (30 mg/mL in chlorobenzene), the gap between CuPc nanorods is completely filled, resulting in a relatively smooth top surface (see Figure 4-10b). However, when a much lower PCBM loading (15 mg/mL in solution) was used, the amount of PCBM molecules deposited was not sufficient to completely fill the spacing between the CuPc nanorods, leading to a corrugated and rough surface as shown in Figure 4-10a. This also suggests that the CuPc nanorods still stand on the substrate and the spin-coating process does not damage the contact of the nanorods with the underlying ITO electrode, which is important for hole collection in PV devices. Figure 4-11 also shows the absorption spectra of a CuPc nanorod film before and after spin-coating of PCBM on top. The increased absorption below wavelength of $\lambda = 500$ nm in CuPc nanorod/PCBM composite film compared with neat CuPc nanorod film indicates reasonable amount of PCBM is loaded into the spacing between the nanorods.

Figure 4-11. Absorption spectra of CuPc nanorod film before (red dash line) and after (blue solid line) infiltration of PCBM.
Optimization of Cupc Nanorods/PCBM Cell

To fabricate CuPc nanorods/PCBM PV devices, CuPc nanorod films with 40-60 nm long nanorods were grown on ITO substrate with α = 75°, and a PCBM solution with 22 mg/mL concentration was spin-coated onto the nanorod films at 1000 rpm. The CuPc/PCBM composite films were then annealed at 90 °C for 15 min to remove solvent residual before the deposition of an 8 nm thick bathocuproine (BCP) exciton-blocking layer\(^\text{122}\) and a 100 nm thick aluminum cathode in high vacuum.

Figure 4-12 shows the current density-voltage \((J – V)\) characteristics under simulated 1 sun AM 1.5 illumination for CuPc nanorods/PCBM devices based on 60 nm long nanorods grown with a stationary or rotational substrate (labeled as “NR-S” and “NR-R”, respectively). The structure of these nanorod-based devices is shown in the inset of Figure 4-12. Shown for

![Diagram of Copper phthalocyanine (CuPc) nanorod solar cell structure.](image)

Figure 4-12. Current density – voltage \((J – V)\) characteristics of three CuPc/PCBM photovoltaic cells under 1 sun AM 1.5 illumination: a bilayer cell (labeled as “Planar”) with a 30 nm thick flat CuPc film, two devices with CuPc nanorods grown on ITO with a stationary (“NR-S”) or rotational (“NR-R”) substrate. The inset schematically illustrates NR-R device structure.
comparison are the $J - V$ characteristics of a bilayer, planar heterojunction CuPc/PCBM device (labeled as “Planar”) with a 30 nm thick flat CuPc film and a PCBM layer deposited under the same condition as the nanorod-based devices. The short-circuit current density reaches $J_{SC} = (4.4 \pm 0.2)$ mA/cm$^2$ for both NR-S and NR-R devices, which is higher than that of the planar heterojunction device, $J_{SC} = (3.4 \pm 0.2)$ mA/cm$^2$. On the other hand, all three devices show the same open-circuit voltage of $V_{OC} = 0.57$ V, which is close to the previously reported value based on the same D – A materials system.$^{123,124}$ The fill factor (FF) of the NR-S device is, however, much lower than that of the NR-R device, 0.40 vs. 0.55. This could be attributed to the differences in the morphology of nanorod arrays. The tilted nanorods obtained using stationary substrate mode may present more difficulties for the complete infiltration with PCBM molecules than the mostly up-right nanorods grown with a rotational substrate as well as a less direct path for charge transport to respective electrodes. Nevertheless, the power conversion efficiency reaches PCE = (0.95 ± 0.05) % in the NR-S device and (1.4 ± 0.1) % in the NR-R device, both of which are higher than PCE = (0.85 ± 0.05) % in the bilayer CuPc/PCBM device.

**Planar Plus Nanorods Cupc/PCBM Cell**

To further improve the efficiency of the nanorod-based devices, a planar CuPc layer can be inserted between the nanorods and the ITO to further enhance the hole transport across the film and also provide additional absorption of the incident photons. Similar structure composed of planar-mixed heterojunction was also applied in the CuPc/C$_{60}$ PV cell by Xue *et. al.*, and enhanced power conversion efficiency is observed.$^{45}$

Figure 4-13a shows the $J - V$ characteristics under simulated 1 sun AM 1.5 illumination for three NR-R devices with 8 nm planar CuPc inserted between nanorod and ITO (labeled as “Planar-NR”). It can be seen that by varying the nanorod height from 40 to 80 nm, $J_{SC}$
Figure 4-13. Current density – voltage ($J - V$) characteristics of three planar plus nanorod CuPc/PCBM photovoltaic cells (label as “Planar-NR”) under 1 sun AM 1.5 illumination: (a) 8 nm thick planar layer plus 40, 60 and 80 nm height nanorod, (b) 5, 10, 20 nm thick planar plus 40 nm height nanorod. Inset: Schematic of Planar-NR device structure.

decreases from (5.0 ± 0.2) mA/cm$^2$ for the 40 nm long planar-NR device to (4.3 ± 0.2) mA/cm$^2$ for the 80 nm long planar-NR device. With similar $V_{OC}$ for the three devices, maximum $\eta_p = (1.7 \pm 0.1\%)$ is achieved in the 40 nm long planar-NR device. This observation suggests that the
additional planar layer can help improve the device efficiency and PCBM infiltration is better with 40 nm long nanorods. Further optimization of the planar-NR device involved varying the planar CuPc layer thickness with fixed 40 nm long nanorods on top. The $J - V$ characteristics of planar-NR devices with 5, 10 and 20 nm planar CuPc under simulated 1 sun AM 1.5 illumination are shown in Figure 4-13b. The three devices exhibit similar $V_{OC} = 0.6$ V, whereas the $J_{SC}$ increases with increased planar layer thickness, exhibiting $J_{SC} = (4.7 \pm 0.2)$ mA/cm$^2$ with 5 nm thick planar layer and $J_{SC} = (5.6 \pm 0.2)$ mA/cm$^2$ with a 20 nm thick layer. With a high FF of 0.53, power conversion efficiency of PCE = (1.8 ± 0.1) % is achieved in the planar-NR device using a combination of 20 nm thick planar layer and 40 nm long CuPc nanorods as donor layer.

Figure 4-14 shows the PV parameters of planar-NR device as a function of incident irradiance ($P_{in}$) along with those of NR-S, NR-R and planar heterojunction devices. It is found that all four devices have almost constant responsivity ($J_{SC}/P_{in}$) over the entire illumination range though the value drop slightly higher intensities region (> 40 mW/cm$^2$), indicating linear

![Figure 4-14. Photovoltaic performance versus incident irradiance ($P_{in}$) of Planar-NR, NR-R, NR-S and Planar device. PCE: power conversion efficiency, FF: fill factor, $J_{SC}/P_{in}$: responsivity and $V_{OC}$: open circuit voltage.](image-url)
dependence of $J_{SC}$ on $P_{in}$. The two nanorod devices show the same level of responsivity, which is higher than that of the planar heterojunction device but lower than that of the planar-NR device. The $V_{OC}$ increases logarithmically with $P_{in}$ for all devices, which follows the trend of conventional p-n junction solar cells. All four devices show lower FF at higher intensity (> 20 mW/cm²) and the low FF for NR-S device is due to poor hole transport. The maximum PCE = (1.80 ± 0.1) % is achieved at 1 sun intensity of the planar-NR device, which is approximately a two-fold enhancement compared with the planar heterojunction device, PCE = (0.85 ± 0.05) %.

Table 4-1 compares some photovoltaic parameters of the Planar, NR-S, NR-R and Planar-NR device under 1 sun illumination.

Table 4-1. Comparison of the open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), fill factor (FF), and power conversion efficiency (PCE) of Planar, NR-S, NR-R and Planar-NR devices under 1 sun illumination.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>0.57</td>
<td>3.4 ± 0.2</td>
<td>0.47</td>
<td>0.85 ± 0.05</td>
</tr>
<tr>
<td>NR-S</td>
<td>0.57</td>
<td>4.4 ± 0.2</td>
<td>0.40</td>
<td>0.95 ± 0.05</td>
</tr>
<tr>
<td>NR-R</td>
<td>0.57</td>
<td>4.4 ± 0.2</td>
<td>0.55</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>Planar-NR</td>
<td>0.60</td>
<td>5.6 ± 0.3</td>
<td>0.53</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>

**Discussion**

In this work, CuPc nanorods with 20 – 50 nm in diameter are successfully grown on top of different substrates using the oblique angle deposition method. In order to promote the growth of one-dimensional nanorods under OAD condition, it is important to maintain a large incident angle. It can be seen from Figure 4-5 that as the incident angle becomes smaller the trend of one-dimensional growth becomes less prominent, leading to shorter nanorods and reduced surface
roughness. However, a large incident angle will increase the spacing between the nanorods due to a stronger shadowing effect. For application of CuPc nanorod arrays in OPV devices, it is desired that not only the diameter of the nanorod is comparable to the exciton diffusion length of CuPc, but also that the spacing between the nanorods is close to the exciton diffusion length of PCBM. Therefore, nanorod arrays with appropriate spacing can be achieved by tuning the incident angle of molecular flux.

In the current study, the diameter of the CuPc nanorods achieved using stationary substrate mode is 20 – 50 nm, while it reaches 40 – 70 nm using rotational substrate mode. Therefore, the nanorod diameter obtained here is still too large to generate efficient exciton diffusion. To further reduce the nanorod diameter, it is crucial to limit the surface diffusivity of the absorbed molecules. As indicated in the nanorod morphology evolution study, the onset of two-dimensional growth is accompanied by initial three-dimensional growth of the existing nuclei due to the diffusion of absorbed molecules from the top of the nuclei to the bottom (see Figure 4-4b and c). Since the diameter of the nanorod grown afterward is determined by the size of the pre-formed nuclei, it is essential to reduce or prevent the initial three-dimensional growth of existing nuclei by limiting the surface diffusivity of molecules. Here, deposition rate as high as ~10 Å/s was used to suppress the molecule surface diffusivity. Although denser nanorod arrays with increased nanorod length was obtained using high deposition rate (see Figure 4-8), there was no significant change in the nanorod diameter. This suggests increasing deposition rate alone may not be sufficiently suppress the molecular surface diffusivity, and lower substrate temperature may be desired as an alternative. Comparison between the performance of NR-S and NR-R OPV devices suggest that infiltration of PCBM is vital to achieve high efficiency in interdigitated BHJ. The up-right orientation of CuPc nanorods in NR-R device results in better
PCBM infiltration, therefore, higher fill factor and power conversion efficiency can be obtained. Even though larger nanorod (40 – 70 nm) is present in the NR-R device, the better PCBM infiltration leads to better performance than the NR-S device, where smaller but tilted nanorods are used.

Based on this investigation, it is believed that further enhancement in the CuPc nanorod/PCBM OPV cell efficiency requires smaller up-right oriented CuPc nanorods. This can be achieved by using OAD with rotational substrate mode, while at the same time keeping the substrate at low temperature to limit the surface diffusivity of molecule. Additionally, planar CuPc and PCBM layers can be used to sandwich the interdigitated BHJ layer to further improve device efficiency.

Conclusions

In conclusion, we have demonstrated that aligned polycrystalline CuPc nanorods with diameters as small as 20 nm can be grown using the oblique angle deposition method. While the growth on a stationary substrate leads to slanted nanorods, growing on a rotational substrate yields mostly up-right, though somewhat larger nanorods. An interdigitated bulk heterojunction structure was realized by infiltrating the CuPc nanorod array with solution processed PCBM molecules. A maximum power conversion efficiency of $\eta_p = (1.8 \pm 0.1)\%$ at 1 sun AM1.5 illumination was achieved in such nanorod based device, approximately twice of that of a bilayer CuPc/PCBM device.
CHAPTER 5

EFFICIENT DEEP-BLUE PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES

Introduction

Research on organic light-emitting diodes (OLEDs) has gained significant advancement over the last two decades since the first heterojunction OLED report by C. W. Tang.\textsuperscript{2} Today, OLEDs have found their way into the flat-panel display (FPD) and lighting applications. However, one of the remaining challenges for OLEDs in widely commercial application is the efficiency and stability of blue-emitting OLEDs.\textsuperscript{125-128} Phosphorescent OLEDs, which utilize triplet excitons to emit light, have been widely studied to enhance the OLED efficiency.\textsuperscript{5} And PHOLEDs with nearly 100\% internal quantum efficiency have been demonstrated in green-emitting device.\textsuperscript{129,130} For blue PHOLEDs, metal-organic complexes of iridium (III) bis[(4,6-difluorophenyl)-pyridinoto-N,C\textsuperscript{2}]picolinate (FIrpic) and iridium (III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6) are two blue phosphorescent emitters that widely employed.\textsuperscript{131-134} The FIrpic-based device exhibits an emission spectrum with two vibronic peaks at 475 and 500 nm and Commission Interntionale de L’Eclairage (CIE) coordinates of approximately (0.17, 0.34).\textsuperscript{134,135} Due to the greenish-blue color, FIrpic-based device is not an ideal blue source for display and lighting application. FIr6-based device, however, exhibits deeper blue color emission than FIrpic-based device with two major vibronic peaks at 458 and 489 nm and CIE coordinates of (0.16, 0.26).\textsuperscript{132,136}

FIr6 has a higher triplet energy ($T_1$) of 2.72 eV, than that of FIrpic ($T_1 = 2.65$ eV), which in turn produce deeper blue color.\textsuperscript{131,136} Therefore, a host material with an even higher triplet energy is needed in order to effectively confine the exciton to the phosphorescent emitter. In a previous work, Holmes et al. showed that direct charge trapping by the FIr6 could be an effective way to improve the device efficiency, which avoids the energy loss during host-guest exothermic
energy transfer commonly found in FIrpic-based device. In their work, a wide bandgap host layer of $p$-bis(triphenylsilyly)benzene (UGH2) doped with FIr6 was employed as the emissive layer (EML). In addition, a 15 nm thick layer of N,N'-dicarbazolyl-3,5-benzene (mCP) is inserted between the hole transport layer (HTL) of bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPD) and EML as the exciton blocking layer (XBL) to confine the exciton as well as to facilitate the hole injection into the EML. On the cathode side, a layer of bathocuporine (BCP) is used as electron transport layer (ETL) and hole blocking layer (HBL). The device achieved a maximum external quantum efficiency (EQE) of $\eta_{\text{EQE}} = 12 \%$ and power efficiency of $\eta_p = 14 \text{ lm/W}$.

To further enhance the efficiency of FIr6-based PHOLEDs, there are still a number of issues to be addressed. In the current FIr6-based device, a 25 nm thick EML is needed to achieve efficient charge trapping for exciton generation, whereas another 15 nm XBL is required to effectively blocking the exciton. It is known that the UGH2 and mCP have relatively low charge carrier mobility and such thick layers will inevitably increase the overall driving voltage and reduce the power efficiency of the device, which is an important factor in determining the practical application of OLEDs.

In this chapter, we focus on improving the performance of the FIr6 PHOLED based on the existing structure, where new materials and device architectures are explored. In the first section, the effect of several new electron and hole blocking materials on improving the device efficiency are compared. A direct proof of efficient electron blocking is shown by comparing the emission spectra of two controlled devices. The second section introduces two major ways to lower the overall driving voltage of the blue PHOLED, which includes optimization of the active layer thickness and using $p$-$n$-doped charge injection layer to achieve $p$-$i$-$n$ structure. The third section
is a discussion of the results in this chapter and how to further improve the blue OLED performance. Finally, the conclusions will be given in the last section.

**Charge Carrier and Exciton Blocking in Phosphorescent OLED**

As shown in the energy level diagram of the FIr6 device (Figure 5-1), the electrons are injected from the LiF/Al anode into the lowest unoccupied molecular orbital (LUMO) of BCP, followed by injection into the FIr6 LUMO. Similarly, the holes are injected into highest occupied molecular orbital (HOMO) of FIr6 through NPD and mCP layer. The electrons and holes, which are trapped by the FIr6 phosphorescent molecules, will recombine to emit photons. Nevertheless, it is found that part of the electrons injected into the EML can overcome the energy barrier at mCP/EML interface and are injected into the NPD layer when mCP layer is thinner than 15 nm. This suggests that the 0.4 eV barrier at the mCP/EML interface cannot efficiently confine the electron with the EML. On the other hand, the triplet exciton formed in the EML will diffuse to the BCP layer due to slightly lower triplet energy of BCP ($T_1 = 2.5$ eV)\(^{138}\) than FIr6. Such an exciton loss mechanism can also happen between FIr6 and NPD ($T_1 = 2.29$ eV)\(^{139}\) when the mCP layer thickness is lower than the exciton diffusion length.

**Effect of Electron and Exciton Blocking Layer**

Here, we investigate the charge carrier and exciton blocking effect of a new hole transport material 1,1-bis[(di-4-tolyamino)phenyl]cyclohexane (TAPC). It is found that a device using TAPC as the ETL shows significantly enhanced performance over the NPD-based device, which could be due to higher triplet energy ($T_1 = 2.87$ eV) yet comparable electron mobility of TAPC compared with NPD.\(^{140-142}\)

Figure 5-1 shows the molecular structure of active materials involved in the current FIr6-based device as well as their energy level diagram and triplet energy. The blue PHOLEDs were fabricated on glass substrates commercially precoated with a layer a layer of indium tin oxide.
Figure 5-1. Schematic energy level diagram of the deep-blue phosphorescent organic light-emitting diodes (PHOLEDs) and molecular structure of the materials involved in the devices.

(ITO) with a sheet resistance of ~20 Ω/sq. The substrates were cleaned with deionized water, acetone, and isopropanol consecutively for 45 min, and then treated in ultraviolet ozone for 15min immediately before loading into a high vacuum deposition chamber (background pressure ~3 × 10^{-7} Torr). Deposition of all materials, including the Al cathode, was conducted in succession without breaking the vacuum. First, devices using NPD and TAPC as HTL were compared. The 40 nm thick HTL consists of TAPC or NPD, followed by 15 nm mCP. The 25 nm EML consisted of FIr6 doped into UGH2 with 10 wt % concentration. 40 nm thick BCP was deposited as the electron transport and hole blocking layer. TAPC, mCP, UGH2 and FIr6 were purchased from Luminescence Technology Corp., BCP from TCI America, and NPD from e-Ray. All organic materials were used as obtained without further purification. The cathode consisting of 0.5 nm thick layer of LiF followed by a 50 nm thick Al was deposited through an
Figure 5-2. Electroluminescence (EL) spectra of two PHOLEDs with the structures of ITO/NPD or TAPC (40 nm)/mCP (15 nm)/UGH2:10 wt % FIr6 (25 nm)/BCP (40 nm)/LiF (1 nm) /Al \textit{in situ} shadow mask, forming a 4 mm\textsuperscript{2} active device area. Current-density-luminance-voltage ($J - L - V$) characteristics were measured using an Agilent 4155C semiconductor parameter analyzer with a calibrated Newport silicon diode. The electroluminescence (EL) spectrum and CIE coordinates of the device were collected through a high sensitivity Ocean Optics spectrometer. The luminance was calibrated using a Minolta luminance meter (LS-100). The external quantum efficiency ($\eta_{EQE}$) was determined by assuming Lambertian emission and following the reported method.\textsuperscript{60}

The EL spectra of the NPD- and TAPC-based devices at $J = 3$ mA/cm\textsuperscript{2} are shown in Figure 5-2. The two devices show very close CIE coordinates, (0.16, 0.28) for the NPD device and (0.16, 0.27) for the TAPC device. However, there is a smaller shoulder peak appeared in EL spectrum at wavelength $\lambda = 435$ nm for NPD device, which becomes more apparent as the mCP
Figure 5-3. Performance of PHOLEDs with either NPD or TAPC as hole transport layer (HTL). (a) Current density-voltage ($J-V$, closed symbols) and luminance-voltage ($L-V$, open symbols) characteristics and (b) Luminance power ($\eta_P$, closed symbols) and external quantum ($\eta_{EQE}$, open symbols) efficiencies as a function of current density. 

The layer becomes thinner than 15 nm. This has been attributed to the emission from NPD when a portion of electrons overcome the barrier at the mCP/EML interface and enter into NPD, where they recombine with holes injected from the ITO and form excitons. However, no TAPC emission ($\lambda = 435$ nm) is observed even at the highest driving voltage or with a much thinner
mCP layer. Figure 5-3a compares the $J$-$L$-$V$ characteristics of the NPD- and TAPC-based
devices. It can be seen that the TAPC-based device shows a slightly lower current density at $V > 5$ V, but the difference in the L-V characteristics is small. The current-density dependencies of
the external quantum and power efficiencies of these two devices are shown in Figure 5-3b. A
peak external quantum efficiency of $\eta_{\text{EQE}} = (12 \pm 1) \%$ and a peak power efficiency of $\eta_P = (14 \pm 1) \text{ lm/W}$ are obtained in the NPD device, which are very similar to the previous report values. For the TAPC device, on the other hand, $\eta_{\text{EQE}}$ reaches a maximum of $(18 \pm 1) \%$. The peak power efficiency of $\eta_P = (16 \pm 1) \text{ lm/W}$, which is nearly 15 % higher than the maximum of the
NPD-based device, is achieved at a luminance of $L = 4 \text{ cd/m}^2$. Moreover, the TAPC device shows a $\eta_P = (13 \pm 1) \text{ lm/W}$ at $L=100 \text{ cd/m}^2$ and $\eta_P = (8.9 \pm 0.6) \text{ lm/W}$ at $L=800 \text{ cd/m}^2$,
approximately 60% higher than the NPD device at these two luminances (7.9 and 5.6 lm/W, respectively).

We believe the significant improvement in the TAPC device is due to better electron and
exciton blocking provided by the TAPC. The electron affinity of TAPC is 0.4 eV smaller than
that of mCP (2.0 eV vs 2.4 eV), i.e., the LUMO level of TAPC is 0.4 eV higher than that of
mCP.\textsuperscript{132,140} Hence, a TAPC layer should provide an additional barrier height for preventing
electrons injected from cathode, which is not available in NPD. Moreover, the higher triplet
energy of TAPC should also enable us to reduce the mCP layer thickness without compromising
the exciton confinement in the EML. Figure 5-4 shows the performance of TAPC-based devices
with the mCP layer thickness varied from 0 to 15 nm. Here, the EML layer thickness is reduced
to 20 nm in an effort to reduce the overall driving voltage. It can be seen that with same 15 nm
thick mCP layer, reducing the EML thickness from 25 nm to 20 nm results in a decrease of
maximum $\eta_{\text{EQE}}$ from $(18 \pm 1) \%$ to $(15 \pm 1) \%$. This is due to incomplete exciton formation in the
Figure 5-4. Luminance power ($\eta_P$, closed symbols) and external quantum ($\eta_{EQE}$, open symbols) efficiency versus current density ($J$) for TAPC-based devices with a varying mCP layer thickness.

A thinner EML. However, the peak $\eta_P$ is slightly increased from (16 ± 1) to (18 ± 1) lm/W because of the reduction in device driving voltage. With the EML thickness fixed at 20 nm, as the mCP layer thickness is reduced from 15 to 10 nm, $\eta_{EQE}$ is almost unaffected, and the maximum $\eta_P$ remains at (18 ± 1) lm/W. However, $\eta_P$ shows slight improvement at high current densities due to the lower driving voltage with reduced mCP layer thickness. Further reducing the mCP layer thickness to 5 nm or lower will lead to a significant reduction in $\eta_{EQE}$. The mCP plays an important role in facilitating the injection of holes into the EML, as its highest occupied molecular orbital (HOMO) level sits between those of TAPC and FIr6. $^{136,143}$ Without the mCP layer, electrons and holes would accumulate at the TAPC/EML interface due to the presence of large energy offset, resulting in a very thin recombination zone close to this interface. Therefore, polaron quenching of exciton and exciplex formation at the interface could significantly lower the quantum efficiency. $^{144-147}$ The device with 5 nm thick mCP exhibits a much faster efficiency
roll-off at high current densities compared to other devices with a thicker mCP layer, although they show almost identical efficiency at low current densities \( J \sim 10^{-3} \text{ mA/cm}^2 \). Since the surface roughness of ITO substrate is typically a few nanometers, the 5 nm thick mCP may not form complete coverage over the whole device area, leading to efficiency reduction in spots where the mCP layer thickness approaches zero.

**Evidence for Effective Electron and Exciton Blocking**

To confirm the improvement on device efficiency is due to better electron and exciton confinement properties of TAPC over NPD, we compared NPD- and TAPC-based devices without the mCP layer. Inset of Figure 5-5 shows the plot of \( \eta_{\text{EQE}} \) as a function of the current density for the two devices. It can be seen that the \( \eta_{\text{EQE}} \) of the TAPC is approximately 5 times higher than that of the NPD device. In addition, as shown in Figure 5-5, strong NPD fluorescent emission \( (\lambda = 435 \text{ nm}) \) can be observed in the EL spectrum NPD device, while no TAPC

![Figure 5-5](image)

Figure 5-5. Electroluminescence (EL) spectra of TAPC-based and NPD-based PHOLEDs without mCP layer. Inset: external quantum efficiency vs. current density of the two devices.
fluorescence ($\lambda = 360$ nm) is found.\textsuperscript{149} This indicates that electron leakage into the HTL is rather significant in the NPD device, but not present in the TAPC device. In the current investigation, there is no discernable triplet emission from NPD ($\lambda = 541$ nm) or TAPC ($\lambda = 430$ nm).\textsuperscript{139} Therefore, it is difficult to directly compare the exciton blocking properties of NPD and TAPC. However, it has been demonstrated previously that the higher triplet energy of TAPC than NPD can enhance the efficiency of green PHOLEDs because of better exciton confinement.\textsuperscript{139}

**Effect of Hole and Exciton Blocking Layer**

So far, the optimized TAPC device composed of 10 nm mCP and 20 nm EML, which has $\eta_{\text{EQE}}$ of $(15 \pm 1)$ % and $\eta_{\text{P}}$ of $(18 \pm 1)$ lm/W. Since TAPC already provides good electron and exciton confinement, further enhancement of the device efficiency may be achieved by improved hole and exciton blocking at the EML/ETL interface. Currently, the BCP has $T_1 = 2.5$ eV, which is slightly lower than that of FIr6. Moreover, the energy barrier of holes is only 0.4 eV at the EML/BCP interface. Both factors may result in inefficient hole and exciton blocking at the EML/BCP interface. Therefore, a thin layer of UGH2 and 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl] phenylene (OXD-7)\textsuperscript{150} is inserted between EML and BCP layer in order to further improve the hole and exciton blocking within the EML.

Figure 5-6a shows the $L - J - V$ characteristics of devices with 5 nm UGH2 or OXD-7 inserted between EML and BCP layer. It can be seen that the UGH2 device has better current injection and luminance than the OXD-7 device, reaching $J = \sim 5$ mA/cm$^2$, $L = \sim 1000$ cd/m$^2$ at 10 V for UGH2 device but only $J = \sim 3$ mA/cm$^2$ and $L = \sim 700$ cd/m$^2$ for OXD-7 device. It is known that OXD-7 has better electron transport than UGH2.\textsuperscript{151} Therefore, the OXD-7 device should show lower driving voltage than the UGH2 device. The presence of high driving voltage in the current OXD-7 device could possibly due to the poor electron injection at the additional EML/OXD-7 and OXD-7/BCP interfaces, which are not present in the UGH2 device.
dependencies of external quantum and power efficiency on current density for OXD-7 and UGH2 devices are shown in Figure 5-6b. It can be seen that both devices show higher maximum $\eta_{\text{EQE}}$ and $\eta_p$ compared with the optimized TAPC device without any hole blocking layer. The

![Figure 5-6. Performance of PHOLEDs with ITO/TAPC (40 nm)/mCP (10 nm)/UGH2:10 wt % Flr6 (20 nm)/HBL (5nm)/BCP (40 nm)/LiF (1 nm)/Al (a) Current density-voltage ($J-V$, closed symbols) and luminance-voltage ($L-V$, open symbols) characteristics and (b) Luminance power ($\eta_p$, closed symbols) and external quantum ($\eta_{\text{EQE}}$, open symbols) efficiencies as a function of current density.](image)
OXD-7 device has peak $\eta_{\text{EQE}}$ of $(15 \pm 1)\%$ and $\eta_p$ of $(21 \pm 1)\text{ lm/W}$, and the UGH2 device show peak $\eta_{\text{EQE}}$ and $\eta_p$ of $(20 \pm 1)\%$ and $(25 \pm 1)\text{ lm/W}$, respectively. This suggests the inserted OXD-7 and UGH2 layer, with their higher triplet energy, do help improve the device efficiency by inducing better exciton blocking. Moreover, due to the higher HOMO level of UGH2 with respect to the OXD-7 and BCP (both have the same HOMO level), the addition hole blocking effect could be expected from a neat UGH2 layer, which contributes the highest peak efficiency achieved. However, it is worth noticing that both OXD-7 and UGH2 devices have very fast efficiency roll-off at high current densities, which is so significant that the efficiency becomes lower than the optimized TAPC device. This suggests that the charge injection become more unbalanced in the high voltage regime.\textsuperscript{152} Considering an additional OXD-7 or UGH2 layer will reduce the electron transport, the EML could become hole dominant at high voltage. Since charge balance also plays an important role in determining the device efficiency, the high triplet energy of the ETL should be the only key factor affecting the device efficiency.

**Reducing Driving Voltage of Phosphorescent OLED**

In the last section, we showed that charge carrier and exciton confinement is of great importance to obtain blue PHOLEDs. And significant improvement of external quantum efficiency has been achieved using TAPC as HTL and UGH2 as exciton blocking layer. Nevertheless, one of the key parameters to determining the practical application of OLEDs is luminance power efficiency, which is the light output of OLED with unit energy input, or say, lumens per watt (lm/W). Therefore, the work in this section focuses on reducing the driving voltage of the blue PHOLEDs by optimizing the active layer thickness and using efficient charge injection layer.
**Efficient Electron and Hole Injection Layer**

One way to effectively reduce driving voltage of the OLEDs is using p- and n-doped charge injection/transport layers. It is believed that the doped organic layer will have higher intrinsic carrier density than the undoped layer. On one hand, such increased carrier density can improve the conductivity of the film. On the other hand, the charge injection barrier between the electrode and the organic layer can be reduced due to band bending at the metal-organic interface, therefore, forming ohmic contact. In the current study, N,N’-diphenyl-N,N’-bis(3-methylphenyl)-[1,1’-biphenyl]-4,4’-diamine (MeO-TPD) doped with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) is used as a p-doped hole injection layer, whereas Li doped 4,7-diphenyl-1,10-phenanthroline (BPhen) layer is used as n-doped electron injection layer.

The improved conductivity of the F4-TCNQ doped MeO-TPD originates from the efficient electron transfer from MeO-TPD to F4-TCNQ molecules due to the strong electron affinity of F4-TCNQ. As a result, additional holes are created in the MeO-TPD layer, increasing the conductivity of the film. Figure 5-7a shows the $J-V$ characteristics of 250 nm F4-TCNQ doped MeO-TPD films sandwiched between gold electrodes, which generate hole-only devices. It can be seen that the current density increased as the F4-TCNQ dopant concentration increases from 0 mol % to 9.0 mol %. The conductivity of the MeO-TPD layer is obtained by fitting the ohmic region, i.e., $J \propto V$, of the $J-V$ curve. As shown in Figure 5-7b, the conductivity is improved from $\sim 10^{-10}$ S·cm$^{-1}$ in the undoped MeO-TPD film to more than $10^{-5}$ S·cm$^{-1}$ in the 9.0 mol % doped sample, which is five order of magnitude higher. Therefore, the voltage drop across the doped MeO-TPD will be significantly lower.

Even though a high conductivity p-doped layer is successfully obtained through doping MeO-TPD, it is still unclear how it works on the current blue PHOLEDs. Therefore, two hole-
Figure 5-7. Conductivity study of F4-TCNQ doped MeO-TPD films (a) Current density-voltage ($J-V$) characteristics of doped and undoped MeO-TPD films. The dots are measured data point, and the lines are the linear fit of the ohmic regime. (b) Conductivity of the doped MeO-TPD films as a function of the F4-TCNQ doping concentration. (Courtesy of T. Tseng and J. Xue)

only devices are fabricated to investigate the hole injection and transport in the FIr6 device. The two hole-only devices involve structures of ITO/TAPC(20 nm) or MeO-TPD:F4-TCNQ (3 mol %, 20 nm)/TAPC (20 nm)/UGH2:FIr6 (10 wt %, 20 nm)/Au (50 nm). Here, BCP is removed to make sure holes can be fully collected at the cathode and Au is used as cathode to reduce electron injection under forward bias. Figure 5-8 compares the $J-V$ characteristics of the two hole-only devices under forward bias. It can be seen that the device using 20 nm doped MeO-TPD as the hole injection layer shows significantly higher current density than the TAPC only device. The current density reaches $J = \sim 50$ mA/cm$^2$ at 10 V for the doped MeO-TPD device, whereas $J = \sim 0.2$ mA/cm$^2$ for the TAPC at same voltage. This suggests that hole injection and transport in the doped MeO-TPD is more efficient than in the TAPC only device. Here, only 3 mol % F4-TCNQ doping concentration is used in the p-doped layer because further increasing the dopant concentration will not significantly enhance the hole current further. Moreover, high dopant concentration will induce strong exciton quenching when the dopants manage to diffuse into the EML with thinner TAPC and mCP layer.
Figure 5-8. Current density-voltage \((J – V)\) characteristics of ITO/TAPC (red) or MeO-TPD: 3 mol % F4-TCNQ (blue) (20nm)/TAPC (20 nm)/UGH2: 10 wt% FIr6 (20 nm)/Au (50 nm) hole-only device. Inset: same plot in linear scale.

The n-doped electron injection and transport layer composed of Li doped BPhen layer, has been successfully used on different OLEDs to reduce driving voltage of the device. It has been shown that the extremely active Li atoms doped into the BPhen will donate electrons to BPhen molecules. As a result, the intrinsic carrier density in BPhen is increased significantly, and high conductivity could be obtained. It has been shown that the conductivity of intrinsic BPhen is approximately \(10^{-10}\) S·cm\(^{-1}\), which is increased by 4 orders of magnitude to \(~10^{-6}\) S·cm\(^{-1}\) in the 1:1(by molar ratio) Li doped BPhen layer.\(^{153}\) Therefore, similar to F4-TCNQ doped MeO-TPD, improvement on electron injection and transport is expected in the device using Li doped BPhen layer. To confirm our hypothesis, two electron-only devices without electron blocking mCP and nm)/Bphen (20 nm)/BPhen:Li (1:1 by molar, 20 nm)/LiF/Al and ITO/ UGH2:FIr6 (10 wt %, 20 nm)/BCP (40 nm)/LiF/Al. Here, the ITO substrate is directly used without UV-ozone treatment,
Figure 5-9. Current density-voltage ($J – V$) characteristics of ITO/UGH2: 10 wt % FIr6 (20 nm)/BCP (40 nm)/LiF/Al (red) and ITO/UGH2: 10 wt% FIr6 (20 nm)/Bphen (20 nm)/Bphen:Li =1:1 (20 nm)/LiF/Al (blue) electron-only device. Inset: same plot in linear scale.

which results in a lower work function of ITO to reduce hole injection from ITO under forward bias. Moreover, a 20 nm thick neat BPhen layer is inserted between the UGH2 and n-doped Bphen layer to prevent diffusion of Li cations into the EML. It is believed that the Li cation can be the quenching center for the triplet exciton, which reduces the luminance efficiency.$^{154,155}$

Figure 5-9 shows the $J – V$ characteristics of the two electron-only devices under forward bias. The device with Li doped BPhen layer show higher current density than the BCP device at the same voltage. For instance, $J = \sim 15 \text{ mA/cm}^2$ at 10 V for the BCP device, whereas $J$ increases to more than 100 mA/cm$^2$ for the n-doped device at the same voltage. This suggests more efficient electron injection and transport is achieved in the device using Li doped BPhen layer as n-doped layer. Another important observation by comparing the two sets of single carrier devices is that
the electron and hole current is more balanced under high driving voltage in the devices with doping layers. It can be seen from Figure 5-8 and Figure 5-9 that $J = \sim 50 \text{ mA/cm}^2$ and $\sim 120 \text{ mA/cm}^2$ at 10 V for the p-doped hole-only and n-doped electron-only devices, respectively, whereas $J = \sim 0.2 \text{ mA/cm}^2$ and $\sim 15 \text{ mA/cm}^2$ for the undoped hole-only and electron-only devices. The current density difference in terms of percentage is much less after using doped charge injection layers. This suggests more balanced charge injection into the EML is achieved; hence improved device efficiency is anticipated.

**Device Using p-i-n Structure**

Based on the previous understanding on the performance of p- and n-doped charge injection/transport layers, it is advisable to incorporate the two efficient doping layers into the blue PHOLED structure to reduce driving voltage and improve luminance power efficiency. The so-called $p$-$i$-$n$ structure typically is composed of an intrinsic EML sandwiched between a p-doped hole injection/transport layer and an n-doped electron compliment. In this Section, the performance of $p$-$i$-$n$ blue PHOLEDs using F4-TCNQ doped MeO-TPD as a p-doped layer and Li doped BPhen as an n-doped layer is investigated. Here, a $p$-$i$-$n$ structure based on the conventional NPD device studied previously is fabricated. Figure 5-10 shows the energy level diagram of the p-i-n devices as well as the device structure under investigation. The conventional NPD device composed of 40 nm NPD, 15 nm mCP, 25 nm 10 wt % FIr6 doped UGH2 as EML and 40 nm BCP, which is reported as the optimized conventional NPD device. In the NPD $p$-$i$-$n$ device, the 40 nm NPD is replaced with 25 nm thick 2 mol% F4-TCNQ doped MeO-TPD and 15 nm pure NPD, whereas the 40 nm BCP is replaced with 20 nm pure BPhen and 20 nm thick Li doped BPhen (1:1 molar mixing ratio).
Figure 5-10. Device structure of the conventional NPD-based deep-blue PHOLEDs and the two \textit{p-i-n} structure PHOLEDs under study as well as the energy level diagram of \textit{p-i-n} PHOLEDs.

Figure 5-11a shows the \textit{J-L-V} characteristics of conventional NPD device and the \textit{p-i-n} NPD device. It can be seen that, with same mCP and EML layer, the \textit{p-i-n} device has higher current density and luminance than the conventional device. At 10 V the current density and luminance reach $J = \sim 50$ mA/cm$^2$ and $L = \sim 4300$ cd/m$^2$ for the \textit{p-i-n} device, whereas $J = 15$ mA/cm$^2$, $L = \sim 2000$ cd/m$^2$ for the conventional device. Moreover, the \textit{p-i-n} structure has significantly reduced the driving voltage of the device. The driving voltage at $L = 1000$ cd/m$^2$ is reduced from $V = 10$ V in the conventional device to $V = 7.5$ V in the \textit{p-i-n} device. This has led to enhanced luminance power efficiency in the \textit{p-i-n} device. Figure 5-11b shows the plot of external quantum and luminance power efficiency as a function of luminance. It should be noted
Figure 5-11. Performance of PHOLEDs of conventional NPD-based device and two $p-i-n$ devices (a) Current density-voltage ($J - V$, closed symbols) and luminance-voltage ($L - V$, open symbols) characteristics and (b) Luminance power ($\eta_P$, closed symbols) and external quantum ($\eta_{EQE}$, open symbols) efficiencies as a function of luminance.

that the external quantum efficiency of the $p-i-n$ device is slightly lower than the conventional device at certain voltages, with peak $\eta_{EQE} = (10 \pm 1)\%$ for the $p-i-n$ device and $\eta_{EQE} = (12 \pm 1)\%$ for the conventional device. Although the peak $\eta_P$ of the $p-i-n$ device is still lower than the
conventional device, (12 ± 1) lm/W versus (14 ± 1) lm/W, the p-i-n device shows higher $\eta_P$ than
the conventional one as $L > 4$ cd/m$^2$, which is more relevant to practical display or lighting
applications. In the current p-i-n and conventional devices, a common 25 nm 10 wt % FIr6 doped
UGH2 layer is used as the EML. Since significantly more charge carriers are injected into the
EML in the p-i-n device, such low FIr6 doping concentration and thin EML layer may not be
sufficient to effectively trap the injected carriers and generate triplet excitons. By considering
this, we increased the FIr6 doping concentration to 15 wt % as well as the EML layer thickness
to 30 nm. As shown in Figure 5-11a, with increased FIr6 concentration and EML layer thickness,
the modified p-i-n device shows slightly lower current density yet higher luminance compared
with the normal p-i-n device, reaching $J = 40$ mA/cm$^2$ and $L = 4700$ cd/m$^2$ at 10 V. Moreover,
due to the presence of more trapping and emitting centers in the EML, the modified p-i-n device
achieves higher external quantum efficiency than the conventional and normal p-i-n devices with
peak $\eta_{EQE} = (13.0 \pm 1.0)$ %. The enhancement in power efficiency of modified p-i-n devices over
conventional ones is more significant, especially at high luminances (see Figure 5-11b).
Noticeably, both p-i-n devices show very fast roll-off of the efficiency curves at $L > 1000$ cd/m$^2$.
This could due to both unbalanced charge injection under high voltage and triplet-triplet
quenching at high luminances when the triplet exciton density is too high within the EML. The
comparison of the efficiencies at different luminance and CIE coordinates of the three devices is
listed in Table 5-1. The p-i-n structure is very effective in improving the power efficiency at the
high luminance, which is much more valuable for applications in displays ($L \sim 100$ cd/m$^2$) and
lighting ($L \sim 1000$ cd/m$^2$). And all these are achieved without a significant change of the EL
spectra and CIE coordinates of the devices.
Table 5-1. Comparison of the turn-on voltage \( (V_T) \), external quantum efficiency \( (\eta_{EQE}) \), power efficiency \( (\eta_P) \), and CIE coordinates of three devices

<table>
<thead>
<tr>
<th>Device</th>
<th>( V_T ) (V)</th>
<th>( \eta_{EQE} ) (%) ( \text{(at peak)} )</th>
<th>( \eta_P ) (lm/W) ( \text{(at peak, } 100 \text{ cd/m}^2, 1000 \text{ cd/m}^2) )</th>
<th>CIE ( (x, y) ) ( \text{(at } 1 \text{ mA/cm}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional (NPD)</td>
<td>4.7</td>
<td>12 ± 1</td>
<td>14, 8, 5 ± 1</td>
<td>(0.16, 0.28)</td>
</tr>
<tr>
<td>Normal ( p-i-n )</td>
<td>4.6</td>
<td>11 ± 1</td>
<td>12, 9, 6 ± 1</td>
<td>(0.17, 0.29)</td>
</tr>
<tr>
<td>Modified ( p-i-n )</td>
<td>4.8</td>
<td>13 ± 1</td>
<td>14, 12, 8 ± 1</td>
<td>(0.16, 0.29)</td>
</tr>
</tbody>
</table>

Discussion

In this chapter, several methods have been successfully applied to the existing deep-blue PHOLEDs to improve the device efficiency. Due to the nature of the blue emitter, achieving efficient blue OLEDs is challenging. For phosphorescent blue OLEDs in particular, the high triplet energy phosphorescent emitter requires even higher triplet energy for the host materials as well as the peripheral charge transport materials. Also, the wider bandgap of the blue emitter usually possess lower HOMO and higher LUMO levels, which makes the charge injection into the corresponding energy levels more difficult. Here, using TAPC as the HTL instead of NPD can increase the efficiency of the FIr6 PHOLED significantly. The improvement originates from better exciton and electron blocking provided by TAPC, who has a \( T_1 = 2.87 \text{ eV} \) and a LUMO level of 2.0 eV. With TAPC, the thickness of mCP and EML can be reduced without largely sacrificing the external quantum efficiency, hence higher luminance power efficiency is achieved. Similarly, high triplet energy ETL of OXD-7 and UGH2 is used to improve the hole and exciton blocking on the cathode side.\textsuperscript{152,156} Even though improved efficiency is observed at low current density, the efficiency actually becomes lower than the device without OXD-7 or UGH2. This is attributed to the poor electron transport after inserting any of these two layers between EML and BCP. To overcome this drawback, a single ETL with high triplet energy and
high electron mobility is desired. In the work after, we used electron transport material tris[3-(3-pyridyl)mesityl] borane (3TPYMB) with electron mobility of $\mu_e = \sim 10^{-5}$ cm$^2$/Vs, triplet energy of $T_1 = 2.95$ eV and HOMO level of 6.77 eV to replace BCP ($\mu_e = \sim 10^{-6}$ cm$^2$/Vs, $T_1 = 2.5$ eV, HOMO of 6.7 eV),$^{157}$ which led to a peak $\eta_{EQE} = (20.0 \pm 1.0)$ %.$^{153}$ Therefore, by incorporating high triplet energy materials as the peripheral charge transport layers, further enhancement of the efficiency of current blue PHOLEDs should be achievable.

Another route demonstrated to be effective in improving device efficiency involves usage of n- and p-doped charge injection layers. The doped charge injection/transport layers are able to achieve lower injection barrier and higher conductivity, which result in reduced driving voltage and higher luminance power efficiency. In the current $p$-$i$-$n$ blue PHOLEDs, the F4-TCNQ doped MeO-TPD as p-doped layer and Li doped BPhen as n-doped layer not only reduced the driving voltage but also significantly increased the amount of charge injected into the EML. Since FIr6 is the phosphorescent emitter as well as the charge transport/trapping center, higher FIr6 doping concentration is desired to maximize the exciton generation in the $p$-$i$-$n$ device. That is why higher efficiency in the $p$-$i$-$n$ device is obtained by increasing the FIr6 concentration in the EML. The current modified $p$-$i$-$n$ device possesses a 30 nm thick 15 wt% FIr6 doped UGH2 as EML, whose thickness can be further reduced to lower the driving voltage. In order to reduce the EML layer thickness without compromising the quantum efficiency of the device, it is possible to further increase the FIr6 concentration to 20 wt % or even greater.

In the current blue PHOLEDs, electrons can still be injected in to the LUMO level of the mCP even though TAPC is used to improve electron confinement. In the next step of research work conducted majorly by Sang-Hyun Eom, we demonstrated that a TAPC device with dual emissive layers consisting of 4 wt % FIr6 doped mCP and 25 wt % doped UGH2 can further
enhance the PHOLED efficiency by utilizing the electron injected into mCP layer. Moreover, application of \textit{p-i-n} structure on such dual emissive layer device resulted in further improvement of the power efficiency to $(25 \pm 2)$ lm/W at 100 cd/m$^2$ and $(20 \pm 2)$ lm/W at 1000 cd/m$^2$\textsuperscript{158}. In the current \textit{p-i-n} devices, a layer 20 nm thick of pure BPhen is inserted between the n-doped BPhen layer and EML to prevent the diffusion of Li ions into the EML, which can cause significant luminance quenching. To reduce the pure BPhen layer or even completely remove it requires way to hinder the diffusion of ion dopant into EML. By doping the BPhen with Cs instead of Li the diffusion of ion dopants into the EML should be reduced due to the large size of the Cs ion. In another work we published, we achieved higher efficiency in the \textit{p-i-n} device using Cs as dopants than that with Li dopants\textsuperscript{153}.

With efficient deep-blue PHOLED, a white PHOLED can be easily achieved by doping certain amount of the green and red phosphorescent emitters into the EML\textsuperscript{159}. With current efficiency blue PHOLEDs, we achieved a white OLED by introducing fac-tris(phenylpyridine) iridium [Ir(ppy)$_3$] as green emitter and iridium(III) bis-(2-phenylquinoly-N, C$^2$) acetylaceto-nate (PQIr) as red emitter. The while PHOLED achieved a peak power efficiency of $(40 \pm 2)$ lm/W, a color rendering index of 79 and CIE of (0.37, 0.40)\textsuperscript{160}.

\textbf{Conclusions}

We have shown that the efficiencies of the FIr6-based deep-blue PHOLEDs significantly depend on the properties of the peripheral charge injection/transport materials. A maximum $\eta_{\text{EQE}} = (18 \pm 1)\%$ was achieved using TAPC as HTL, which is approximately 50% higher than the device using NPD as HTL. This improvement is attributed to the better electron and exciton confinement provided by the TAPC. The maximum $\eta_{\text{EQE}}$ is further enhanced to $(20 \pm 1)\%$ by introducing a thin neat UGH2 as hole and exciton blocking layer. We also have shown that incorporation of F4-TCNQ doped MeO-TPD hole injection and Li doped BPhen electron
injection layer can substantially reduce device driving voltage. The modified $p$-$i$-$n$ device achieved a power efficiency of $\eta_p = (11 \pm 1) \text{ lm/W}$ at 100 cd/m$^2$, which is nearly 45% higher than the conventional device at the same luminance.
CHAPTER 6
LOW TURN-ON VOLTAGE OF MEH-PPV POLYMER LIGHT-EMITTING DIODES

Introduction

One important category of organic light-emitting diodes (OLEDs) is the polymer light-emitting diodes (PLEDs), which differ from small molecule OLEDs by the use of conjugated polymers as emissive layer. The research on PLEDs started in 1990 when the first electroluminescence from a polymer was observed in poly(phenylene vinylene) (PPV), and significant advances have been achieved in PLEDs in the two decades since. Compared with small molecule OLEDs, PLEDs have an advantage of being able to be fabricated through solution processes, where the active layers are deposited through spin-casting or ink-jet printing from a polymer solution. Therefore, the PLEDs are more suitable for large-area low-cost fabrication by eliminating the need for expensive, material-costly vacuum deposition. Nevertheless, the current PLEDs suffer a few drawbacks compared with small molecule OLEDs, and one of the issues remaining is the relatively high driving voltage. As we learned in Chapter 5, a multi-layer \( p-i-n \) structure was achieved through vacuum thermal evaporation to successfully reduce the driving voltage. With such a multi-layer structure, the various functional materials separate the roles of charge injection, transport and light emission, which shows the versatility of the small molecule OLEDs. Achieving such a multi-layer structure, however, is rare in PLEDs. This is mainly due to the difficulty of achieving solvent orthogonality, which requires the solvent during the subsequent layer deposition does not dissolve the previously deposited layer. Because of this, most of the PLEDs are composed of poly(ethylenedi-oxythiophene) polystrylene sulphonate (PEDOT:PSS) as hole injection layer, a polymer as the emitting layer (EML) and a vacuum deposited small molecule electron injection/transport layer.
Since most of the light-emitting conjugated polymers are p-type semiconductors, balanced injection and transport in the hole-dominant PLEDs requires sufficient electron injection into the EML during device operation. Even though low-work-function cathodes of Ca, Ba and LiF/Al are widely used to reduce the electron injection barrier, their air and water sensitivity significantly reduce device stability and lifetime. Over the past few years, great efforts have been made by different research groups to provide an efficient electron injection cathode with ambient stability and ease of fabrication. Wu et. al. reported a bilayer cathode consisting of aluminum and alcohol-/water-soluble conjugated polymer, which shows comparable performance to the Ba/Al cathode. Cao et. al. showed that addition of an organic surfactant between the polymer EML and Al can improved PLED performance. Another way to improve the electron injection includes inserting a layer of polystyrene sodium sulfonate between the polymer EML and Al.

In this chapter, we present a novel and efficient electron injection cathode composed of ZnO nanoparticles (NPs) and Al. The poly[2- methoxy-5-(2’-ethylhexyloxy)-1, phenylene vinylene] (MEH-PPV) PLED with ZnO NPs/Al cathode shows remarkably improved electron injection over the conventional LiF/Al cathode. Electroluminescence from MEH-PPV is observed at a driving voltage as low as (1.3 ± 0.1) V. It is believed that the ultra low turn-on voltage achieved by the ZnO NPs/Al cathode could be attributed to an efficient Auger process that took place at the MEH-PPV/ZnO NPs heterojunction. An electron can gain additional energy during the Auger process and can overcome the injection barrier at the MEH-PPV/ZnO NPs interface. Therefore, electrons can be injected into the MEH-PPV at a much lower driving voltage. Such a method to improve electron injection is significantly different from the conventional fashion of seeking low-work-function cathode to reduce injection barrier. The content in this chapter is arranged in the following order. Structure and morphology
characterization of the ZnO NP layer as well as device performance of MEH-PPV PLED with ZnO NPs/Al as cathode are presented in the first part. The second part will focus on the mechanism study of the low turn-on voltage phenomenon, which is conducted based on the hypothesis of Auger process at the MEH-PPV/ZnO NPs interface. The discussion and partial conclusion will be given in the last part.

**Low Turn-on Voltage with ZnO Nanoparticles as Electron Injection Layer**

To study the mechanism of efficient electron injection, hence the ultra low turn-on voltage, it is of great importance to first gain information of the particular structure and morphology of ZnO NPs as well as the device performance of the MEH-PPV PLED with ZnO NPs/Al cathode.

**Morphology and Structure of ZnO Nanoparticles**

The ZnO nanoparticles were synthesized through the sol-gel method. In a typical experience, ZnO NPs were prepared by dropwise addition of a stoichiometric amount of tetramethyl ammonium hydroxide dissolved in ethanol (concentration 0.55 M) to 30 mL of 0.1 M Zinc acetate (dehydrate) dissolved in dimethyl sulfoxide (DMSO) followed by stirring for an hour. The ZnO nanoparticles were then precipitated and washed thoroughly using heptanes/ethanol twice to remove the residual chemicals. ZnO NPs were then dispersed in ethanol with a concentration of ~ 30 mg/mL.

Here, transmission electron microscopy (TEM) and X-ray diffraction (XRD) are employed to characterize the morphology and structure of ZnO NPs. The TEM measurement is conducted using JOEL TEM 200CX, whereas the XRD pattern is recorded using Philips X’pert MRD diffractometer with Cu-Kα source operated in \( \theta - 2\theta \) mode. Figure 6-1a shows the transmission electron microscopy (TEM) images of ZnO NPs synthesized through the above method. The nearly spherical shape ZnO NPs have diameter ranging from 2.5 nm to 3.5 nm. Figure 6-1b
Figure 6-1. Morphology of ZnO nanoparticles. (a) Transmission electron microscope (TEM) image of ZnO NPs. Inset: high resolution TEM image of same ZnO NPs, where ZnO NPs form “peanut” like pair-wise particle. (b) Histogram for size distribution of the ca. 50 ZnO NPs. The scale bar is 20 nm. (Courtesy of Lei Qian)

shows a histogram of ZnO NP sizes for a population of ~50 isolated nanocrystals, which suggests a fairly narrow distribution of the nanoparticle size with an average diameter of 3.2 ± 0.3 nm.

The XRD patterns of the ZnO NPs along with that of bulk ZnO single crystal are shown in Figure 6-2. Bulk ZnO is known to adopt a wurtzite structure with space group of $P6_{3}mc$ and lattice constant of $a = 3.250$ Å and $c = 5.207$ Å.\cite{171} Comparison of the XRD patterns of the ZnO NPs with that of bulk ZnO suggests that the ZnO NPs are crystalline with similar wurtzite structure and lattice constant to bulk ZnO. However, the diffraction peaks are significantly broadened in the XRD pattern of ZnO patterns, which could due to the reduced size of these nanoparticles. By measuring the full width at half maximum (FWHM) through curve fitting, the size of the ZnO nanoparticle can be obtained through the Scherrer formula:\cite{172}

$$d = \frac{K\lambda}{B \cos \theta}$$
Here, $d$ is the diameter of the nanoparticle, $\lambda$ is the x-ray wavelength, which is 1.54Å for Cu-K$\alpha$ source, $B$ is the FWHM, $\theta$ is the Bragg angle, and $K$ is a shape factor, which equals 1.2 assuming a spherical shape.$^{171}$ The calculation using the above formula suggests an average particle size of 3.1 nm, which matches very well with the value obtained through TEM study.

**LiF versus ZnO Nanoparticle as Electron Injection Layer**

The performance of two typical MEH-PPV PLEDs using LiF/Al and ZnO NPs/Al as cathodes is studied in this part. The devices are fabricated on glass substrates pre-coated with a layer of indium-tin-oxide (ITO) with as sheet resistance of ~ 20 $\Omega$\square. The ITO substrate is cleaned by de-ionized water, acetone and isopropanol consecutively followed by ultraviolet-ozone treatment for 15 minutes. A 40 nm thick PEDOT:PSS (Baytron Al 4083) is then spin-coated on to the ITO followed by baking at 150 °C in air for 15 minutes to remove residual water. MEH-PPV with a concentration of 5 mg/mL in chloroform is spin-coated at 4000 rpm on
the PEDOT:PSS to provide a ~ 80 nm thick film. For the device using LiF/Al as the cathode, the MEH-PPV layer is annealed at 150 °C in nitrogen for 30 minutes before loading into a custom-made vacuum chamber (background pressure: ~ $1 \times 10^{-6}$ Torr) for LiF and Al deposition. For the device using ZnO NPs/Al as cathode, the ZnO NPs are spin-coated at 4000 rpm on top of the fresh MEH-PPV layer from an ethanol solution to provide a 40 nm thick film. The MEH-PPV plus ZnO NPs layer are then annealed at 150 °C for 30 minutes in nitrogen to remove residual solvent followed by Al deposition. The device area is 4 mm$^2$. Current-density-luminance-voltage ($J – L – V$) characteristics were measured using an Agilent 4155C semiconductor parameter analyzer with a calibrated Newport 818-UV silicon diode. The luminance was calibrated using a Minolta luminance meter (LS-100). The external quantum efficiency ($\eta_{\text{EQE}}$) was determined by assuming Lambertian emission. The electroluminescence (EL) spectrum is obtained through a highly sensitive JASCO FP-6500 fluorescence spectrometer. All measurements are conducted in air without encapsulation of the device.

Figure 6-3a compares the $J – L – V$ characteristics of MEH-PPV PLEDs with ZnO NPs/Al and LiF/Al as cathodes. The ZnO-based device always displays higher current injection than the LiF-based device at the same voltages and the difference is more significant at the low voltage region. At the driving voltage of 2 V and 9 V current densities $J = \sim 6$ mA/cm$^2$ and $\sim 2.47 \times 10^3$ mA/cm$^2$ were obtained in the ZnO-based device, whereas $J = \sim 0.03$ mA/cm$^2$ and $\sim 1.29 \times 10^3$ mA/cm$^2$ in LiF-based device. On the other hand, the ZnO-based device shows higher luminance than the LiF-based device when $V < 5.5$ V but lower luminance when $V > 5.5$ V. It is noted that the ZnO-based device has remarkably lower turn-on voltage $V_T$ (defined as the voltage at $L = 0.1$ cd/m$^2$) than the LiF-based device, with $V_T = 1.36$ V in the ZnO-based device and $V_T = 2.08$ V in the LiF-based device. Figure 6-3b shows the $\eta_{\text{EQE}}$ and power efficiency $\eta_p$ of the two devices.
Although higher current injection is achieved in the ZnO-based device, the ZnO-based device exhibits lower $\eta_{\text{EQE}}$ and $\eta_P$ than the LiF-based due to less improvement in luminance. Maximum efficiencies of $\eta_{\text{EQE}} = 0.20\%$ and $\eta_P = 0.31\, \text{lm/W}$ are obtained in the ZnO-based device, whereas $\eta_{\text{EQE}} = 0.85\%$ and $\eta_P = 1.47\, \text{lm/W}$ in the LiF-based device.
The surprisingly high current injection and low turn-on voltage in the ZnO-based device is intriguing. Generally, the $V_T$ of light-emitting diodes should be close to the value of the emitted photon energy divided by electron charge (photon energy voltage). To ensure the light emission originated from excited state MEH-PPV (emission peak at the wavelength of 580 nm) but not from any exciplex states between MEH-PPV and ZnO NPs, the EL spectrum at different driving voltages of the ZnO-based device is measured using a high sensitivity fluorescence spectrometer. Figure 6-4 shows the EL spectra from the ZnO-based device with driving voltages from 1.3 V to 5 V. It can be seen that the ZnO-based device shows consistent EL spectra under all driving voltage. Emission peaks located at the wavelength $\lambda = 580$ nm corresponds to a photon energy of $\sim 2.14$ eV, which is consistent with the reported EL spectrum from MEH-PPV PLED. Notably, weak light emission from MEH-PPV can be observed with a driving voltage as low as 1.3 V, which is approximately 0.8 V lower than the value of 2.14 V photon energy voltage.

Figure 6-4. Electroluminescence (EL) spectra of ZnO NPs device under different forward bias. Inset: normalized EL spectra.
Application of ZnO Nanoparticles on Other Polymer Light-Emitting Diodes

With the low turn-on voltage observed in ZnO-based MEH-PPV PLED, the turn-on voltages of two other PLEDs using ZnO NPs as electron injection layer are investigated. In the current study, two PLEDs comprising ITO/PEDOT:PSS/poly(9,9’-dioctylfluorene-co-benzothiadiazole) (F8BT) or poly[2-methoxy, 5-(3’,7’dimethyl-octyloxy)]-p-phenylenevinylene (MDMO-PPV)/ZnO NPs/Al are fabricated. Figure 6-5a and b show the $L - V$ and $J - V$ characteristics of

![Graph](image-url)

Figure 6-5. Performance of other PLEDs with ZnO NPs as electron injection layer. (a) Luminance-voltage ($L - V$) and (b) current density-voltage ($J - V$) characteristics of ITO/PEDOT:PSS/MDMO-PPV or F8BT/ZnO NPs/Al PLEDs. Inset: normalized EL spectra of the two devices.
the two devices. Due to poor photoluminescence efficiency of MDMO-PPV compared with MEH-PPV, the MDMO-PPV device displays very low luminance with a peak value of $L = \sim 30$ cd/m$^2$. Nevertheless, both devices show low turn-on voltage of $V_T = 2.8$ V for the F8BT device and $V_T = 2.0$ V, which are close to the emitted photon energy voltage (2.33 eV for F8BT and 2.16 eV for MDMO-PPV based on wavelength of the emission peak). The inset of Figure 6-5a shows the normalized EL spectra of F8BT and MDMO-PPV device at the driving voltage of 2.4 V and 2.0 V, respectively, which are consistent with the reported F8BT and MDMO-PPV spectra.$^{166,174,175}$ On the other hand, the current density reaches $J = \sim 1000$ mA/cm$^2$ at $V = 5$ V in the F8BT device. This value is much higher than the report value of F8BT PLED using Ca as cathode, in which $J = \sim 300$ mA/cm$^2$ at $V = 5$ V.$^{166}$ Similarly, the current MDMO-PPV PLED also achieves $J = \sim 800$ mA/cm$^2$ at $V = 5$ V, which is twice higher than the report value of MDMO-PPV PLED with LiF/Al as cathode at same driving voltage.$^{175}$

All these suggest that ZnO NPs is an efficient electron injection layer for a number of PLEDs. Improved charge injection and low turn-on voltage are realized in PLEDs using MEH-PPV, F8BT or MDMO-PPV as emissive layer and ZnO NPs as electron injection layer.

Mechanism Study for Low Turn-on Voltage Phenomenon

Usually, the $V_T$ of the organic or inorganic light-emitting device is close to the emitted photon energy.$^{176,177}$ In the current ZnO-based MEH-PPV PLED, however, 2.14 eV photons originated from MEH-PPV bandgap emission is observed with $V_T$ as low as 1.36 V, which is approximately 0.8 V lower than the photon energy voltage of 2.14 V. While such significant reduction of $V_T$ is not observed in the device with the LiF/Al cathode, this could particularly relate to the ZnO NPs layer inserted between MEH-PPV and Al. In this section the mechanism for the ultra low turn-on voltage in ZnO-based is investigated.
Auger Assisted Injection Model

Ideally, the driving voltage necessary to obtain red, green, and blue emission in light-emitting diodes is ~ 1.65, 1.95 and 2.28 V, respectively. Therefore, the thermodynamic limit for $V_T$ of the orange-emitting MEH-PPV PLED should fall in the region of 1.65 - 1.95 V. Observation of light emission at $V_T = 1.36$ V in the ZnO-based device definitely required an efficient energy up-conversion process to meet the thermodynamic requirement.

Figure 6-6a shows the energy level diagram of the ZnO-based device. It can be noted that the hole injection at the PEDOT:PSS/MEH-PPV interface is very efficient due to the negligible hole injection barrier. Since MEH-PPV has higher hole mobility than electron mobility, the injected holes can easily transport across the MEH-PPV layer and be blocked at the MEH-PPV/ZnO NPs interface due to the large energy offset between the MEH-PPV HOMO and ZnO valence band. On the other side, the electrons can be efficiently injected into ZnO NPs from the Al because of the matched ZnO conduction band level and Al work function. However, because

Figure 6-6. Interfacial Auger recombination in ZnO NPs device. (a) Energy level diagram of ZnO NPs device. (b) Interfacial Auger recombination and electron injection process at the MEH-PPV/ZnO NPs interface, which involves 1) interfacial recombination, 2) energy transfer, 3) excitation of hot electron, 4) injection of hot electron across the MEH-PPV/ZnO NPs interface, and 5) radiative recombination in MEH-PPV.
of the 1.2 eV barrier between the MEH-PPV LUMO and ZnO conduction, the electrons will also be blocked at the MEH-PPV/ZnO NPs interface. The blocked electrons and holes will create a strong electric field at the MEH-PPV/ZnO NPs interface under forward bias.

Conceptually, ZnO-based devices should not display very efficient electron injection into the MEH-PPV layer due to the large electron injection barrier at the MEH-PPV/ZnO NPs interface. However, experimental observation of MEH-PPV emission at a driving voltage of 1.36 V suggests that electrons accumulated at the MEH-PPV/ZnO NPs interface can gain additional energy to overcome the 1.2 eV barrier. One possible argument for electron injection at low driving voltage could be that the high energy electrons, which based on the Boltzmann distribution (assuming non-degenerate case), were swept into the MEH-PPV by the strong electric field formed at the MEH-PPV/ZnO NPs interface. Nevertheless, simple calculation suggests the chance of electrons of occupied energy states 1.2 eV above the bottom of ZnO conduction band is approximately $10^{-20}$. By assuming effective density of states in the conduction band at the level of $\sim 10^{19} \text{ cm}^{-3}$, the amount of electrons injected through such a process should only support a maximum $\eta_{\text{EQE}}$ of $\sim 10^{-20} \%$, which is significantly lower than the measured $\eta_{\text{EQE}} = \sim 10^{-3} \%$ at 1.6 V.

To explain the origin of the additional energy for electron injection, we proposed an energy up-conversion process through interfacial Auger recombination at the MEH-PPV/ZnO NPs interface, which is depicted schematically in Figure 6-6b. The electron injection and sequential emission process can be divided into the following steps. First, one electron from the ZnO conduction band and one hole from the MEH-PPV HOMO will recombine, and the energy released will transfer to another electron on the ZnO conduction band. With the additional energy, the hot electron will occupy a higher energy state, from where the hot electron is quickly
swept into the MEH-PPV LUMO by the strong interfacial electric field. The injected electron will recombine with a hole accumulated on the MEH-PPV side and emit a photon. As matter of fact, such an energy up-conversion process through interfacial Auger recombination is not rare, and samples have been observed in a few inorganic heterojunctions.\textsuperscript{179-181} Seidel et. al. reported an energy up-conversion phenomenon in a type-II inorganic heterojunction by optically pumping the heterojunction.\textsuperscript{180} In their case, the accumulated yet spatially separated pools of electrons and holes created through light excitation of the heterojunction is required for efficient Auger recombination to take place. This resembles the scenario in our current MEH-PPV/ZnO NP heterojunction, where pools of electrons and holes are created at the heterojunction through electrical injection. Therefore, it is reasonable to believe such energy up-conversion through the Auger process could be used to explain the ultra low turn-on voltage in the ZnO-based device.

**Comparison of Different ZnO Materials**

In order to understand whether the Auger process is common to the MEH-PPV/ZnO heterojunction or only particular to the current ZnO NPs, we compare effect of different ZnO electron injection layers on the MEH-PPV PLED. Here, three additional types of ZnO are deposited on top of MEH-PPV and their turn-on voltages are compared. The three additional types of ZnO layer involve: 1) ZnO NPs with average particle size of ~5 nm, 2) ZnO layer deposited through sol-gel precursor followed by annealing at 150 °C for 30 minutes to transform the precursor into oxide, 3) electron-beam deposited 15 nm thick continuous ZnO layer. Figure 6-7 shows the TEM image of 5 nm ZnO NPs along with their XRD pattern as well as the tapping mode atomic force microscope (AFM) images of sol-gel ZnO layer. It can be seen that the 5 nm ZnO NPs display similar spherical shape to the 3 nm ZnO NPs, and the XRD pattern indicates these larger particles adopt the same wurtzite structure as that of 3 nm ZnO NPs. The AFM
Figure 6-7. Morphologies of different ZnO materials. (a) Transmission electron microscope (TEM) image of ZnO NPs with 5 nm diameter. Inset: the XRD pattern of same ZnO NPs. (b) Atomic force microscope (AFM) image of ZnO layer prepared through sol-gel precursor. The scale bar is 20 nm and the scanning area is $1.5 \times 1.5 \, \mu m^2$. (TEM image courtesy of Lei Qian)

image, on the other hand, suggests a fairly smooth surface of sol-gel deposited ZnO layer and grains with size as small as ~20 nm can be observed.

With the same device structure but different ZnO electron injection layers, the four MEH-PPV PLEDs display different $J - V$ and $L - V$ characteristics. It can be seen from Figure 6-8a that the devices using ZnO NPs and sol-gel ZnO as electron injection layers have a similar level of current injection at the same voltage, whereas the device with e-beam deposited ZnO layer show significantly lower current injection. The current density is $J = ~9.0 \times 10^{-2} \, mA/cm^2$ in the e-beam deposited ZnO device, which is more than two orders of magnitude lower than the other three devices. The $L - V$ characteristics in Figure 6-8b of the four devices, however, indicate a gradual decrease of the luminance as the ZnO transformed from small nanoparticles to continuous film. The luminance at 9 V for 3 nm, 5 nm ZnO NPs, sol-gel ZnO and e-beam ZnO devices is $L = ~8700$, ~100, ~60 and ~0.08 cd/m$^2$, respectively. Such a decrease of luminance is
Figure 6-8. Performance of device with different ZnO electron injection layer. (a) Current density-voltage ($J - V$) and (b) luminance-voltage ($L - V$) characteristics. Inset: normalized EL spectra ZnO NPs, sol-gel ZnO and e-beam ZnO device.

achieved without significant change of EL spectra of the devices (see inset). Quite surprisingly, the ultra low $V_T$ phenomenon does not appear in the devices using larger ZnO NPs, sol-gel and e-beam deposited ZnO as electron injection layer. The $V_T$ actually increases from 1.36 V in 3 nm
Temperature Dependence of Turn-on Voltage

In this part, the temperature dependence of the $J - V$ and $L - V$ characteristics of the device using 3 nm ZnO NPs as electron injection layer is investigated, while behavior of device using LiF/Al as cathode under the same conditions is also recorded for comparison. The temperature study is conducted in a low vacuum cryostat cooled by liquid nitrogen. The temperature of the device is monitored by a thermocouple and a temperature controller is used to accurately control the temperature to be ± 0.1 K within the setpoint. During the measurement, the temperature is gradually increased from 177 K to 357 K, and the $J - L - V$ scan of the device is executed 2 minutes after temperature becomes stable at the setpoint. Figures 6-9a and b is the comparison of the $J - V$ characteristics of the ZnO NPs based device and that of the LiF device. Both devices displayed improved current injection as the temperature increased, and such improvement becomes less significant as the temperature goes beyond 297 K. In the LiF based device, the $J - V$ curves display two distinct regimes: $J \propto V$ (ohmic regime) at the low voltage and $J \propto V^n$ ($n > 2$) at high voltage. And the transition point between the two regimes decreases from 2.4 V at 179 K to 1.4 V at 357 K. On the other hand, the ZnO NP device always shows higher current injection than the LiF based device at the same temperature, especially at voltage of $V < 2$ V. Even though the ZnO NP based device displays a similar ohmic regime at low voltages, the range of the regime with $J \propto V^n$ ($n > 2$) characteristic is much smaller. The transition point between the two regimes is much lower than the LiF based device, which is “pinned” at 0.8 V when temperature $T > 297$ K. Moreover, for the ZnO NP based
device, the $J - V$ curves show fast transition to space-charge limited (SCL) regime ($J \propto V^2$) at high voltages when temperature $T > 297$ K.

The temperature dependent $L - V$ characteristics of the two devices are shown in Figure 6-10a and b. The ZnO NP based device shows improved luminance as the temperature increases from 177 K to 357 K, whereas the luminance from the LiF based device actually decreases as the
Figure 6-10. Temperature dependence of luminance-voltage ($L - V$) characteristics of (a) ZnO NPs and (b) LiF device. Inset: comparison of turn-on voltage as function of temperature of the two devices.

Temperature increases when $T > 297$ K. The decrease of luminance at elevated temperatures in the LiF device may result from the fast degradation of the MEH-PPV/LiF interface. The decrease of luminance at elevated temperatures in the LiF device may result from the fast degradation of the MEH-PPV/LiF interface.167 Inset of figure 6-10 compares the $V_T$ of the two devices as function of the temperature. In the current case, the threshold for $V_T$ is set to be 1 cd/m$^2$ due to the different luminance measurement geometry inside the cryostat. For LiF based device, the $V_T$ decreases from 4.2 V at 177 K to 2.2
V at 357 K, whereas the $V_T$ decreases from 2.9 V at 177 K to 1.25 V at 357 K for ZnO NP based device. Notably, $V_T$ become almost unchanged when $T > 300K$ for both devices.

**Electron-only Device**

The current interfacial Auger recombination model requires the presence of a high density of electrons and holes at the MEH-PPV/ZnO NPs interface so that the three-particle process (two electrons and one hole) can effectively take place. Therefore, by significantly reducing the density of one type of charges at the interface, the Auger recombination rate will become much lower, leading to reduced electron current coming from such a process. Based on this consideration, electron only devices are fabricated to probe the validity of above assumption.

The two electron-only devices comprise Al/MEH-PPV (80 nm)/ZnO NPs (40 nm) or LiF (1 nm)/Al deposited in sequence. Here, Al is used as anode to prevent hole injection into the MEH-PPV layer. The inset of Figure 6-11 shows the energy level diagram of the ZnO NPs based electron-only device. Under forward bias, electrons will accumulate at MEH-PPV/ZnO NPs interface. Since the hole density is much lower at the interface in this scenario, the interfacial Auger recombination rate is suppressed.

Figure 6-11 shows the $J – V$ characteristics under forward bias of the two electron-only devices along with that of the two normal bipolar MEH-PPV PLEDs with ITO/PEDOT:PSS as anode. It is found that both electron-only devices display much lower current density than the bipolar ones due to the absence of hole current. It is noted that without the hole current, the ZnO NP based electron-only device actually has even lower electron current than the LiF based device. For instance, at $V = 1.5$ V the current density reduces from $J = 0.85$ mA/cm$^2$ in the normal PLEDs to $J = 4.1 \times 10^{-6}$ mA/cm$^2$ in the electron-only device for ZnO NPs, whereas it reduces from $J = 6.5 \times 10^{-4}$ mA/cm$^2$ to $J = 8.9 \times 10^{-5}$ mA/cm$^2$ for LiF based devices. This
Figure 6-11. Current density-voltage ($J - V$) characteristics of ZnO NPs and LiF electron-only device. $J - V$ characteristics of bipolar devices are shown for comparison. Inset: energy level diagram of ZnO NPs electron-only device.

suggests that without the hole current, electrons accumulated at the MEH-PPV/ZnO NPs interface cannot obtain additional energy from the Auger recombination to jump over the interfacial barrier, which leads to such reduced current density. Plus, the Auger recombination itself in the bipolar device will also contribute to a certain portion of the forward current density. Moreover, the lower electron current device reflects that the electron injection barrier is actually higher in the ZnO NP based than that in the LiF based device, in which an interfacial dipole layer is formed to reduce injection barrier.\(^{167}\)

**Discussion**

In the current study, an electron injection layer composed of ~ 3 nm ZnO nanoparticles is applied to a MEH-PPV PLED to successfully reduce the turn-on voltage of the device. It is
proposed that an interfacial Auger recombination is responsible for the ultra low $V_T$. As a matter of fact, the interfacial Auger recombination has been reported in a number of inorganic or even organic heterojunction, such as InP/AlInAs, rubrene/C$_{60}$ heterojunction. Nevertheless, observation of the Auger process at the organic/inorganic interface is rare.

Owing to the negligible hole (electron) injection barrier at the PEDOT:PSS/MEH-PPV (ZnO NPs/Al) interface and large energy barrier at the MEH-PPV/ZnO NP heterojunction, charges of opposite signs can accumulate at the interface under low forward bias ($V < 1.5$ V). Electrons from the ZnO NPs and holes from MEH-PPV can form interfacial charge transfer (CT) state excitons, or say, exciplex. The energy released from the recombination of CT excitons is subsequently transferred to another electron on the ZnO NPs through a resonant process. One important observation in the current MEH-PPV/ZnO NPs heterojunction is that the appearance of interfacial Auger recombination strongly depends on the size of the ZnO NPs. The current minimum 3 nm ZnO NPs still have a size larger than the Bohr radius of ZnO ( ~ 1.4 – 1.8 nm) and strong quantum confinement effect should not be expected. Nevertheless, the reduced particle size does provide a higher surface area-to-volume ratio and increased density of surface states. These surface states can serve as electron trapping centers. Therefore, the increased density of trapped electrons could result in more efficient resonant energy transfer in the reduced size ZnO NPs, in which the coupling between the interfacial CT exciton and the electrons is stronger. As the particle size increases, the energy may release in the form of heat instead of transferred to the electron, which is less confined. This is indirectly proven in Figure 6-7a and b, where devices with different size of ZnO NPs display fairly similar $J – V$ characteristics but significantly different $L – V$ performance.
Temperature study of the ZnO NP based device reveals that the current density increases as the temperature increases, a similar trend is also observed in LiF based device. This could be partially due to the common hole injection process at the PEDOT:PSS/MEH-PPV interface through thermionic emission. Nevertheless, the transition point between the two regimes (ohmic regime and $J \propto V^n (n > 2)$) on $J - V$ curves of LiF based device is sensitive to temperature, and it shifts to lower voltages as the temperature increased. On the other hand, the transition point on $J - V$ curves of ZnO NP based devices is pinned at 0.8 when $T > 297$K, which support the fact that the interfacial Auger recombination is less sensitive to the temperature as long as sufficient charges are built up at the interface. Even though both ZnO NPs and LiF based devices display similar trends on the $V_T$ versus temperature, the consistently lower $V_T$ in ZnO NPs under the same temperature may suggest the presence of the Auger process, which is insensitive to temperature. Finally, investigation of electron-only devices further confirms the electron injection through the interfacial Auger recombination. By removing the hole accumulation at the MEH-PPV/ZnO NPs interface, the Auger recombination rate is significantly reduced. And the current density shows approximately five orders of magnitude reduce in ZnO NPs device compared to only one order of magnitude change in the LiF device. Such abnormal yet significant reliance of electron injection on hole current may only be explained by the Auger process at the MEH-PPV/ZnO NPs interface. A more direct way to probe the validity of the Auger process may involve transient absorption measurements of the interfacial CT excitons and the hot electrons on ZnO NPs, from which their corresponding lifetime can be extracted as well.

**Conclusions**

In this chapter, we demonstrated ultra low turn-on voltage can be achieved in MEH-PPV PLED by using ZnO nanoparticles as electron injection layer. The ultra low turn-on voltage can be explained by Auger recombination assisted electron injection at the MEH-PPV/ZnO NPs...
interface. Such an electron injection process is peculiar to the current material system, which allows both electrons and holes to accumulate at the MEH-PPV/ZnO NPs heterojunction. ZnO NP size dependence of the turn-on voltage suggest strong coupling of electrons and CT excitons are required for efficient energy transfer during the Auger process. Temperature study and the electron-only device further support the hypothesis of interfacial Auger recombination for assisting electron injection. The current ZnO NPs can be applied to a variety of polymer light-emitting devices and pave a new way to achieve low turn-on voltage through Auger-assisted electron injection.
CHAPTER 7
CONCLUSIONS AND FUTURE WORK

Conclusions

The rapid development of knowledge in the field of organic electronics has facilitated the transformation of lab-based research into commercial products. Nevertheless, there are still many issues need to be addressed before mass production of organic electronic devices. The work presented in this thesis has focused on investigation of novel material processing techniques and device architectures for efficient organic optoelectronic devices. Of particular interest, organic photovoltaic (OPV) cells and organic light-emitting diodes (OLEDs), both of which are on the edge of commercialization, are extensively studied.

Even though donor-acceptor mixed bulk heterojunctions (BHJ) have been widely accepted for improving the efficiency of OPV cells, the thermodynamics and kinetics process behind the formation of nanoscale phase separated mixed BHJ is still not clear. Molecular dynamic (MD) simulation combined with experimental investigation of pentacene:C$_{60}$ mixtures reveals that the intermolecular interaction plays an major role on determining the degree of phase separation in the mixture (Chapter 3). And the strong interaction between pentacene molecules leads to large aggregates, which reduce exciton diffusion efficiency. Although processing conditions may still be varied to manipulate the degree of phase separation, the controllability is quite limited. Based on the knowledge obtained from study of pentacene:C$_{60}$ mixtures, we show in Chapter 4 that interdigitated BHJ composed of organic nanorod grown by oblique angle deposition (OAD) can overcome the disadvantages present in the molecular mixed BHJ and, at the same time, provide efficient exciton diffusion and charge collection. Copper phthalocyanine (CuPc) nanoaggregates with different morphology are obtained by control the incident angle, substrate rotation and deposition rate during the OAD process. It is found that the optimized interdigitated BHJ
composed of vertical aligned CuPc nanorod and infiltrated PCBM show twice higher efficiency than the CuPc/PCBM planar heterojunction device.

Deep blue phosphorescent OLEDs (PHOLEDs) are studied in Chapter 5. Due to high triplet energy of the blue phosphorescent emitter, it is crucial to secure good exciton confinement by using high triplet energy charge transport layers. On the other hand, improved charge confinement with EML can be obtained by increasing the energy offset between the LUMO or HOMO of EML and that of the adjacent layers. For practical application of OLEDs, high power efficiency of the device is more concerned. Using p- and n-doped organic layer can significantly reduce the driving voltage due to lower charge injection barrier at the metal-organic interface and increased conductivity of charge transport layer. Polymer light-emitting diodes (PLEDs), which is another important category of OLEDs, have advantage of solution processability. In Chapter 6, an electron injection layer composed of ZnO nanoparticles is inserted between the MEH-PPV and the Al to significantly reduce the turn-on voltage. The observed ultra low turn-on voltage is attributed to the efficient electron injection through an Auger recombination at the MEH-PPV/ZnO NPs interface.

The work presented in this thesis is to understand the physical process behind the formation of different organic nanostructure for efficiency OPV cells as well as operation principle of novel device architecture for efficiency OLEDs. Fruitful results are obtained from the current research work, which is helpful for future fabrication of efficient and low-cost OPV cells and OLEDs.

**Future Work**

Based on the knowledge obtained from the work present in this thesis, there is future research that can be conducted to expand the existing work so that large-area, low-cost efficient OPV cells and OLEDs can realized.
Control Growth of Organic Nanostructure

The organic photovoltaic (OPV) cells have been long viewed as a renewable energy to replace the current fossil fuels due to their potential to provide inexpensive and abundant electrical power from the sun, while generate zero emission of greenhouse gases. Even though the power conversion efficiency of OPV cells has been improved to more than 5% over the past two decades, it is still below the requirement for wide commercialization of OPV cells. In this thesis, we demonstrated that control growth of donor-acceptor (D-A) nanostructure is crucial to achieve both efficient exciton diffusion and charge collection so that enhanced OPV cell efficiency can be obtained (Chapter 3 and 4). With the acquired knowledge, there is a number of other ways to better control the formation of desired organic nanostructure, where both efficient exciton diffusion and charge collection can be achieved.

As we have learned in the study of pentacene:C\textsubscript{60} mixtures and OAD grown CuPc nanorods, the surface and bulk diffusivity of the molecules can strongly affect the morphology of the nanostructure. Since the surface diffusivity of the molecule can be affected by the deposition rate, the large portion of the work in this thesis has been focusing on the nanostructure morphology dependence on deposition rate. Nevertheless, another factor that deserves investigation is the substrate temperature, which strongly influences both surface and bulk diffusion of molecule. Low substrate temperature will suppress the diffusion of molecule and induce less segregated structure in the D-A mixtures or reduced nanorod diameter during OAD process. It is believed that different nanostructure can be grown by varying the substrate temperature and deposition rate over a large range.

Another way to control the formation of certain organic nanostructure involves utilizing pre-existing template. Figure 6-1a shows the AFM image of 10 nm pentacene:tetracene mixed film and SEM images of gold nanoparticle deposited on top of the ITO substrate. It can be seen
that the pentacene:tetracene mixed film display a surface morphology with uniformly distributed domains with 50 – 70 nm. Figure 7-1b, on the other hand, shows the Si nanorod arrays achieved by inductively coupled plasma (ICP) ion etching the Si substrate using Au nucleation as masks. Both nanostructured thin films can be used as a template to replace the intrinsic nucleation layer during OAD process so that desired nanorod diameter and packing density can be obtained when appropriate incident angle and surface diffusivity are provided.

**Organic Light-Emitting Diodes**

The research on OLEDs has gained fruitful results over the past decade with commercial viable product appeared on the market already. Phosphorescent OLEDs (PHOLEDs) have been considered as the most promising technology due to their capability to achieve nearly 100% internal quantum efficiency. In this thesis, we found that improved exciton and charge blocking is crucial to achieve high quantum efficiency, whereas doped charge injection layer can significantly reduce the driving voltage, leading to higher power efficiency.
Nevertheless, there are a few challenges need to be addressed in the current deep-blue PHOLEDs. For the practical application of OLEDs, the power efficiency at high luminance is more relevant (100 cd/m² for display and 1000 cd/m² for lighting). However, the fast roll-off of efficiency curves observed in the current p-i-n device results in low power efficiency at high luminance. This fast roll-off is mainly attributed to the imbalanced injection of electrons and holes. One way to address this issue is to control the doping concentration in the n- and p-doped injection layer so that more balance injection of opposite charges can be maintained at high luminance. This could partially address the issue of fast roll-off in the efficiency curve observed in p-i-n devices.

Since 3 nm ZnO nanoparticles (NPs) can be used as efficient electron injection layer to significantly reduce the turn-on voltage of MEH-PPV PLED, it is worth applying such ZnO NPs on other types of PLEDs to see the reduction of turn-on voltage. In the current study, a few experiments have been conducted to demonstrate the presence of Auger recombination at the MEH-PPV/ZnO NPs interface. Nevertheless, a more direct proof of such process requires transient absorption measurement to confirm the existence of interfacial charge transfer (CT) excitons or excited hot electrons generated by the Auger process and their lifetime as well.

**Afterword**

Instead of competing with the existing inorganic electronic device, the future of organic electronics lies in the fabrication of high-efficiency, low-cost and large-area devices with reasonable lifetime. The works presented in this thesis have paved the way to this goal so that organic photovoltaic cells and organic light-emitting diodes with improved efficiency are achievable.
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BIOGRAPHICAL SKETCH

Ying Zheng was born in Guangzhou, China in 1982. As a son of the People’s Liberation Army (PLA) officer, he lived a happy childhood in the biggest military base in South China and finished his primary school in 1995. He graduated from Zhixin High School in 2001.

With his outstanding academic performance, he graduated *summa cum laude* from South China University of Technology in 2005 with a Bachelor of Engineering majored in polymer science and engineering. In fall 2005, he started his graduate study in Department of Materials Science and Engineering at University of Florida. With research topics on organic photovoltaic cells and organic light-emitting diodes, he is the author and co-author of ten journal publications. In 2009, he received his Doctor of Philosophy in materials science and engineering under the supervision of Prof. Jiangeng Xue.