Growth and characterization of organic/inorganic thin films for photonic device applications

Jon Wai Yu Sit
Hong Kong Baptist University

Follow this and additional works at: https://repository.hkbu.edu.hk/etd_oa

Recommended Citation
Sit, Jon Wai Yu, "Growth and characterization of organic/inorganic thin films for photonic device applications" (2015). Open Access Theses and Dissertations. 179.
https://repository.hkbu.edu.hk/etd_oa/179

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at HKBU Institutional Repository. It has been accepted for inclusion in Open Access Theses and Dissertations by an authorized administrator of HKBU Institutional Repository. For more information, please contact repository@hkbu.edu.hk.
Growth and Characterization of Organic/Inorganic Thin Films for Photonic Device Applications

SIT Wai Yu

A thesis submitted in partial fulfilment of the requirements

for the degree of

Master of Philosophy

Principal Supervisor: Prof. SO Shu kong

Hong Kong Baptist University

May 2015
Declaration

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

Signature:_________________

Date: May 2015
Abstract

Thin film transistors (TFTs) can be used to determine the bulk-like mobilities of amorphous semiconductors. Different organic hole transporters (HTs) are under investigation including spiro-TPD, 2TNATA, NPB and TPD which are commonly used in organic light-emitting diodes (OLEDs). In addition, we also measure the TFT hole mobilities of two iridium phosphors: Ir(ppy)$_3$ and Ir(piq)$_3$. These materials were grown on two different gate dielectric surfaces which were SiO$_2$ and polystyrene (PS). On SiO$_2$, the TFT mobilities are found to be 1-2 orders smaller than the bulk hole mobilities as evaluated independently by time-of-flight (TOF) technique. On the other hand, on PS gate dielectric layer, the TFT mobilities of these hole transporters are found to be in good agreement with TOF data. A thickness dependence measurement was carried out on TFT with PS. We found that only 10nm of organic semiconductor is sufficient for TFTs to achieve TOF mobilities. We further investigate why organic semiconductors on SiO$_2$ have such huge reduction of mobilities. Temperature dependent mobility measurements were carried out and the data were analyzed by the Gaussian Disorder Model (GDM). We found that on SiO$_2$ surface, when compared to the bulk values, the energetic disorders ($\sigma$) of the HTs increase and simultaneously, the high temperature limits ($\mu_\infty$) of the carrier mobilities decrease. Both $\sigma$ and $\mu_\infty$ contribute to the reduction of the carrier mobility. The increase in $\sigma$ is related to the presence of randomly oriented polar Si-O bonds. The reduction of $\mu_\infty$ is topological in origin and is related to the orientations of the more planar molecules on SiO$_2$. The more planar molecules tend to lie horizontally on the surface and such orientation is unfavorable for charge transport in TFT configuration.

Hybrid organic/inorganic perovskites have emerged as an outstanding material for photovoltaic cells. In the second part of this work, we setup a repeatable
perovskite recipe and optimized the system under different conditions. Under certain circumstances, a perovskite solar cell with power conversion efficiency ~9% can be achieved with PEDOT:PSS as hole transporting layer with the conventional structure.
Acknowledgements

I would like to express my sincere gratitude to all the people who have given their support of my M. Phil study and research.

I would like to thank Prof. S. K. So, my principle supervisor, for giving me a precious chance to study in his research group even I was not his project student during my undergraduate studies. I am extremely thankful and indebted to him for his patience, motivation, excellent guidance, and providing me with an excellent atmosphere for doing research.

Co-workers in laboratory T916, Kevin Chan, Cyrus Chan, Harrison Lee, Ken Tsung, Ken Cheung, Winky Leung, Carr Ho, Anson Hung, Yin Hang, Rocky Chan, and Cyrus Yiu, for their help and support. It would have been a lonely lab without them.

Mr. W. H Choi in T911 who gave me guidance and advises in my research.

Mr. Thomas Yeung, for the maintenance of instruments and technical supports.

Mr. Edward Chan, Mr. Benson Leung for teaching and supporting in the X-ray deflection and scanning electron microscope experiments and analysis.

Last but not least, my parents, my brother. They always support me and encourage me with their best wishes.
Table of Contents

Declaration.................................................................................................................I
Abstract.....................................................................................................................III
Acknowledgements..................................................................................................V
Table of Contents......................................................................................................VI
List of Figures............................................................................................................IX
List of Tables...........................................................................................................XII

Chapter 1 Introduction..............................................................................................1
  1.1 Background ........................................................................................................1
  1.2 Organic materials .............................................................................................1
  1.3 Applications and recent studies in organic semiconductors .........................4
  1.4 Motivations for this thesis work .....................................................................7

Chapter 2 Fundamental Concepts..........................................................................13
  2.1 Charge transport in organic semiconductor ..................................................13
    2.1.1 Introduction to organic semiconductors ...................................................13
    2.1.2 Molecular orbitals ....................................................................................14
    2.1.3 Hopping and Poole-Frenkel models .........................................................14
    2.1.4 Gaussian Disorder Model .......................................................................17
  2.2 Charge injection in organic semiconductor ...................................................20
  2.3 Theory of organic thin film transistor ..............................................................22
    2.3.1 Organic thin film transistor (OTFT) ..........................................................22
    2.3.2 Structures of organic thin film transistors .................................................22
    2.3.3 The I-V characteristics ............................................................................23
    2.3.4 Threshold voltage ......................................................................................24
    2.3.5 Current-voltage characteristics of OTFTs .................................................25
  2.4 Some limitations of organic thin film transistors ............................................27
    2.4.1 Hysteresis ................................................................................................27
    2.4.2 Charge transport direction ......................................................................28
  2.5 Hybrid organic/inorganic perovskite solar cells ......................................29
    2.5.1 Characterization of solar cells ..................................................................31
4.3.6.2 Electroluminescent properties

Chapter 5 Hybrid organic/inorganic perovskite solar cells

5.1 Introduction
5.2 Experimental Details
5.3 Result and discussion
  5.3.1 Structural and optical characterizations
  5.3.2 Optimization of perovskite solar cell
    5.3.2.1 Optimization of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ annealing duration
    5.3.2.2 Optimization of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ spin speed
    5.3.2.3 Optimization of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ annealing temperature
    5.3.2.4 Employing other hole transporting layer
  5.3.3 Importance of ZnO buffer layer
  5.3.4 Future improvements
    5.3.4.1 Replacing hole transporting layer
    5.3.4.2 Thermal evaporation of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ layer
    5.3.4.3 Inverted structure
  5.4 Summary

Chapter 6 Conclusion

Curriculum Vitae
List of Figures

Fig. 1.1 Curved TV introduced by Samsung in 2014. ............................................ 5
Fig. 1.2 A flexible organic solar cell ........................................................................ 6
Fig. 1.3 OTFT-driven OLED display developed by Sony ........................................ 7
Fig. 2.1 Hopping conduction in an organic semiconductor ..................................... 15
Fig. 2.3 Energy diagrams of organic/metal interfaces .............................................. 21
Fig. 2.6 Transfer characteristics with hysteresis in an OTFT .................................. 28
Fig. 2.7 Charge transport direction in OTFTs and OPVs ........................................ 29
Fig. 2.9 Working principles of a perovskite solar cell .............................................. 31
Fig. 2.10 J-V characteristics of a perovskite solar cell ............................................ 33
Fig. 2.11 Equivalent circuits for a solar cell ............................................................. 35
Fig. 2.12 Crystal structure of ABX$_3$ perovskite .................................................... 36
Fig. 2.13 I-V characteristics of a solar cell with hysteresis ...................................... 37
Fig. 3.1 Chemical structures of NPB and Ir(ppy)$_3$ ............................................... 41
Fig. 3.2 Chemical structures of MAI and PbCl$_2$ .................................................... 43
Fig. 3.3 Experimental setup of sublimation ............................................................. 44
Fig. 3.4 Top view of a silicon dioxide wafer ............................................................ 45
Fig. 3.5 ITO substrate used for OPV measurements ................................................. 47
Fig. 3.6 Schematic diagram showing the procedures of spin-coating ...................... 50
Fig. 3.7 Circular and square mounts used in thermal evaporation ......................... 52
Fig. 3.8 Schematic diagram of J-V measurements of a solar cell ............................ 53
Fig. 3.9 Schematic diagram of output current measurement of OTFTs .................. 55
Fig. 3.10 Middle diagram represents typical data obtained from the setup ............ 57
Fig. 4.1 Chemical structures and the HOMO values of four organic amine-based hole transporters, and two iridium-based compounds, Ir(piq)$_3$, and Ir(ppy)$_3$ ........................................ 61
Fig. 4.2 Bottom gate top contact TFT device structure ......................................... 63
Fig. 4.3 (a) Typical TFT output characteristics for NPB grown on SiO₂ and on PS gate dielectric layers. (b) TFT transfer characteristics of NPB transistors grown on SiO₂ and on PS. The data were taken at a Vds = -60V.

Fig. 4.4 Transfer characteristics of four amine-based compound.

Fig. 4.5 Bar graphs of TOF (dotted line), linear and saturation mobilities for all the amine-based compounds.

Fig. 4.6 Thickness dependent NPB hole mobilities.

Fig. 4.7 Temperature dependent TFT-derived mobilities data for all the four amine-based compounds analyzed by the GDM model.

Fig. 4.8 AFM images of NPB films on PS.

Fig. 4.9 AFM images of NPB films on SiO₂.

Fig. 4.10 Molecular orientations of NPB on SiO₂ and PS.

Fig. 4.11 3-D molecular structures of NPB and spiro-TPD.

Fig. 4.12 a) 3-D molecular structure of Ir(piq)₃ b) Transfer characteristics of Ir(piq)₃ and NPB on PS and SiO₂ gate dielectric layers.

Fig. 4.12 Temperature dependent measurement of Ir(ppy)₃ and Ir(piq)₃ on PS and SiO₂.

Fig. 4.14 Chemical structure of BAnF derivatives and mADN.

Fig. 4.15 Transfer characteristics of BAnF derivatives and mADN.

Fig. 4.16 EL spectra of DPAVBi and C545T-doped devices at 8V.

Fig. 4.17 J-V characteristics and the external quantum efficiency (EQE) of four devices.

Fig. 5.1. Energy diagram of a perovskite solar cell.

Fig. 5.2 XRD pattern of a thin film of CH₃NH₃PbI₃-xClₓ.

Fig. 5.3. SEM image of a thin film of CH₃NH₃PbI₃-xClₓ thin film.

Fig. 5.4. PDS spectrum of a thin film of CH₃NH₃PbI₃-xClₓ.

Fig. 5.5. PDS spectrum of thin film of CH₃NH₃I (MAI).

Fig. 5.6 J-V characteristics of CH₃NH₃PbI₃-xClₓ solar cell with different annealing durations at 90°C.
Fig. 5.7 J-V characteristics of CH₃NH₃PbI₃₋ₓClₓ solar cells prepared at different spin speeds.................................................................110

Fig. 5.8 J-V characteristics of CH₃NH₃PbI₃₋ₓClₓ solar cells prepared at different annealing temperature ..................................................................................112

Fig. 5.9 Performance of the perovskite solar cells prepared at different annealing temperatures........................................................................................................113

Fig. 5.10. a) Chemical structures of MoO₃ and HAT-CN. b) Energy levels of MoO₃, HATCN and perovskite .........................................................................................114

Fig. 5.11 J-V characteristics of CH₃NH₃PbI₃₋ₓClₓ solar cell with PEDOT:PSS, MoO₃, and HAT-CN as HTL........................................................................................................115

Fig. 5.12 SEM images of perovskites on MoO₃ and on PEDOT:PSS layers… ....117

Fig. 5.13 J-V characteristics of perovskite solar cells with or without ZnO .........118
List of Tables

Table 1.1 Examples of organic small molecules and polymers ........................................... 3
Table 2.1 Work functions of metals ...................................................................................... 22
Table 2.2 Commonly used ions in perovskite solar cell ......................................................... 36
Table 3.1 HOMO and LUMO energy levels of NPB and Ir(ppy)3 ......................................... 42
Table 3.2 Chemical names and structures of solvents and solutes used in this thesis ............ 49
Table 4.1 Energetic disorders and high temperature limits of the mobility obtained from TFT and TOF techniques .......................................................................................... 75
Table 4.2 $\mu_\infty$ and average hopping distances of all amine compounds on PS and SiO$_2$ surfaces as computed by Eq.(4.6). ....................................................................................... 76
Table 4.3 HOMO, LUMO and optical bandgaps of BAnF and mADN .................................. 88
Table 4.4 Hole mobilities of the BAnF derivatives and mADN .............................................. 90
Table 4.5 Electroluminescence performance of OLED devices ........................................... 94
Table 5.1 CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (perovskite) properties ...................................................... 98
Table 5.2 Approximate wavelength of C-H and N-H vibrations .......................................... 106
Table 5.3 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different annealing durations at 90°C ................................................................................................. 108
Table 5.4 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different spin-speeds ................................................................................................................................. 110
Table 5.5 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different annealing temperatures ........................................................................................................ 112
Table 5.6 Performances of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells with PEDOT:PSS, MoO$_3$, and HATCN as HTL .................................................................................................................. 116
Table 5.7 Device performances of the perovskite solar cell with or without ZnO ............... 118
Chapter 1 Introduction

1.1 Background

The research of organic semiconductors began in the early 1960s.\cite{1} However, activities remained quite limited. Then in 1977, a seminal discovery was made by Alan Heeger and his co-workers. They reported a high electrical conductivity in polymer, polyacetylene.\cite{2} Because of this discovery, they were awarded the Nobel Prize in Chemistry in 2000. Since then, many groups considered using organic materials in electronic devices.\cite{3,4} In 1980s, Ching Tang and Steven van Slyke in Kodak invented efficient thin film light emitting diodes (OLEDs) which employed organic molecules by tris(8-hydroxyquinolinate)aluminum (Alq3) and aromatic diamine.\cite{5,6} Based on this work, Samsung and LG invested on OLEDs development. Nowadays, these two companies have embraced OLED technology and integrated OLED displays in their cell phones and televisions. In this chapter, we will explore the nature of organic semiconductors and their general applications.

1.2 Organic materials

Organic semiconductors are hydrocarbon based materials. There are generally two classes of organic semiconductors: (1) conjugated polymers or (2) small molecules containing conjugated $\pi$-bonds. Many organic semiconductors are aromatic based compounds. Table 1.1 shows, as examples, the two very important chemical
structures and their related compounds that are commonly used in organic electronic devices. Thiophene, triphenylamine, and carbazole (not shown in Table 1.1) are being used widely because of their excellent electrical and optical properties.\textsuperscript{[7–10]} Major applications of these organic materials can be found in organic light emitting diodes (OLEDs), organic solar cell (OPVs), organic thin film transistors (OTFTs), and organic sensors.
<table>
<thead>
<tr>
<th>Chemical Groups</th>
<th>Common organic molecules/polymers</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td><img src="image" alt="PEDOT:PSS" /></td>
<td>OPV[^11]</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="P3HT" /></td>
<td>OLED[^12]</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="PCDTBT" /></td>
<td>OPV[^13]</td>
</tr>
<tr>
<td>Triphenylamine</td>
<td><img src="image" alt="NPB" /></td>
<td>OLED[^14]</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="TPD" /></td>
<td>OPV[^16]</td>
</tr>
</tbody>
</table>

Table 1.1 Examples of organic small molecules and polymers that were commonly used in different applications

[^11]: Reference 11
[^12]: Reference 12
[^13]: Reference 13
[^14]: Reference 14
[^15]: Reference 15
[^16]: Reference 16
1.3 Applications and recent studies in organic semiconductors

Electronic devices using organic semiconductors have many advantages. They are light in weight, flexible, solution processable, and compatible with large area processing. There are two approaches to deposit thin films of organic semiconductors. First, organic materials, if they are in the forms of small molecules, can be deposited by vacuum evaporation. Large vacuum chambers are required which greatly increase the cost of fabrication. Second, molecules or polymers can be dissolved in a solvent. Thin films can be deposited by spin-coating, spray coating, roll-to-roll coating, and blade coating.\[^{17}\] By employing solution processing, organic devices are expected to be cheaper in the future. Below, we very briefly review different classes of organic electronic devices.

First, organic light emitting diodes (OLEDs) are electroluminescent (EL) devices. The organic based light emissive layers are sandwiched between two electrodes. When a potential difference $V$ is applied between electrodes, holes and electrons in the organic semiconductor recombine to emit light. Flexible or curved devices are possible to fabricate due to the flexibility of organic materials. Companies like LG and Samsung already invested their research in OLEDs in the past decade. In the past
two years, the development of organic display technologies accelerate. LG and Samsung introduced their new curved OLED TV in 2014 (Fig. 1.1).

![Curved TV introduced by Samsung in 2014](image)

Fig. 1.1 Curved TV introduced by Samsung in 2014.\[18\]

Secondly, organic photovoltaic cells (OPVs) are devices that convert sunlight into electricity. When the device is illuminated under the sun or a suitable light source, photogenerated holes and electrons inside the device will diffuse towards the anode and cathode, respectively. Photocurrent is then generated from the device. Organic solar cells utilize the green and renewable solar energy and they offer a very appealing application of organic semiconductors. Fig. 1.2 shows a flexible organic solar cell. In 2013, H. J. Snaith made use of organic/inorganic hybrid materials to fabricate perovskite solar cells which yielded 12.2% power conversion efficiency (PCE).\[19\] Since then, up to 20.1% PCE has been reported in the field.\[20\] Since the
perovskite solar cells are low cost, solution processable, and they do not require high temperature processing, the research in perovskite solar cell is still expanding very rapidly. However, in a typical perovskite solar cell involve lead, which is, an environmental unfriendly heavy metal. It is still a hindrance to employ organic/inorganic hybrid perovskite solar cell to real-life applications.

Fig. 1.2 A flexible organic solar cell.[21]

Besides OLEDs and OPV cells, organic thin film transistors (OTFTs) are under steady investigations. A TFT employs an organic semiconductor as the active material. It has three electrodes: source, drain, and gate electrodes. The current can flow from source to drain via the organic layer. The current can be controlled by the voltage applied on the gate electrode. OTFTs employing high mobility organic materials have been reported in the recent researches.[22,23] Nowadays, OTFTs can be used as fast
switches. Besides, OTFTs are found important applications in organic sensors.[24,25]

Sensing devices can be printed on an array of substrate and they can determine the concentration of certain target analytes in the sample.[25] Fig. 1.3 shows the OTFT-driven OLED display developed by Sony.

Fig. 1.3 OTFT-driven OLED display developed by Sony.[26]

1.4 Motivations for this thesis work

In organic materials, charge transport properties are of paramount importance in order to understand the operations of organic electronic devices such as OPVs and OLEDs. Many techniques have been established to measure charge transport properties. Among these techniques, time-of-flight (TOF) is the most reliable.[27] In TOF, free charge carriers are optically generated by a laser. So, there is no contact or injection problems. However, TOF measurement requires a thick film of few microns and consumes a lot of material for measurement. Therefore, other techniques such as
dark injection space charge limited current (DI-SCLC),\[^{28}\] admittance spectroscopy (AS), \[^{29}\] and organic thin film transistors (OTFTs) \[^{30}\] have been used to probe mobilities with reduced material consumption. Chapter 4 of this thesis describes an alternative approach of using an OTFT to probe the bulk carrier transport of organic semiconductors. Because the conducting path of an OTFT usually within the first few monolayers above the gate dielectric,\[^{31}\] we are able to show TOF mobility can be achieved in TFT configuration, but in much reduced film thickness. The second part of this thesis describes an initial attempt to develop and characterize hybrid organic/inorganic perovskite solar cells. Perovskite solar cells with high efficiencies emerged within 5 years and by now have already achieved a PCE exceeding 20%.\[^{20}\] Perovskite material possess excellent optical and electrical properties such as small bandgap, low binding energy, and high ambipolar mobilities.\[^{32-34}\] Since organic/inorganic hybrid perovskite solar cell is a novel material to achieve ultrahigh PCE, we hope to develop a reliable recipe to fabricate the perovskite solar cell in a simple, and a conventional structure with acceptable PCE.

This thesis is organized as follows. Fundamental concepts of organic electronics and the experimental details will be outlined in Chapter 2 and Chapter 3 respectively. In depth investigation of charge transport properties of thin film transistors will be discussed in Chapter 4. We discovered that after employing PS as gate dielectric layer,
one can probe bulk mobilities of organic semiconductors in TFT configuration. By varying the film thickness of the active layer in TFT, we investigated the hole mobility, film morphology, and molecular orientation of organic semiconductors on polar or non-polar surfaces. Transport properties of planar molecules and 3-D molecules will be discussed. In Chapter 5, the structural, and electrical properties of organic/inorganic perovskite material will be examined, and a repeatable recipe of perovskite solar cell will be outlined. Different fabrication conditions were explored to optimize the solar cell to ~9% PCE. Finally, a detailed conclusion will be drawn in Chapter 6.
References:


[18] Samsung U9000 Curved Ultra HD TV Series


[26] Sony OTFT-driven OLED display


Nanoscale 2014, 6, 6679.


Mater. 2015, 5, 1401855
Chapter 2 Fundamental Concepts

This chapter presents a few foundation concepts that are useful for understanding charge transport and charge injection in organic semiconductors. We start with an introduction to organic semiconductors. Besides charge transport and injection, we discuss the essential device physics of organic thin film transistors and solar cells.

2.1 Charge transport in organic semiconductor

2.1.1 Introduction to organic semiconductors

Organic electronics employing $\pi$-conjugated organic materials is enjoying rapid growth. Using organic semiconductors, one can fabricate flexible devices such as large-area displays and solar cells.$^{[1-5]}$ However, the performance of these devices are strongly dependent on the optical, electrical, and morphological properties of the materials. Among them, the electrical property plays a special role as all devices need to transport charges. Therefore, charge carrier mobility becomes an important parameter because it measures how charge carriers move within the electrical devices.

For example, balancing hole and electron mobilities can help the development of organic photovoltaic cells (OPVs).$^{[6-8]}$ High mobility organic thin film transistors (OTFTs) may be used as fast switches in different electric circuits or devices. Therefore, studies of carrier mobility are of paramount importance.

Organic semiconductors are formed by aggregates of organic molecules in solid
states. Usually, the molecules interact with each other by weak van der Waal’s forces. Furthermore, organic semiconductors are usually insulators and there are few free carriers in room temperature. Unlike inorganic semiconductors which can be described by the band theory, organic semiconductors are often amorphous. Their energy states are usually discrete and disordered. Therefore, hopping model is introduced to describe the charge transport in organic semiconductors.

2.1.2 Molecular orbitals

Organic semiconductors possess carbon-based aromatic small molecules or polymers. In these aromatic molecules, σ electrons are localized and bind the carbon atoms together. In contrast, π-electrons are more extended spatially and they are more delocalized. In the presence of a strong, external electric field, π-electrons become mobile. Positive charges, i.e., holes, transport along the highest occupied molecular orbital (HOMO) while negative charges, i.e., electrons, transport along the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO energy states are similar to the valence band and conduction band of inorganic semiconductors.

2.1.3 Hopping and Poole-Frenkel models

Fig. 2.1 shows the energy diagram in an organic semiconductor. Black solid lines represent hopping sites which possess discrete energy states. Pink circles represent free charge carriers and the dotted hollow red circles represent the target
sites of the free carriers before hopping. The intrinsic HOMO and LUMO energy states in organic semiconductors are discrete and disordered because of the random distribution of molecules in the materials.\textsuperscript{[9]} Energy is often required when a carrier hops from one localized state to another molecule if the target site is empty. The energy for hopping is derived from thermal energy.

\[ \mu = \frac{v_d}{E} \quad (2.1) \]
where \( \mu \) is the mobility of the free carriers, \( v_d \) is the drift velocity, and \( E \) is the applied electric field. The unit of mobility is \( \text{cm}^2/\text{Vs} \). It can be interpreted as the average velocity of a free charge carrier per unit electric field.

Poole-Frenkel model is an important model to describe charge transport in insulators and semiconductors.\(^{[10,11]}\) The conductivity of an organic semiconductor in the presence of an electric field, \( E \), can be written as

\[
\sigma = \sigma_0 \exp\left(\frac{q^3}{\varepsilon k_B T} \sqrt{E}\right) = \sigma_0 \exp(\beta\sqrt{E})
\]

(2.2)

\[
\beta = \sqrt{\frac{q^3}{\varepsilon k_B T}}
\]

(2.3)

where \( \sigma \) is the conductivity in the material, \( \sigma_0 \) is the conductivity of the material at zero electric field, \( q \) is the elementary charge unit, \( \varepsilon \) is the permittivity of the material, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( E \) is the electric field. One can also correlate the mobility and the conductivity by introducing Ohm’s law,

\[
J = \sigma E
\]

(2.4)

where \( J \) is the current density. By the definition of current density,

\[
J = \frac{I}{A} = \rho v_d = qnv_d
\]

(2.5)

where \( I \) is the electric current, \( A \) is the cross-section area of the material, \( \rho \) is the
charge density, \( n \) is the carrier concentration, and \( v_d \) is the drift velocity. Combining Eq. (2.1), Eq. (2.4), and Eq. (2.5), one obtains,

\[
\sigma = qn\mu \tag{2.6}
\]

Thus, the conductivity is proportional to the carrier mobility. Finally we relate the Poole-Frenkel model and mobility by combining Eq. (2.2) and Eq.(2.6) to obtain,

\[
\mu = \mu_0 \exp(\beta \sqrt{E}) \tag{2.7}
\]

where \( \mu_0 \) is the zero field mobility and \( \beta \) is the temperature dependent Poole-Frenkel slope. This model has been used by different groups to obtain the hole mobility. However, the values of \( \beta \) obtained from experiments seem to be different from the theoretical values.\(^{[12-15]}\) Therefore, another model is required to describe the intrinsic properties in organic semiconductor.

### 2.1.4 Gaussian Disorder Model

The Gaussian disorder model (GDM) was originally proposed by H.Bässler. It is the most widely used model to describe carrier transport in amorphous organic small molecules and polymers.\(^{[16]}\) Bässler used Monte Carlo simulation to deduce an empirical equation,

\[
\mu(\sigma, T, \Sigma, E) = \mu_0 \exp\left[\frac{2}{3} \frac{\sigma}{k_B T} \right] \exp\left[\frac{C \left( \frac{\sigma}{k_B T} \right)^2 - \Sigma^2}{\sqrt{E}} \right] \tag{2.8}
\]
where $\mu_\infty$ is the high temperature limit mobility, $\sigma$ is the energetic disorder, $C$ is a fitting parameter which is related to charge concentration, and $\Sigma$ is the positional disorder, and $E$ is the applied external field. When $E=0$, the mobility is dependent on $\sigma$ and $T$ only.

$$\mu(\sigma, T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3k_BT}\right)^2\right] \quad (2.9)$$

The physical meaning of energetic disorder is illustrated in Fig. 2.2. The energetic disorder has the same mathematical meaning of standard deviation in statistics. It serves as the parameter to measure the variation and dispersion of energy states in the organic semiconductors. Fig. 2.2 shows the spreads of the energetic disorder, $\sigma$ of the HOMO/LUMO in an organic semiconductor.
Fig. 2.2 Spreads of HOMO/LUMO in an organic semiconductor. $\sigma_L$ and $\sigma_H$ are the standard deviations of energy states in the LUMO and HOMO, respectively.
2.2 Charge injection in organic semiconductor

At room temperature, there are few free charge carriers in organic semiconductors. Appreciable electric conduction can occur when carriers are injected externally through a metallic contact electrode. For hole conduction, holes can be injected into the HOMO level of the organic semiconductor. On the other hand, electrons can be injected into the LUMO for electron conduction. When there is no charge transfer in the interface, the vacuum level between organic layer and metal layer should be aligned. However, in most of the cases, charge transfer occurs between the interfaces and creates interface dipoles and therefore the vacuum level is not aligned. In such a case, the hole/electron injection is limited by the hole injection barrier ($\phi_h$) or electron injection barrier ($\phi_e$). In the Schottky-Mott model, $\phi_h$ and $\phi_e$ are defined by: $^{[11,17]}$

$$\phi_h = I_p - \Phi_m \quad (2.10)$$

$$\phi_e = \Phi_m - A_e \quad (2.11)$$

where $I_p$ is the ionization energy, $A_e$ is the electron affinity, and $\Phi_m$ is the metal work function. Table 2.1 shows the work function values of the typical metals are used in organic devices. If there are no injection barriers (i.e. $\phi_h = \phi_e = 0$ eV), the interface is defined as Ohmic contact.
However, in reality, interfacial dipoles cause a change of the vacuum level across the interface by $\Delta$. Therefore Eq. (2.10) and (2.11) become:\cite{17}

$$\phi_h = I_p - \Phi_m + \Delta$$  \hspace{1cm} (2.12)

$$\phi_e = \Phi_m - A_e - \Delta$$  \hspace{1cm} (2.13)

Fig. 2.3 shows the energy diagram of organic/metal interface with or without interface dipole. In our studies, the metallic contact between electrodes and organic semiconductors can be described by this model.

Fig. 2.3. Energy diagrams of organic/metal interfaces with or without interface dipole.
2.3 Theory of organic thin film transistor

2.3.1 Organic thin film transistor (OTFT)

The first practical organic field effect transistor was reported by Tsumura et.al by using polythiophene as semiconductor.\cite{18} Since then, OTFTs found many applications including switches in OLEDs, humidity sensors, pH sensors and pressure sensors.\cite{19,20,21,22,23} In addition, various companies have developed flexible OLEDs with the technique of OTFT. Other than real-life applications, OTFT is also a promising device to test carrier mobilities of different organic semiconducting materials because the amount of material consumption is significantly less than other techniques such as time-of-flight (TOF).\cite{24,25}

2.3.2 Structures of organic thin film transistors

An OTFT is a device which contains three basic parts: 1) contact electrodes consisting of source, drain, and gate electrodes; 2) an insulating layer which acts as the gate dielectric; 3) an organic thin film semiconducting layer. Fig. 2.4 shows a

<table>
<thead>
<tr>
<th>Metals</th>
<th>Au</th>
<th>Al</th>
<th>Ca</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work functions (eV)</td>
<td>-5.1</td>
<td>-4.3</td>
<td>-2.9</td>
<td>-4.3</td>
</tr>
</tbody>
</table>

Table 2.1 Work functions of the typical metals used in organic electronic devices
typical bottom gate top contact OTFT structure. Various metal oxides such as Al$_2$O$_3$, SiO$_2$ and TiO$_2$ have been used as gate dielectric layers. Oxide-based bottom gate OTFT wafers are commercially available. Therefore, bottom gate OTFT structure is common for laboratory use. However, top gate OTFT structures can also used for n-type OTFT to prevent the degradation of organic semiconductors due to air exposure.

Fig. 2.4 Schematic diagram of an organic thin film transistor

2.3.3 The I-V characteristics

In order to operate an OTFT, two voltage sources are needed. One is gate voltage, $V_g$. When a $V_g$ is applied, charges are induced in the organic semiconductor. If $V_g$ is larger than a threshold voltage, a conducting channel is formed between the source and drain electrodes. At the same time, a drain voltage ($V_{ds}$) can be applied to mobilize the charges in the conducting channel and therefore drain current ($I_{ds}$) can be measured. At low $V_{ds}$, $I_{ds}$ is directly proportional to $V_{ds}$ and obey Ohm’s law. So the
conducting channel has a linear profile of charge density. On the other hand, when $V_{ds}$ is comparable to $V_g$, the voltage drop at drain contact will become zero and the conducting channel is pinched off and it is defined as the saturation region. Fig.2.5 shows the typical current-voltage characteristics from OTFT measurements.

![Fig. 2.5 Typical current-voltage characteristics from OTFT measurements.](image)

2.3.4 Threshold voltage

Threshold voltage ($V_t$) can be regarded as the minimum $V_g$ required to form a conducting channel in an OTFT. In the ideal case, $V_t$ should be zero, which means a conducting channel can be formed once $|V_{gs}| > 0$. However, there are a few factors that will affect $V_t$. For example, bad film contacts, traps, impurities may also increase $V_t$ so that higher $V_g$ is required to complete the conducting channel.
2.3.5 Current-voltage characteristics of OTFTs

The discussion below is based on the following assumptions: i) negligible leakage current; ii) direction of electric field is from source to drain only; iii) channel thickness is uniform; iv) mobility is constant in the organic semiconductor.[26,27]

After applying \( V_g \) and \( V_{ds} \) in an organic thin film transistor, the induced charges \( Q \) at the semiconductor is proportional to the potential difference \( V_g - V(x) \) where \( V(x) \) is the potential at position \( x \) under the influence of \( V_{ds} \).

\[
Q = C_i [V_g - V_t - V(x)]
\]

In Eq. (2.14), \( C_i \) is the capacitance of the gate dielectric layer per unit area and \( V_t \) is the threshold voltage. For a small \( V_{ds} \), the average induced charge density \( \bar{Q} \) is equal to the induced charge density at the middle of the conducting channel:

\[
Q = \bar{Q} = C_i (V_g - V_t - \frac{V_{ds}}{2}) = \bar{n} q t
\]

where \( \bar{n} \) is the average induced carrier density in the conducting channel. By Ohm’s law, we can correlate \( V_{ds} \) and \( I_{ds} \).

\[
J = \sigma E = \sigma \frac{V_{ds}}{L} = \frac{I_{ds}}{W t}
\]

where \( J \) is the current density, \( \sigma \) is the conductivity of the conducting channel, \( E \) is the
electric field between the source and drain electrodes, $L$ is the channel length, $W$ is the channel width and $t$ is the film thickness. Making use of the definition of conductivity,

$$\sigma = qn\mu$$  \hspace{1cm} (2.17)

Eq. (2.16) becomes

$$I_{ds} = \frac{W}{L} \mu C_i \left[ (V_g - V_i)V_{ds} - \frac{V_{ds}^2}{2} \right]$$  \hspace{1cm} (2.18)

which is the classic current-voltage equation for thin film transistor. In the linear region, $(V_{ds} \ll V_g - V_i)$. So Eq.(2.18) can be simplified as

$$I_{ds} = \frac{W}{L} \mu_{lin} C_i (V_g - V_i)V_{ds}$$  \hspace{1cm} (2.19)

On the other hand, in the saturation region, $V_{ds} = V_g - V_i$, and Eq. 2.18 becomes

$$I_{ds} = \frac{W}{2L} \mu_{sat} C_i (V_g - V_i)^2$$  \hspace{1cm} (2.20).

Therefore, we can obtain the linear mobility by plotting $I_{ds}$ against $V_g$ and the saturation mobility by plotting $\sqrt{I_{ds}}$ against $V_g$. 
2.4 Some limitations of organic thin film transistors

2.4.1 Hysteresis

The drain current of an OTFT may depend on the history of the past measurement. Sweeping $V_g$ in different directions (from –ve to +ve or from +ve to –ve) may result in different output currents in the transfer characteristics. Fig.2.6 shows typical hysteresis in OTFTs. According to Orgiu et.al.\cite{28} the hole mobility of pentacene thin film transistor depends on how $V_g$ is swept. Sweeping $V_g$ from -100V to +100V (forward) and from +100V to -100V (backward) result in different $I_{ds}$ and therefore different extracted mobilities. The hysteresis originates from electron trapping, moisture, oxygen or other impurities.\cite{28,29,30} Such behavior can also affect the stability of the device.\cite{30}
Fig. 2.6 Transfer characteristics with hysteresis in an OTFT. The blue dashed curve and orange curve represent the sweeping direction of $V_g$ was from positive to negative and from negative to positive, respectively.

2.4.2 Charge transport direction

In organic photovoltaics (OPVs) cells and organic light emitting diodes (OLEDs), charges transport in the organic layers in the vertical direction (perpendicular to the substrate). However, in an OTFT, charges transport differently and they move horizontally from the source to drain through the organic semiconductor just above the gate dielectric. Due to the film morphology such as crystallinity, molecular packing and orientation, carrier mobility obtained from OTFT may not reflect the bulk mobility when the organic semiconductors are employed into device applications.

Fig.2.7 shows the charge transport directions of OTFTs and OPVs.
2.5 Hybrid organic/inorganic perovskite solar cells

Hybrid organic/inorganic perovskite solar cells are capturing huge attentions in recent years because of their high power conversion efficiencies (PCEs).[31–35] Recently, the National Renewable Energy Laboratory (NREL) confirmed that Seok’s group from the Korea Research Institute of Chemical Technology (KRICT) achieved 20.1% efficiency which is the highest perovskite solar cell to date.[36] Fig. 2.8 shows the latest best research-cell efficiencies from NREL (on 28-Mar-2015).[37] Perovskite solar cells have abundant advantages compared to silicon solar cells. They are: 1) low temperature processable, usually not higher than 120°C, 2) solution processable, which makes such kind of solar cell potentially useful in large area fabrication, 3) conformable, so they be coated on flexible substrates.[2,38]
Fig. 2.8. Best research-cell efficiencies from the National Renewable Energy Laboratory (NREL) in March 2015.
2.5.1 Characterization of solar cells

In organic/inorganic perovskite solar cells, light energy is converted into electrical energy. The mechanism is very similar to organic photovoltaic cells. There are four cascade processes in the working principles in perovskite solar cells as shown in Fig. 2.9. 1) Perovskite absorbs photons and generates electron-hole pairs (excitons). 2) Exciton may dissociate spontaneously or diffuse towards the interface of hole transporting layer (HTL) and electron transporting layer (ETL). 3) Holes move towards the HOMO of HTL and electrons move towards the LUMO of ETL. 4) Holes and electrons are then transport to anode and cathode respectively. Therefore a photocurrent can pass through an external load.

![Diagram](image)

Fig. 2.9. Working principles of a perovskite solar cell: 1) photon absorption and exciton generation, 2) exciton diffusion, 3) charge separation, and 4) charge transportation
Fig. 2.10 shows a typical current density-voltage (J-V) characteristic curve of a solar cell under illumination. The power conversion efficiency of a solar cell, $\eta$, is defined as:

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{max}} \cdot J_{\text{max}}}{P_{\text{in}}}$$  \hspace{1cm} (2.21)

where $P_{\text{max}}$ is the maximum power density output from the solar cell, $P_{\text{in}}$ is the input incident light density, $V_{\text{max}}$ and $J_{\text{max}}$ are the voltage and current density at the maximum power point. The fill factor ($FF$) can be defined as the ratio of the areas of maximum power rectangle, and the area defined by $V_{\text{oc}}$ and $J_{\text{sc}}$,

$$FF = \frac{V_{\text{max}} \cdot J_{\text{max}}}{V_{\text{oc}} \cdot J_{\text{sc}}}$$  \hspace{1cm} (2.22)

From Eq. (2.22), the power conversion efficiency, can be rewritten as

$$\eta = \frac{FF \cdot V_{\text{oc}} \cdot J_{\text{sc}}}{P_{\text{in}}}$$  \hspace{1cm} (2.23)
2.5.2 Equivalent circuit of a solar cell \([39]\)

A solar cell can be modeled as the parallel combination of a light-dependent current source, and a diode as shown in Fig. 2.11 (a). However, in a real device, there exist a series resistance \((R_s)\), and a shunt resistance \((R_{sh})\). So a more realistic device model is shown in Fig. 2.11 (b). \(R_s\) is related to the intrinsic conductivity of the device. It is a complex function of mobility, resistance, morphology, interfaces and thickness of the semiconductor. On the other hand, \(R_{sh}\) expresses the loss of photocurrent due to leakage, carrier recombination, impurities, and defects in the semiconducting layer. In such a device, the J-V characteristics can be modeled by Eq.(2.24) and Eq.(2.25): \([39]\)
Diode current:

\[ J_{\text{diode}} = J_s \left[ \exp \left( \frac{qV_{\text{diode}}}{nk_BT} \right) - 1 \right] \]  \hspace{1cm} (2.24)

Shunt current:

\[ J_{\text{sh}} = \frac{V_{\text{diode}}}{R_{\text{sh}}} \]  \hspace{1cm} (2.25)

where \( J_s \) is the saturation current density, \( n \) is the diode ideality factor, and \( V_{\text{diode}} \) is the voltage across the diode. Since,

\[ J = J_{\text{diode}} + J_{\text{sh}} - J_{\text{ph}} \]  \hspace{1cm} (2.26)

where \( J_{\text{diode}} \) is the current through the diode, \( J_{\text{sh}} \) is the current through the shunt resistor, and \( J_{\text{ph}} \) is the photocurrent

\[ J = J_s \left[ \exp \left( \frac{qV_{\text{diode}}}{nk_BT} \right) - 1 \right] + \frac{V_{\text{diode}}}{R_{\text{sh}}} - J_{\text{ph}} \]  \hspace{1cm} (2.27)

Making use of \( V_{\text{diode}} = V - JR_s \), the generalized Shockley equation can be derived: \[ ^{[39]} \]

\[ J = \frac{R_{\text{sh}}}{R_s + R_{\text{sh}}} \left[ J_s \left\{ \exp \left( \frac{q(V - JR_s)}{nk_BT} \right) - 1 \right\} + \frac{V}{R_{\text{sh}}} - J_{\text{ph}} \right] \]  \hspace{1cm} (2.28)

In the ideal case, \( R_{\text{sh}} \to 0 \) and \( R_s \to \infty \), Eq. (2.28) is reduced to:
\[ J = J_s \left\{ \exp \left( \frac{q(V - JR_s)}{nk_BT} \right) - 1 \right\} - J_{ph} \]  

(2.29)

Fig. 2.11. Equivalent circuits for a solar cell. a) an ideal solar cell. b) a real device.
2.5.3 Chemical structure of perovskite compounds

The general chemical formula of perovskite is $\text{ABX}_3$ where A is the larger cation, B is the smaller cation, and X is the anion. Fig. 2.12 shows the crystal structure of $\text{ABX}_3$ perovskite. Table 2.2 shows the common $\text{ABX}_3$ elements used in perovskite solar cell. Different choices of A and X lead to the difference in diffusion length, optical band gap, wetting, and different device performances.\(^{[36,40,41]}\)

![Fig. 2.12 Crystal structure of ABX₃ perovskite.][36]

<table>
<thead>
<tr>
<th>Commonly used ions</th>
<th>A (large cations)</th>
<th>B (small cations)</th>
<th>X (anions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{CH}_3\text{NH}_3$(^{[36]})</td>
<td>$\text{Pb}^{2+}$</td>
<td>$\text{Cl}^-$</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{NH}_3$(^{[42]})</td>
<td>$\text{Sn}^{2+}$</td>
<td>$\text{Br}^-$</td>
</tr>
<tr>
<td></td>
<td>$\text{HC(NH}_2)_2$(^{[42]})</td>
<td></td>
<td>$\text{I}^-$</td>
</tr>
</tbody>
</table>

Table. 2.2 Commonly used ions in perovskite solar cell

2.5.4 Measurement difficulties
Many perovskite solar cells are known to exhibit non-negligible hysteresis. The output I-V curve is found to be dependent on the direction in which the applied voltage is swept as shown in Fig 2.13.\cite{34,43} For the data reported in this thesis, power conversion efficiency can vary from 6% to 9% on the same perovskite solar cell. Several methods were also reported to eliminate the hysteresis of perovskite solar cell such as changing the voltage sweeping rate, sweeping time, different direction of bias and passivation by fullerenes.\cite{44,45} However, the effectiveness of such methods turn out to be ineffective. The origin of hysteresis is still yet to be confirmed.

Fig. 2.13 I-V characteristics of a solar cell with hysteresis. The blue dotted line represents a forward bias (from \(-V\) to \(+V\)). The orange line represents a reverse bias (from \(+V\) to \(-V\)).
Reference

[1] OTFT-Driven OLED Display that can be rolled up onto a Pen


Chapter 3 Experimental Details

3.1 Material preparation

3.1.1 Material introduction

Two kinds of organic molecules were selected in this thesis work for in-depth characterization as active materials in OTFTs. The results will be presented and discussed in Chapter 4. The molecules are \((\text{N,N’-Di(1-naphthyl)-N,N’-diphenyl-}(1,1’-\text{biphenyl})-4,4’-\text{diamine (NPB)})\) and \(\text{tris[2-phenylpyridinato-2,N]iridium(III)}\) \([\text{Ir(ppy)}_3]\). Both molecules have wide applications in organic light emitting diodes (OLEDs).\[^1\text{–}^3\]\ Fig. 3.1 shows their chemical structures. In this work, thin films of these two molecules were deposited by vacuum deposition. These films are generally smooth and amorphous, and the film thicknesses can be controlled accurately. Table 3.1 shows the HOMO and LUMO energy levels of NPB and \text{Ir(ppy)}_3

![Chemical structures of NPB and Ir(ppy)_3](image)

**Fig. 3.1** Chemical structures of NPB and \text{Ir(ppy)}_3.
<table>
<thead>
<tr>
<th></th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>-5.5[^{[4]}]</td>
<td>-2.5[^{[4]}]</td>
</tr>
<tr>
<td>Ir(ppy)(_3)</td>
<td>-5.6[^{[2]}]</td>
<td>-2.8[^{[2]}]</td>
</tr>
</tbody>
</table>

Table 3.1 HOMO and LUMO energy levels of NPB and Ir(ppy)\(_3\)

In Chapter 5, we will present data related to the growth and characterization of perovskite solar cell materials. The materials used in the fabrication of perovskite thin film were lead(II) chloride (PbCl\(_2\)) and methyl ammonium iodide (MAI). Fig. 3.2 shows their chemical structures. A perovskite thin film was obtained by spin coating a solution consisting a mixture of PbCl\(_2\) and MAI on a substrate after. Such a spin coating method enables us to form a film in a convenient way because the entire process does not require a vacuum chamber. In contrast to the organic films of NPB and Ir(ppy)\(_3\), perovskite films prepared in this way are quite rough, and they are polycrystalline.
3.1.2 Material purification by sublimation

Purity of materials is of paramount importance because charge traps arise the impurities.\cite{5,6} Such traps can affect charge transport properties of an organic semiconductor because the energy required to remove a hole or an electron from the trap state may be larger than the average thermal energy, $k_B T$.\cite{7,8} Such impurities may come from side products or residues from chemical synthesis. Moreover, materials may react with ambient air or moisture to form impurities. Therefore, in this work, some of the materials were purified by sublimation.

Fig. 3.3 shows the experimental setup of sublimation. The raw material with a known weight was placed in a small bottle in the Pyrex tube. The Pyrex tube was then inserted into a furnace heater (Barnstead / Thermolyne Co., F21130-26) which was then evacuated by a diffusion pump to high vacuum of $4 \times 10^{-6}$ torr. Under high
vacuum, the raw material may vaporize or sublime into gas form under heating and condensed as solid near the cooler region of the Pyrex tube. Finally, the condensed organic material was scratched off from the Pyrex tube. By measuring the mass of the “scratched off” material, the sublimation yield can be calculated with the following equation,

\[ \text{yield} = \frac{m_{\text{final}}}{m_{\text{initial}}} \cdot 100\% \]  

(3.1)

where \( m_{\text{initial}} \) is the mass of the material before sublimation and \( m_{\text{final}} \) is the mass of the material after sublimation. The average yield obtain in our work was around 90%.

Fig. 3.3 Experimental setup of sublimation
3.2 Sample fabrication

3.2.1 Sample preparation for organic thin film transistors (OTFTs) measurements

3.2.1.1 Etching

P-doped silicon wafer was prepared by etching one side of a silicon dioxide wafer as shown in Fig. 3.4. Since p-doped silicon is sandwiched between two layers of silicon dioxide, hydrofluoric acid (HF) was used to remove one of the silicon dioxide layers. The etched wafer was then cut into chips with a dimension of 1.5cmx2cm for further treatment.

Fig. 3.4 (a) Top view of a silicon dioxide wafer viewed from top. (b) Side view of the wafer before and after etching
3.2.1.2 Substrate treatment

The 1.5cmx2cm substrate was then cleaned by acetone using cotton rod to remove impurities. The substrate was immersed into an ultrasonic bath with filtered acetone twice for 20 minutes each. Finally, the substrate was put into the ultraviolet-ozone cleaner for 13 minutes to remove any hydrocarbon contamination. The substrate was ready for organic layer deposition.

3.2.1.3 Sample preparation for organic photovoltaics (OPVs) measurements

A 2.5mmx2.5mm pre-patterned indium tin oxide (ITO) substrate with a sheet-resistance of 15-20Ω/□ was purchased from Tinwell Technology Limited. Fig. 3.5 shows the pattern and details of the ITO substrate. The substrate underwent cleaning procedures before organic layer deposition. First, the substrate was cleaned by analytical reagent (A.R.) grade acetone (Lab-scan, A.R. grade) with a cotton rod to remove any observable dusts or particles. Then the substrate was cleaned by scrubbing with detergent and immersed into a diluted Deconex at 70°C for 10 minutes to remove excess detergent, followed by immersing into deionized water, acetone (A.R grade), and isopropanol (A.R. grade) for 20 minutes each in an ultrasonic bath (Branson commercial Ultra sonic cleaner, Model 1210). Finally, the substrate was transferred into an ultra-violet ozone cleaner (UVO cleaner, Jeligt Company, Inc. UVO cleaner, Model 42-220) to remove residual hydrocarbon on the substrate.


![Image of ITO substrate](image)

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Sheet resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5x2.5cm²</td>
<td>15-20Ω/□</td>
</tr>
</tbody>
</table>

* Shaded area --- ITO coated

Fig. 3.5 (a) ITO substrate used for OPV measurements showing the pattern, dimensions, and the sheet resistance.

### 3.2.2 Material deposition

#### 3.2.2.1 Spin-coating

Table 3.2 shows the common solvents used for spin-coating in our study. An electronic balance was used to weigh the target solute materials in a small glass bottle. Then, suitable amount of solvent was added into the bottle via a pipette. A magnetic stirrer and heating were also used to achieve good solubility. The precursor solution was then filtered by a 0.45µm polytetrafluoroethylene (PTFE) or poly-1,1-dofluoroethene (PVDF) filter to remove insoluble particles. Then the precursor solution was then ready for spin-coating.

Spin-coating can be done in air or in N₂ environment. The substrate was placed on a horizontal chuck in the spin coater (VTC 100 Vacuum Spin Coater). The substrate was sprayed with compressed gas was used to remove any dusts or large...
particles on the substrate. A known volume of the precursor solution was then transferred on the substrate with a pipette. By controlling the spin speed (in rpm) and time, a film with well-controlled thickness can be obtained. In general, high spin speed and long spin time would make a thin film.

After spin-coating, the film was transferred onto a hot plate or baked inside an oven for thermal annealing. The annealing temperature can be varied from 40°C to 120°C in our studies. Annealing would remove extra solvents in the film. Higher annealing temperatures were needed if the materials contained metal oxides or had been dissolved in a high boiling point solvent. Annealing plays a key role to enhance crystal formation in perovskite solar cell.\textsuperscript{[9,10]} Fig.3.6 shows the schematic diagram of the spin coating process.
<table>
<thead>
<tr>
<th>Solvents</th>
<th>Chemical Structures</th>
<th>Solutes</th>
<th>Chemical Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1-2-trichloroethane</td>
<td><img src="image1" alt="Structure" /></td>
<td>Polystyrene</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td><img src="image3" alt="Structure" /></td>
<td>Lead chloride,</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Chloroform</td>
<td><img src="image5" alt="Structure" /></td>
<td>Methyl ammonium iodide</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td><img src="image7" alt="Structure" /></td>
<td>ZnO nano particles</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td><img src="image9" alt="Structure" /></td>
<td>PC₆₀BM</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
</tbody>
</table>

Table 3.2 Chemical names and structures of solvents and solutes used in this thesis
Fig. 3.6 Schematic diagram showing the entire preparation procedures of thin films prepared by spin-coating.
3.2.2.2 Thermal deposition

For thermal deposition of thin films, substrates were mounted on a circular or a square plate as shown in Fig. 3.7a. The circular mount was then secured inside the Denton vacuum evaporator (DV-502V) for organic and transition metal oxide thin film deposition. An Edwards evaporator (AUTO 306) was used to evaporate metallic materials (e.g. gold and aluminum). Fig.3.7b shows the experimental setup of a thermal evaporator. The circular mount was used for organic film deposition while the square mount was used for transition metal oxide film deposition. In the thermal evaporator, the operating pressure was at 4x10^{-6} torr, which was evacuated by a diffusion pump. Coating rate can be controlled and monitored by the current controlling unit (Sorensen DLM 8-75) and the thickness sensor (Sycan STM 100/MF), respectively.
Fig. 3.7 (a) Circular and square mounts used in thermal evaporation. (b) Schematic diagram of a thermal evaporator (side view).
3.2.3 Device characterizations

3.2.3.1 Organic photovoltaic cell measurement

The experimental setup for OPV cells measurement is shown in Fig.3.8. The output I-V curves of an OPV cell were measured by a source meter (Keithley Instruments Inc. Model 2400 source meter) under AM 1.5G illuminations (100mW/cm²) which simulated by a commercial solar simulator (Newport Corp., Oriel Model 96000 150W) with a calibrated power density of $P=100\text{mW/cm}^2$. The solar simulator was further calibrated in our lab by a power meter (Thorlabs, Inc., Model PB100D). The source meter provided potential difference between the anode and cathode in the cell and measured its output current.

![Fig.3.8 Schematic diagram of J-V measurements of a solar cell.](image-url)
3.2.3.1 Organic thin film transistor measurements

After the fabrication of organic thin film transistors, samples were transferred and mounted into a temperature controllable cryostat (Oxford Instruments, Optistat DN-V). The experimental setup for the data acquisition is shown in Fig. 3.9. Source and drain electrodes were connected to a source meter (Keithley 236 Source Measure Unit) to provide $V_{ds}$ and measure $I_{ds}$ simultaneously. On the other hand, an independent voltage source (Xantrex XT 120-0.5 DC supply) was used to provide the gate voltage underneath the sample. After mounting the sample into the cryostat, a rotary pump was used to evacuate the cryostat to low vacuum at $10^{-3}$ torr. A temperature controller (Oxford Instruments, ITC-502) was used to regulate the temperature of the sample for temperature dependence measurements. The sample could be regulated between 80-450K with liquid nitrogen and an electronic heater inside the cryostat.
Figure 3.9: Schematic diagram of output current measurement of OTFTs in a liquid-nitrogen-cooled cryostat.
I_{ds}-V_{ds} output characteristics can be obtained from the setup to the computer.

The method for measuring the mobilities of any organic semiconductors was outlined in Chapter 2. Typical output characteristics are shown in Fig. 3.10. The field effect mobility in both the linear and saturation regions, \( \mu_{\text{lin}} \) and \( \mu_{\text{sat}} \), can be expressed as,

\[
I_{ds} = \frac{W}{L} \mu_{\text{lin}} C_i (V_g - V_i) V_{ds}
\]  
(3.2)

\[
I_{ds} = \frac{W}{2L} \mu_{\text{sat}} C_i (V_g - V_i)^2
\]  
(3.3)

From Eq(3.2) and Eq(3.3), we get, by differentiation,

\[
\frac{\partial I_{ds,\text{linear}}}{\partial V_g} = \frac{W}{L} C_i \mu_{\text{lin}} V_{DS}
\]  
(3.4)

\[
\frac{\partial \sqrt{I_{ds,\text{sat}}}}{\partial V_g} = \sqrt{\frac{W}{2L} C_i \mu_{\text{sat}}}
\]  
(3.5)

As a result, from Eq.(3.4) and Eq.(3.5), \( \mu_{\text{lin}} \) and \( \mu_{\text{sat}} \) can be extracted from the I-V characteristics as shown in Fig. 3.10. In addition, the threshold voltage, \( V_t \), can be obtained from the x-intercept of the fitted curve.
Fig. 3.10 Middle diagram represents typical data obtained from the setup. Left and right diagrams represent the data points obtained from the linear region and saturation regions, respectively.
References:


Chapter 4 Probing bulk transport of amorphous semiconductors, interfacial disorders, and molecular orientations in a thin-film transistor configuration

4.1 Introduction

This chapter describes an approach of measuring bulk carrier transport of amorphous organic semiconductors. We found that thin film transistor technique can serve as a purpose. We demonstrate the bulk mobilities of amine-based hole transporters (HTs) can be evaluated when polystyrene (PS) is employed as the gate dielectric layer in organic thin film transistors. In contrast to a PS gate dielectric layer, TFT mobilities are 1-2 orders lower than the bulk values for organic semiconductors grown on SiO\(_2\). Temperature dependent measurements were carried out to examine the origins of reduced mobilities. It can be shown on SiO\(_2\) surface, the energetic disorders (\(\sigma\)) of the HTs increase. Simultaneously, the high temperature limits (\(\mu_\infty\)) of the carrier mobilities decrease. Both \(\sigma\) and \(\mu_\infty\) contribute to the reduction of the carrier mobility. The increase in \(\sigma\) is related to the presence of randomly oriented polar Si-O bonds. The reduction of \(\mu_\infty\) is topological in origin and is related to the orientations of the more planar molecules on SiO\(_2\) as revealed by analysis of the initial growth of molecules on SiO\(_2\) and PS surfaces. The more planar molecules tend to lie horizontally on the surface and such an orientation is unfavorable for charge transport in a TFT configuration. Therefore, we introduce two non-planar molecules, Ir(ppy)_3.
and Ir(piq)$_3$. We found that such 3-D molecules do not have any preferential orientations and therefore the hole mobilities of Ir(ppy)$_3$ and Ir(piq)$_3$ do not have drastic change on SiO$_2$ nor PS.

Fig. 4.1(a) shows the chemical structures and the HOMO values of the four HTs, as well as Ir(ppy)$_3$ and Ir(piq)$_3$. Furthermore, making use of the PS gate dielectric, we probed the hole mobilities of BAnF derivatives from Prof. Zhaoxin Wu’s group.\textsuperscript{[1]} The results suggest that one of the BAnF derivatives, BAn-4-F possesses balanced and high hole and electron mobilities. When BAn-F derivatives was adopted as a host materials in OLEDs application, the device possesses high luminescence and external quantum efficiency (EQE).
Fig. 4.1 Chemical structures and the HOMO values of four organic amine-based hole transporters, and two iridium-based compounds, Ir(piq)$_3$, and Ir(ppy)$_3$. 
4.2 Experimental Details

NPB, Spiro-TPD, 2TNATA, TPD, Ir(piq)$_3$ and Ir(ppy)$_3$ were purchased from e-Ray Optoelectronics Technology Co., Ltd. All materials were used as received. MoO$_3$ was purchased from Strem Chemicals, Inc. Polystyrene (PS) was purchased from Sigma Aldrich. Co.. Heavily doped p$^+$-silicon substrates were thermally grown with 300nm of SiO$_2$. Before device fabrication, the substrates were cleaned by deionized water, filtered acetone and iso-propanol with 20 minutes each. After 13 minutes of UV-Ozone treatment, PS (optional layer) was dissolved in 1,1,2-trichloroethane at a concentration of 6.5mg/ml and spun on the silicon substrate at 2000rpm for 1 minute. The substrates were then stored in a vacuum oven at 60°C for 12 hours to remove any unwanted solvents. Both SiO$_2$ and PS surfaces possess smooth surfaces with mean surface roughnesses of 0.13 and 0.17 nm, respectively, as revealed by atomic force microscopy (AFM). Organic semiconductors were thermally evaporated on the substrates at 4x10$^{-6}$ torr at a rate of 0.2Å/s. Both source and drain electrodes were made by 20nm of MoO$_3$ and 100nm of Au. MoO$_3$ could enhance the hole injection efficiency in the hole transporters.$^{[2,3]}$ All TFT devices were bottom-gate top-contact as shown in Fig. 4.2. Unless stated otherwise, the thickness of the organic layers were 100 nm. The TFT mobilities in the linear ($\mu_{\text{lin}}$) and saturation ($\mu_{\text{sat}}$) regions were evaluated by standard equations $^{[4]}$:
where $I_{ds}$ is the source-to-drain current, $W$ is the channel width, $L$ is the channel length, $C_i$ is the capacitance of the gate dielectric per unit area; $V_{ds}$, $V_g$ and $V_t$ are the applied source to drain voltage, the gate voltage, and the threshold voltage of the OTFT respectively. Besides TFT, the hole mobilities of some of the HTs were also examined by time-of-flight (TOF) technique.\textsuperscript{[5]} For TOF measurement, a thick organic layer with an average thickness of 5 μm was needed for reliable measurements.
4.3 Result and discussion†

4.3.1 Achieving bulk mobility in TFT configuration

The TFT output characteristics of NPB on PS and NPB on SiO\(_2\) are shown in Fig. 4.3 (a). The output currents for the NPB transistors varied from 0-20nA on SiO\(_2\). On the other hand, the output currents increased to the range of 0-400nA when NPB was grown on PS. The transfer characteristics are shown in Fig. 4.3(b), which are consistent with the data in Fig. 4.3(a). The results indicate the output currents are much more favorable for the NPB grown on PS. Besides, NPB similar experiments have been conducted on other hole transporters, TPD, Spiro-TPD, and 2TNATA. The transfer characteristics are shown in Fig. 4.4. The results show that all the amine-based compounds have improved output currents on PS. The TFT mobilities in the linear and saturation regions for all amine-based compound are computed and the data are summarized in Fig. 4.5 in the form of a bar graph. We can see for all amine compounds, the TFT mobilities on SiO\(_2\) are consistently lower than the TFT mobilities on PS gate dielectric. In Fig. 4.5, we also show the hole mobilities of all amine compounds (dashed line) as measured independently by time-of-flight (TOF) technique at low electric field. It can be seen that the TOF mobilities are essentially the same as the TFT mobilities on PS. Thus we conclude that, from a metrology point of view, TOF mobility, which is a measure of the bulk carrier transport of the HTs, can be achievable in a TFT configuration but with much reduced film thicknesses.

† Some data in 4.3.1 were acquired by former M.Phil. Student, Cyrus Y.H. Chan.
Fig.4.3 (a) Typical TFT output characteristics for NPB grown on SiO\(_2\) (top) and on PS (bottom) gate dielectric layers. (b) TFT transfer characteristics of NPB transistors grown on SiO\(_2\) and on PS. The data were taken at a \(V_{ds} = -60\) V.
Fig. 4.4 Transfer characteristics of four amine-based compound. All data were taken at a $V_{ds}=-60V$. 
Fig. 4.5 Bar graphs of TOF (dotted line), linear and saturation mobilities for all the amine-based compounds.

4.3.2 Thickness dependence measurement

To check how much organic material is needed for TFT characterization of carrier mobility, we chose NPB as the reference material, and performed a detailed thickness dependent measurement on its hole mobilities on both SiO$_2$ and on PS. Figure 4.6 presents the thickness dependent results. We first focus on the data using PS gate dielectric layer. Above 10 nm, the TFT mobility is essentially constant and independent of the thickness of the organic layer. The values are between $4 \times 10^{-4}$ cm/Vs. The horizontal blue color band in the mobility plot represents the bulk mobility region obtained from TOF. After employing PS as gate dielectric layer in
TFT configuration, one could achieve bulk mobility even when the thickness of the organic layer is down to 10 nm. The result here should be contrasted with TOF results in which at least 100 times thicker film is required. These results should enable the characterization of many newly synthesized organic small molecules when they are still available in limited quantities.

For those TFT with NPB thickness below 10 nm, the mobility drops rapidly as thickness is further reduced, and no reliable mobility can be obtained below 5 nm. Dinelli proposed a model to characterize the thickness dependent TFT mobility with:[6]

\[
\mu = \mu_s \left( 1 - e^{-\frac{d}{d_0}} \right)^{\alpha}
\]  

(4.3)

where \( \mu \) is the mobility of the organic semiconductor, \( \mu_s \) is the saturation mobility of the organic semiconductor (when the film is thick enough), \( d \) is the film thickness, \( d_0 \) is the critical thickness required to obtain an acceptable mobility value, and \( \alpha \) is the exponent parameter to represent the quality of the charge conduction. Using Eq.(4.3), we fitted the data, and obtained a \( d_0 \) of 7.6 nm.

In Fig. 4.6, we also show the TFT mobilities of NPB grown on SiO\(_2\). The overall thickness dependence in this case is very similar to the case on PS, except that the data on SiO\(_2\) are about one and half orders smaller. The hole mobility levels off when
the film thickness exceed 10 nm. Increasing the thickness of NPB to 100 nm does not help to improve the mobility further. The results on SiO$_2$ confirm the notion that in a TFT, the transport of charge carriers occurs within those layers that are in proximity of the gate dielectric layer. (If charge transport were to involve layers well above the gate dielectric, the bulk value of $\mu$ should be achievable for NPB grown on SiO$_2$). Despite the similarities in the thickness dependences on PS and SiO$_2$, the transport of holes above SiO$_2$ is distinctly lower. Below we will examine the origins of reduced mobilities on SiO$_2$. 
Fig. 4.6 Thickness dependent NPB hole mobilities on SiO$_2$ and on PS gate dielectric layers. The solid curves are fitted curves to experimental data using Eq.(4.3). The horizontal band represents the range of mobilities from TOF measurements.
4.3.3 Temperature dependence transport measurements of organic films on SiO$_2$ and PS gate dielectric layers.

To look into the origins of different TFT mobilities on SiO$_2$ and on PS, temperature dependence TFT measurements were performed between 235K and 360K. The extracted hole mobilities were analyzed by the well-known Gaussian Disorder model (GDM).\(^7\) In the GDM, the mobilities are electric field ($F$) and temperature ($T$) dependent.

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

(4.4)

where $k_B$ is the Boltzmann constant, $\mu_\infty$ is the high temperature limit of the mobility, and

$$\beta = C \left( \frac{\sigma}{k_B T} \right)^2 - \Sigma^2 \right)$$

(4.5)

$\beta$ is the Poole-Frenkel slope and $C$ is a fitting constant. The charge carriers experience an energetic disorder ($\sigma$) and positional disorder ($\Sigma$) which can be understood as the width of the Gaussian distribution of the energy states and the positional/orientational fluctuations for the transport sites, respectively. At low field ($F \to 0$), the second exponential term in Eq. (4.4) approaches 1 and $\mu(0,T) \sim \exp \left[ \frac{4}{9} \left( \frac{\sigma}{k_B T} \right)^2 \right]$. A semi-log plot of low field mobilities (using $\mu_{lin}$) versus $1/T^2$ should yield a straight line. $\sigma$ and
can be extracted from the slope and y-intercept of the line, respectively.

Figure 4.7 shows the temperature dependent TFT-derived mobilities data for all the four amine-based compounds analyzed by the GDM model. In addition, we also show hole mobility data obtained independently by TOF experiments. Several features can be noted. First, there are excellent agreements between the TFT data on PS and the TOF results at all temperatures. This observation substantiates that the bulk-like transport behavior from TOF can be realized in a TFT structure. Thus, TFT can be considered to be a low-sample demand tool to evaluate bulk-like mobility of an organic semiconductor. Second, for all organic semiconductors shown in Fig. 4.6, TFT data on SiO$_2$ possess distinctly steeper slopes when compared to TFT data on PS.

According to Eq.(4.4), the energetic disorders can be evaluated from these slopes and that results are summarized on Table 4.1. On PS, the energetic disorders $\sigma$ are in the narrow range between 71-77 meV, and the values are very similar to $\sigma$ obtained from TOF.$^{[8]}$ On the other hand, the energetic disorders, $\sigma$ are much larger when the organic semiconductors are grown on SiO$_2$. A model, which is consistent with observed increase in $\sigma$, can be attributed to the presence of randomly oriented dipoles associated with polar Si-O bonds on the thermally grown SiO$_2$ surface. These random dipoles broaden the density-of-states of the charge hopping manifold, and give rise a larger $\sigma$. In contrast to SiO$_2$ surface, PS is non-polar.$^{[9,10]}$ As a result, holes (once
injected from the source electrode) only experience the intrinsic energetic disorder, which is very similar to the environment encountered in a TOF sample environment.
Fig. 4.7 Temperature dependent TFT-derived mobilities data for all the four amine-based compounds analyzed by the GDM model. Black triangles (△) and red circles (●) represent the TFT mobility on SiO$_2$ and PS respectively. Hollow squares (■) represent the hole mobilities obtained from TOF measurements. The data shown here were originally acquired by former M.Phil. student, Cyrus Y.H. Chan, and are re-analyzed here.
Besides differences in the energetic disorder parameters, we also note from Fig. 4.7 that TFT data on SiO₂ surfaced possess reduced $\mu_\infty$ for all organic semiconductors when compared to the TFT data obtained on PS. Table 4.1 summarized the $\mu_\infty$ data obtained from both gate dielectric surfaces. Following the concept of the GDM, $\mu_\infty$ is related to the hopping rate across the neighboring transporting sites. The rate can be described by:

$$\mu_\infty = \frac{v_0a^2e}{\sigma} \exp(-2\gamma a)$$  \hspace{1cm} (4.6)

where $v_0$ is the attempt-to-hop frequency, $a$ is the average hopping distance, $e$ is the elementary charge, and $\gamma$ is the inverse localization radius. $\gamma$ is primarily determined by the active site for charging hopping. In Fig. 4.7, all compounds are amine-based and the amine moieties are the electron donating sites. So $\gamma$ can be taken as a constant.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{TFT, SiO_2}$ (meV)</th>
<th>$\sigma_{TFT, PS}$ (meV)</th>
<th>$\sigma_{TOF}$ (meV)</th>
<th>$\mu_{\infty, SiO_2}$ (cm²/Vs)</th>
<th>$\mu_{\infty, PS}$ (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-TPD</td>
<td>98</td>
<td>73</td>
<td>75</td>
<td>1x10⁻²</td>
<td>1.5x10⁻²</td>
</tr>
<tr>
<td>2TNATA</td>
<td>91</td>
<td>77</td>
<td>71</td>
<td>1.7x10⁻³</td>
<td>4.7x10⁻³</td>
</tr>
<tr>
<td>NPB</td>
<td>95</td>
<td>74</td>
<td>76</td>
<td>5x10⁻³</td>
<td>1.8x10⁻²</td>
</tr>
<tr>
<td>TPD</td>
<td>94</td>
<td>71</td>
<td>74</td>
<td>7x10⁻³</td>
<td>1.9x10⁻²</td>
</tr>
</tbody>
</table>

Table 4.1 Energetic disorders and high temperature limits of the mobility obtained from TFT and TOF techniques.
can only arise from a difference in the effective hopping distance \(a\). The results from Fig. 4.7 somehow suggest that the average charge hopping distance on SiO\(_2\) surface is larger than on PS surface. Therefore, using Eq(4.6) and assume \(v_0=10^{14}\)Hz, we can compute \(a\) and the result are shown in Table 4.2. Summarizing the temperature dependence experiments, we conclude that the TFT mobilities on SiO\(_2\) surface are reduced compared to the data on PS. Two factors give rise to the reduced mobilities. The first factor is energetic in origin which is attributed to the randomly oriented polar Si-O bonds on the oxide surface. The second factor is related to the charge hopping distance. As we see below, the latter factor is topological in origin and is closely correlated to the orientation of the organic molecules right above the gate dielectric layer.

<table>
<thead>
<tr>
<th></th>
<th>(\mu_{\infty,\text{SiO}_2}) (cm(^2)/Vs)</th>
<th>(\mu_{\infty,\text{PS}}) (cm(^2)/Vs)</th>
<th>(a_{\text{SiO}_2}) (nm)</th>
<th>(a_{\text{PS}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-TPD</td>
<td>1x10(^{-2})</td>
<td>1.5x10(^{-2})</td>
<td>1.04</td>
<td>1.03</td>
</tr>
<tr>
<td>2TNATA</td>
<td>1.7x10(^{-3})</td>
<td>4.7x10(^{-3})</td>
<td>1.87</td>
<td>1.70</td>
</tr>
<tr>
<td>NPB</td>
<td>5x10(^{-3})</td>
<td>1.8x10(^{-2})</td>
<td>1.20</td>
<td>0.93</td>
</tr>
<tr>
<td>TPD</td>
<td>7x10(^{-3})</td>
<td>1.9x10(^{-2})</td>
<td>1.14</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 4.2. \(\mu_{\infty}\) and average hopping distances of all amine compounds on PS and SiO\(_2\) surfaces as computed by Eq.(4.6).
4.3.4 Morphology study on organic thin films

To check if the difference in $\mu_c$ is related to the morphologies of the organic films, we use NPB as an example, and took a series of AFM images for different thicknesses of NPB on SiO$_2$ and PS. Special attention is given to the initial growth of the NPB films on the two different surfaces. Figures 4.8 and 4.9 show the images for nominal NPB thicknesses between 0-5 nm. First, we note that the bare surfaces of SiO$_2$ and PS are generally smooth and the roughnesses are less than 0.2 nm. On the PS surface, between a nominal thickness between 1.5 and 3nm, NPB molecules form discrete islands. These islands are circular or oval in shapes and are quite homogeneous. They grow in sizes until they start to percolate at around 5 nm. The growth of NPB on PS is consistent with the thickness dependent TFT measurements shown in Fig. 4.6 in which we observed negligible mobilities below a film thickness of 5 nm on PS. In fact, the thin film growth of NPB on PS can be well described by the Volmer-Weber growth (VW growth).[11] This kind of growth mode occurs when the intermolecular reaction of NPB is stronger than the interaction between NPB and the surface (PS). The molecules tend to reduce the surface energy and thus the interfacial (contact) area because the substrate (PS) has weak influence on the orientation of NPB. The VW film of NPB on PS percolates at about 5 nm. We expect in relation to the substrate, the molecular orientation of an NPB molecule is random
on PS as gate dielectric. This kind of orientation mimics the bulk film and the hopping distance is similar to the bulk. Therefore, one can obtain bulk mobility (TOF mobility) when well-connected NPB molecules are deposited on PS.
<table>
<thead>
<tr>
<th>NPB AFM images on PS</th>
<th>Nominal thicknesses</th>
<th>Roughnesses ($R_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="74x573_to_231x731.png" alt="Image" /></td>
<td>0nm</td>
<td>0.17nm</td>
</tr>
<tr>
<td><img src="73x410_to_231x569.png" alt="Image" /></td>
<td>1.5nm</td>
<td>1.91nm</td>
</tr>
<tr>
<td><img src="73x248_to_231x406.png" alt="Image" /></td>
<td>3nm</td>
<td>2.74nm</td>
</tr>
<tr>
<td><img src="73x85_to_232x244.png" alt="Image" /></td>
<td>5nm</td>
<td>1.61nm</td>
</tr>
</tbody>
</table>

Fig.4.8 AFM images of NPB films on PS
<table>
<thead>
<tr>
<th>NPB AFM images on SiO₂</th>
<th>Nominal thicknesses</th>
<th>Roughnesses ($R_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Image](71x573 to 231x731)</td>
<td>0nm</td>
<td>0.13nm</td>
</tr>
<tr>
<td>![Image](72x410 to 231x569)</td>
<td>1.5nm</td>
<td>2.20nm</td>
</tr>
<tr>
<td>![Image](72x248 to 231x406)</td>
<td>3nm</td>
<td>0.91nm</td>
</tr>
<tr>
<td>![Image](72x85 to 231x244)</td>
<td>5nm</td>
<td>0.32nm</td>
</tr>
</tbody>
</table>

Fig. 4.9 AFM images of NPB films on SiO₂
In contrast to PS, the growth of NPB on SiO\textsubscript{2} is very different. On PS surface, NPB molecules form discrete islands between 1.5 and 3nm. But the islands are larger and their shapes are more irregular. Compared to the islands on a PS surface, these NPB islands on SiO\textsubscript{2} have much larger lateral dimensions, suggesting that NPB molecules interact much stronger with SiO\textsubscript{2} than with PS. The interaction between an NPB molecule and the surface would favor a configuration in which the molecule prefers to orient itself parallel (horizontal) to the surface, with their $\pi$-orbitals facing down. As the NPB film grows from 1.5 to 3 nm, the roughness of the film significantly reduces from 2.2 nm to 0.9 nm. At the same time, most of the voids between the islands disappear, indicating that fresh incoming molecules prefer to sit on bare SiO\textsubscript{2} regions, consistent with a model in which NPB orients its horizontally with respect to the surface.

Fig.4.10 shows a model for the molecular orientations of NPB on SiO\textsubscript{2} and PS. On SiO\textsubscript{2}, As NPB molecules prefer to lie horizontally on the surface, their $\pi$ orbitals would be perpendicular to the surface, which is not favorable for charge transport along the surface as required by TFT measurement. This will result in an effective increase in the average charge hopping distance $a$, reduced $\mu_\infty$, and reduced carrier mobility even when the energetic disorder contribution is negligible at high temperatures as suggested by Eq.(4.4). Besides NPB, other molecules that can adopt
planar conformations are expected to behave in very similar manners on SiO$_2$ surface. We conclude that on SiO$_2$ surface, molecules that have planar conformations tend to lie horizontally with respect to the substrate. Such an orientation leads to poor $\pi$-$\pi$ overlaps and is unfavorable for charge transport parallel to the surface and suppress of the TFT hole mobility of these molecular films. On the other hand, when PS is used as the gate dielectric layer, these molecules orient themselves randomly as shown in Fig. 4.10. This kind of growth imitates the bulk-like orientation and results in a carrier mobility similar to TOF mobility. The molecules we discuss here, namely, NPB, TPD, and 2TNATA, they all possess planar conformations (3D chemical molecular model of NPB is shown in Figure 4.11) in which they can interact with the polar SiO$_2$ surface, adopt horizontal orientations, and results in reduced $\mu_\infty$. In all three cases, the reduction in $\mu_\infty$ is 25% to 35% of the bulk value of about $2 \times 10^{-2}$ cm$^2$ V$^{-1}$s$^{-1}$. Spiro-TPD, however, is different. Due to the presence of the spiro core, spiro-TPD possesses a 3-D structure as shown in Figure 4.11. The two amine moieties can still orient horizontally, but now the two phenyl rings linking the amines groups are lifted up. So we anticipate a weaker interaction between spiro-TPD and SiO$_2$, and the reduction of $\mu_\infty$ should not be as large as the other planar compounds. In fact, this is what we observe from the nearly overlapping $y$-intercepts in Fig. 4.7 for the spiro-TPD data.
Fig. 4.10 Molecular orientations of NPB on SiO$_2$ and PS.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>NPB</th>
<th>Spiro-TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top view</td>
<td><img src="image1" alt="NPB Top View" /></td>
<td><img src="image2" alt="Spiro-TPD Top View" /></td>
</tr>
<tr>
<td>Front view</td>
<td><img src="image3" alt="NPB Front View" /></td>
<td><img src="image4" alt="Spiro-TPD Front View" /></td>
</tr>
<tr>
<td>Side view</td>
<td><img src="image5" alt="NPB Side View" /></td>
<td><img src="image6" alt="Spiro-TPD Side View" /></td>
</tr>
<tr>
<td>Conformation</td>
<td>Planar</td>
<td>3-D</td>
</tr>
</tbody>
</table>

Fig. 4.11 3-D molecular structures of NPB and spiro-TPD. The 3D molecules were simulated by ChemOffice 2004.
4.3.5 Morphology and transport studies on 3D molecules

In the last section, we show that the difference in mobility between SiO$_2$ surface and PS surface partially originates from the planar conformations of NPB, TPD, and 2TNATA. To substantiate our conclusion, we introduce two non-planar molecules, Ir(ppy)$_3$ and Ir(piq)$_3$. The HOMO energy levels and chemical structures of the iridium compounds are shown in Fig. 4.1. We performed TFT measurements for both Ir(ppy)$_3$ and Ir(piq)$_3$ on SiO$_2$ and PS. The 3-D molecular structure of Ir(piq)$_3$ is shown in Fig. 4.10a and the transfer characteristics of Ir(piq)$_3$ and NPB on PS and SiO$_2$ are shown in Fig. 4.10b. The difference in output currents of NPB on both surfaces has more than one order in magnitudes. However, using a 3-D molecule, Ir(piq)$_3$, the output currents on both surfaces have no significant change. We expect the non-planar conformation of Ir(piq)$_3$ leads to similar output currents as shown in Fig. 4.10. Since Ir(piq)$_3$ is a 3-D molecule, the $\pi$-$\pi$ overlap between the molecules are similar no matter the molecules are grown on SiO$_2$ or PS. Therefore, the output currents of Ir(piq)$_3$ on both surfaces are similar. Besides Ir(piq)$_3$, we also measured the hole mobilities of Ir(ppy)$_3$ and similar conclusions can be drawn as in the case of Ir(piq)$_3$. 
Fig. 4.12 a) 3-D molecular structure of Ir(piq)$_3$ b) Transfer characteristics of Ir(piq)$_3$ and NPB on PS and SiO$_2$ gate dielectric layers.

Figure 4.13 shows the temperature dependent measurement of Ir(ppy)$_3$ and Ir(piq)$_3$ on PS and SiO$_2$. The results are consistent with Fig. 4.12. The hole mobilities of Ir(ppy)$_3$ and Ir(piq)$_3$ show insignificant change on SiO$_2$ or PS.
In conclusion, non-polar PS provides an ideal surface to probe bulk carrier transport of amorphous organic semiconductors. First, PS is nonpolar and the effects arising from surface dipolar disorder can be eliminated. Second, its inert surface favors 3D bulk-like growth of amorphous organic semiconductors even when the film thickness is below 10nm. With the help of thin film transistor and PS gate dielectric, one can probe bulk-like mobility with little amount of material.

Fig 4.13 Temperature dependent measurement of Ir(ppy)$_3$ and Ir(piq)$_3$ on PS and SiO$_2$.
4.3.6 OLED device application

In this section, we use TFT technique to measure hole mobility of four newly synthesized host materials in OLEDs from Prof. Zhaoxin Wu, Xi’an Jiaotong University in order to optimize the OLEDs performances.[1] A series of fluorinated BAnF derivatives have been reported to serve as deep-blue dopants in organic devices.[11] Fluorination of a benzene ring can enhance ambipolar transport by modifying the energy levels in polymers and in small molecules. In addition, C-F bond in fluorination forms a typical π stack arrangement which also enhances charge carrier mobility.[12-15] In addition, we chose a similar blue host material, 2-methyl-9,10-di(2-naphthyl)anthracene (mADN) for comparison. Fig.4.14 shows the chemical structure of 10,10’-bis(n-fluorophenyl)-9,9’-bianthracene (BAnF) and mADN. Table 4.3 shows the HOMO, LUMO, and bandgaps of all investigated chemical compounds.
Table 4.3 HOMO, LUMO and optical bandgaps of BAnF and mADN$^{[1]}$
4.3.6.1 Charge transport properties

The TFT hole only device structure in this study is p⁺Si/SiO₂/PS/ BAnF or mADN/MoO₃/Au and their transfer characteristics are shown in Fig. 4.15. The output current increases monotonically as distance increases between the main chain and the fluorine atom (i.e. Output current: BAn-2-F<BAn-3F<BAn-4F). This trend is attributed to the incorporation of the highly electronegative fluorine atom which hinders the charge transport in the film. The mobilities of the BAnF derivatives and mADN are summarized in Table 4.4. The our reference material, mADN has a hole mobility of 1-4.5x10⁻⁴ cm²/Vs while the champion material, BAn-4-F has a large mobility of 1.2-2.4x10⁻³ cm²/Vs. Furthermore, the mobility is also consistent with Fig. 4.12 (i.e. \( \mu_{BAn-2-F} < \mu_{BAn-3-F} < \mu_{BAn-4-F} \)). The electron mobility of the BAn-4-F film was characterized by the time-of-flight (TOF) transient photocurrent technique by Prof. Wu’s group. BAn-4-F possesses high electron mobility (~10⁻³ cm²/Vs) which is comparable to its hole mobility. With the balanced ambipolar conductivity of BAn-4-F, OLED devices are expected to have good performances.
Table 4.4 Hole mobilities of the BAnF derivatives and mADN. Obtained by TFT measurements. All organic compounds were grown on a PS gate dielectric layer. The reference compound is mADN which is available commercially.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{lin}$ [cm$^2$/Vs]</th>
<th>$\mu_{sat}$ [cm$^2$/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAn-2-F</td>
<td>1.7x10^{-4}</td>
<td>8.7x10^{-5}</td>
</tr>
<tr>
<td>BAn-3-F</td>
<td>2.2x10^{-4}</td>
<td>2.3x10^{-4}</td>
</tr>
<tr>
<td>BAn-4-F</td>
<td>2.4x10^{-3}</td>
<td>1.2x10^{-3}</td>
</tr>
<tr>
<td>BAn-(2,4)-F</td>
<td>1.5x10^{-6}</td>
<td>2.7x10^{-6}</td>
</tr>
<tr>
<td>mADN</td>
<td>1.0x10^{-4}</td>
<td>4.5x10^{-4}</td>
</tr>
</tbody>
</table>

Fig. 4.15 Transfer characteristics of BAnF derivatives and mADN
4.3.6.2 Electroluminescent properties†

BANF derivatives, especially BAn-4-F is expected to have better performance than ordinary host materials because it has wide band gap, balanced and high ambipolar mobility. Our collaborator, Prof. Z. Wu’s group had fabricated two sets of devices using N,N-diphenylamino phenyl vinyl biphenyl (DPAVBi) and 10-(2benzothiazoyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro1H,5H11H-benzo[l]pyrano(6,7,8,-ij)quinolinizin-11-one (C545T) as blue fluorescent dopant and green fluorescent dopant, respectively. The control materials for blue host and green host are 2-tert-butyl-9,10-di(2-naphthyl)anthracene (TBADN) and tris-(8-hydroxy-quinoine) aluminum (Alq3), respectively. The device configurations are shown below:

**Device B1**: ITO/MoO₃ (3nm)/NPB (30nm)/TcTa (10nm)/BAn-4-F:DPAVBi (3 wt%) (30nm)/TPBi (40nm)/LiF (1nm)/Al(100nm)

**Device B2**: ITO/MoO₃ (3nm)/NPB (30nm)/TcTa (10nm)/TBADN:DPAVBi (3 wt%) (30nm)/TPBi (40nm)/LiF (1nm)/Al(100nm)

**Device G1**: ITO/MoO₃ (3nm)/NPB(30nm)/TcTa (10nm)/BAn-4-F:C545T (2 wt%) (30nm)/TPBi (40nm)/LiF (1nm)/Al(100nm)

**Device G2**: ITO/MoO₃ (3nm)/NPB (30nm)/TcTa (10nm)/Alq₃:C545T (2 wt%) (30nm)/TPBi (40nm)/LiF (1nm)/Al(100nm)

Fig. 4.16 shows the normalized electroluminescence spectra for the four devices.

† OLED devices were fabricated and characterized by Prof. Z. Wu in Xi’an Jiaotong University, China
Device B1 and B2 show the same peaks at 492nm and 468nm while Device G1 and G2 show green emission of C545T with the peaks at 524nm and 504nm, respectively.

Fig. 4.16 EL spectra of DPAVBi and C545T-doped devices at 8V\textsuperscript{[1]}

Fig.4.17 shows the J-V characteristics and the external quantum efficiency (EQE) of four devices. The current density of four devices have no significant change after employing BAn-4-F as the host material. However, luminescence and the external quantum efficiency (EQE) of both BAn-4-F based devices were increased. Table 4.5 summarizes the device performances. The EQE of Device B1, B2, G1, and G2 are 5.42%, 3.13%, 5.20%, and 3.52%, respectively. Maximum luminescence of the BAnF employed devices were increased from 22573cd/m\textsuperscript{2} to 26992 cd/m\textsuperscript{2} in DPAVBi based
devices and increased from 58006 cd/m² to 72829 cd/m² in C545T based devices.

Fig. 4.17 J-V characteristics and the external quantum efficiency (EQE) of four devices [1]
<table>
<thead>
<tr>
<th>Device</th>
<th>Emissive layer</th>
<th>Luminance$_{\text{max}}$ (cdm$^{-2}$)</th>
<th>$\eta_{\text{ext}}$ (%)</th>
<th>CIE (x,y) at 8V</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>BAn-4-F:</td>
<td>26992</td>
<td>5.42</td>
<td>(0.15,0.27)</td>
</tr>
<tr>
<td></td>
<td>DPAVBi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>TBADN:</td>
<td>22573</td>
<td>3.13</td>
<td>(0.16,0.27)</td>
</tr>
<tr>
<td></td>
<td>DPAVBi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>BAn-4-F: C545T</td>
<td>72829</td>
<td>5.20</td>
<td>(0.25,0.61)</td>
</tr>
<tr>
<td>G2</td>
<td>Alq: C545T</td>
<td>58006</td>
<td>3.52</td>
<td>(0.31,0.64)</td>
</tr>
</tbody>
</table>

Table 4.5 Electroluminescence performance of DPAVBi- and C545T- doped devices.\cite{1}

To conclude, the carrier transport and photoluminescence properties of BAnF derivatives have been evaluated. Substituting fluorine atom(s) at different positions will affect the transport properties and OLED performances. Electroluminescence measurements suggest that BAn-4-F: DPAVBi and BAN-4-F: C545T devices have high EQE of 5.43%, and 5.2% respectively.

The enhanced of performance is attributed to the twisted charge-transfer (CT) state in BAn-4-F, which leads to a higher intersystem crossing rate for the transition $^3\text{CT} \rightarrow ^1\text{CT}$. Therefore the singlet generation is enhanced in the device.\cite{10}
References:


Chapter 5  Hybrid organic/inorganic perovskite solar cells

5.1 Introduction

Hybrid organic/inorganic perovskite solar cells are now recognized as a class of very promising devices in the area of optoelectronics. Perovskite solar cells are solution processable and flexible, low bandgaps, low exciton binding energy, high and ambipolar carrier mobilities, and high power conversion efficiencies.\(^{[1-4]}\) The earliest perovskite solar cells were fabricated from CH\(_3\)NH\(_3\)PbI\(_3\). Later on, it was discovered the presence of Cl\(^-\) ions during the crystallization process will improve device performances.\(^{[3]}\) In addition, some groups reported that the lead chloride serves as a nucleation site for iodide perovskite to enhance the morphology.\(^{[3]}\) Table 5.1 summarizes selected physical parameters reported from the literature for CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\). Below, we describe our study of a special methyl ammonium based compound, CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\). Since perovskites are an emerging materials, their electronic and optical properties have not been fully investigated. Before investigating such properties, a recipe for making reproducible, stable perovskite solar cell is required.
Table 5.1 CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (perovskite) properties

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical formula</strong></td>
<td>CH$_3$NH$<em>3$PbI$</em>{3-x}$Cl$_x$</td>
</tr>
<tr>
<td><strong>Binding energy</strong></td>
<td>37meV-50meV$^{[5,6]}$</td>
</tr>
<tr>
<td><strong>Diffusion length</strong></td>
<td>100nm-1000nm$^{[7-9]}$</td>
</tr>
<tr>
<td><strong>Dielectric constant</strong></td>
<td>70-1000$^{[10,11]}$</td>
</tr>
<tr>
<td><strong>Band gap</strong></td>
<td>1.5eV-1.55eV$^{[12-14]}$</td>
</tr>
</tbody>
</table>

5.2 Experimental Details

Fig. 5.1 shows the energy levels diagram of a perovskite solar cell that has been tested repeatedly in our lab. PEDOT:PSS was purchased from H.C Starck, CH$_3$NH$_3$PbI$_3$ (MAI) and PbCl$_2$ were purchased from Sigma Aldrich Co. LLC. ZnO nano particles were synthesized by Dr. Stephen Tsang’s group in the City University of Hong Kong. PC$_{60}$BM was purchased from Nano C, Inc., and aluminum was purchased from Alfa Aesar.
The structure of our perovskite was ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/ZnO/PC$_{60}$BM/LiF/Al. PEDOT:PSS layer was prepared by spin-coating its aqueous solution on an ITO substrate at 7000 rpm for 1 minute and dried at 140°C for 10 min in air. A layer of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, was prepared by spin-coating a precursor solution on PEDOT:PSS at 2000rpm for 30s. The precursor solution consists of PbCl$_2$ and methylammonium iodide with a molar ratio of PbCl$_2$:MAI =1:3 in DMF. The film was then annealed at different temperatures and durations. We have not yet determined x.
for our CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ film, but recent study showed that $x$ is in the range of 0.02~0.04$^{[15,16]}$. So our films should be treated as CH$_3$NH$_3$PbI$_3$. For solar cells fabrication, ZnO nanoparticles were further deposited on the CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ film. ZnO nanoparticles were prepared as a suspension in chloroform. The suspension was spun at 2000rpm for 30 seconds on the perovskite films. PC$_{60}$BM (30mg/ml in DCB) was then spun on top of ZnO nanoparticles at 2000rpm for 180s. Finally, the sample was transferred into a vacuum chamber for the deposition of cathode. The cathode was made by evaporating 1nm of LiF and 130nm of Al at a rate of 0.1nm/s and 0.2nm/s respectively. Immediately after cathode deposition, the device’s photovoltaic performance was examined under AM 1.5G conditions. The sample was given a constant $+2V$ bias for 3 seconds the measurement. Reversed bias measurement method ($+V$ to $-V$) was used. For some of the perovskite films, no additional layer were added. The bare films were used for structural, optical and morphological characterization.

5.3 Result and discussion

5.3.1 Structural and optical characterizations

After the fabrication of the CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ thin film, X-ray diffraction (XRD) was used to examine it crystal structure. Fig. 5.2 shows the standard XRD pattern of such a perovskite film. Intense peaks can be seen at 14°, 28.4°, and 43.3° which
correspond to (110), (220), and (330) planes respectively. The peaks are originated from the crystal structure of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. In addition, the XRD pattern is very similar to the reports from other groups.$^{[2,17,18]}$ Moreover, scanning electron microscope (SEM) images of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ films were acquired. Fig. 5.3 shows the SEM image of perovskite under 50k magnification. This image reveals that there are many pinholes on the surface which can lead to short circuit problem in the device. The optoelectronics properties of the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin film were then examined by photothermal deflection spectroscopy (PDS).$^{[19]}$

![XRD pattern](image)

Fig. 5.2 XRD pattern of a thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. 
PDS is a highly sensitive technique for measuring the subgap optical absorption of semiconductors. Its principles of operation have been extensively documented and is very well developed in our research group.\textsuperscript{[20]} PDS enables us to probe the absorption coefficient, bandgap, sub-bandgap states, and impurities in a semiconductor. It is sensitive to small optical absorption. In this study, PDS was used to analyze the bandgap and molecular vibrations in perovskite materials.

Figure 5.4 shows the PDS spectrum of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. The sharp decrease of absorption coefficient at around 800nm reveals the bandgap of our material is around 1.55eV which matches the reported value in Table 5.1. Besides the optical gap

Fig.5.3. SEM image of a thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin film
transition, we can observe the peaks of C-H and N-H vibrations. $\nu_{N-H}$ and $\nu_{C-H}$ are the fundamental frequencies of N-H and C-H stretching respectively. The peaks at 1600nm and 1240nm correspond to the first and the second overtone of C-H vibrations, respectively. Similarly, the peaks at 1390nm and 1140nm correspond of to the first and the second overtone of N-H vibrations, respectively.\[21\] Both C-H and N-H vibrations can be observed for the perovskite films. The intensity of N-H peaks are generally stronger than C-H peaks (Both first and second overtones). The peak at 850nm corresponds to the unreacted MAI inside the film. Fig. 5.5 shows the PDS spectrum of MAI which has a sharp peak at 850nm. In our perovskite films, there appear to have excess MAI that remains after the crystallization process. Table 5.2 summarizes the absorption peaks observed from our perovskite film. C-H and N-H stretches are obtained from the literature. The results show that our observed values are consistent with their gas phase values.\[21\]
Fig. 5.4. PDS spectrum of a thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. The arrows with labels identify the origins of the spectral peaks. The peak assignments are shown in Table 5.2. The peak at about 1.5 eV can be associated with unreacted MAI from the precursor solution.
850 nm peak observed from CH$_3$NH$_3$PbCl$_x$I$_{3-x}$

Fig. 5.5. PDS spectrum of thin film of CH$_3$NH$_3$I (MAI).
Table 5.2 Approximate wavelength of C-H and N-H vibrations. \(\nu_1\), \(2\nu_1\), and \(3\nu_1\) are fundamental, first, and second overtone of the vibration respectively. \(^a\) 1st overtone of N-H absorption is consistent with Fig.3 in Dianov et al.. \(^b\) Similar value of 0.85eV was reported in Futami et al..

5.3.2 Optimization of perovskite solar cell

We optimize our perovskite solar cells by tuning the following factors. 1) CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) annealing durations, 2) CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) annealing temperatures, 3) Spin speeds of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\).

5.3.2.1 Optimization of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) annealing duration

In the preparation of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) film, the samples were annealed to 75 °C for 1 hour in order to remove residual solvents. Subsequently, the sample was further heated to 95°C to promote perovskite crystallization. It has been reported that the optimum annealing temperatures are between 88 and 110 °C. The annealing duration
is also very critical.\textsuperscript{[18,24,25]} Therefore we optimize the system by varying the annealing duration. Fig.5.6 and Table 5.3 show devices performances under four different annealing times. CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3-x}Cl\textsubscript{x} is very sensitive to the annealing duration because the annealing temperature is a key parameter to tune the crystallinity of the perovskite. Crystal size, rate of crystallization and crystallographic planes of perovskite are closely related to the annealing temperature and duration. If the annealing duration is too short, the crystal formation is not complete and results in low J\textsubscript{sc}. On the other hand, if the annealing duration is too long (green pentagons), crystal deformation occurs and the performance goes down. An annealing duration of 60 minutes (red circles) gives the best performance among three different samples.
Fig. 5.6 J-V characteristics of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cell with different annealing durations at 95°C.

<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>45 minutes</td>
<td>11.8</td>
<td>0.78</td>
<td>59.2</td>
<td>5.5</td>
</tr>
<tr>
<td>60 minutes</td>
<td>12.4</td>
<td>0.86</td>
<td>63.2</td>
<td>6.8</td>
</tr>
<tr>
<td>90 minutes</td>
<td>13.5</td>
<td>0.88</td>
<td>50.6</td>
<td>6.0</td>
</tr>
<tr>
<td>120 minutes</td>
<td>4.06</td>
<td>0.72</td>
<td>43.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 5.3 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different annealing durations at 95°C.
5.3.2.2 Optimization of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ spin speed

In polymeric organic solar cell, one may optimize the power conversion efficiency by tuning the thickness bulk heterojunction layer. However, in our perovskite solar cell, the films consist of rough crystallites (Fig. 5.3) and have many pin holes. So it is difficult to measure the exact film thickness from a profilometer. As a result, we optimize the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cell system by varying the spin speed of perovskite solution. Fig. 5.7 shows the devices performances under different spinning speeds. Table 5.4 summarizes the resulting device performances. A slow spin speed gives thicker films and vice versa. If the film is too thin, optical absorption will be suppressed. If the film is too thick, however, charge transport may limit the $J_{sc}$ because excitons have better chances of recombination. A spin speed of 2000rpm for 30s yields the best device with a power conversion efficiency 7.4%. Although the exact thickness of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ cannot be determined easily as the film thickness varies even with the same spin speed, the average thickness should be around 200nm-300nm as determined by many trials using profilnometer.
Fig. 5.7 J-V characteristics of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different spin speeds.

Table 5.4 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different spin-speeds.

<table>
<thead>
<tr>
<th>Spin speed (rpm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>15.9</td>
<td>0.84</td>
<td>49</td>
<td>6.7</td>
</tr>
<tr>
<td>2000</td>
<td>16.7</td>
<td>0.87</td>
<td>50</td>
<td>7.4</td>
</tr>
<tr>
<td>3000</td>
<td>11.7</td>
<td>0.83</td>
<td>63</td>
<td>6.4</td>
</tr>
<tr>
<td>4000</td>
<td>11.7</td>
<td>0.85</td>
<td>64</td>
<td>6.6</td>
</tr>
<tr>
<td>6000</td>
<td>12.0</td>
<td>0.88</td>
<td>55</td>
<td>5.9</td>
</tr>
</tbody>
</table>
5.3.2.3 Optimization of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ annealing temperature

The crystallization of a perovskite film is expected to strongly depend on the annealing duration and temperature. So we optimize the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cell by varying the annealing temperature. Fig. 5.8 shows the devices performances under different annealing temperature. Table 5.5 summarizes devices performances. All the temperatures shown were the calibrated temperatures measured on the hot plate by a pair of thermocouple wires. With an annealing temperature of 114°C, we get a reproducible perovskite solar cell with >9% PCE. In addition, we notice that the perovskite film is very sensitive to the annealing temperature. When the temperature was decreased to 95°C, PCE drops from 9.4% to 1.1%. Such a drastic change can only be attributed to the incomplete perovskite crystal formation. The annealed film appears to have decomposed and results in a yellowish film. Therefore we concluded that the optimum annealing temperature of perovskite solar cell should be between 112°C to 117°C. The optimized processing window indeed is very narrow and occur within a temperature range of about 5°C. Further optimization should be needed in future in order to have a better yield. Fig. 5.9 shows the parameters of the perovskite solar cell under different annealing temperatures.
Fig. 5.8 J-V characteristics of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different annealing temperature

<table>
<thead>
<tr>
<th>Annealing temp.(°C)</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>3.13</td>
<td>0.79</td>
<td>47.5</td>
<td>1.1</td>
</tr>
<tr>
<td>107</td>
<td>12.8</td>
<td>0.81</td>
<td>48.4</td>
<td>5.0</td>
</tr>
<tr>
<td>112</td>
<td>15.3</td>
<td>0.87</td>
<td>69.9</td>
<td>9.3</td>
</tr>
<tr>
<td>114</td>
<td>16.8</td>
<td>0.86</td>
<td>64.7</td>
<td>9.4</td>
</tr>
<tr>
<td>117</td>
<td>16.3</td>
<td>0.88</td>
<td>64.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Table 5.5 Summary table of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cells prepared at different annealing temperatures
Fig. 5.9 Performance of the perovskite solar cells prepared at different annealing temperatures.
5.3.2.4 Employing other hole transporting layer

The performance of a perovskite cell can be affected by the electron transporting layer (ETL) and the hole transporting layer (HTL). For example, there are reports that hole conducting polymers and small molecules are suitable for perovskite solar cells through thermal evaporation with reasonable PCE because $V_{oc}$ can be increased and exceed 1V.\textsuperscript{10,26} Below, we give some very preliminary results with alternate HTL. We employed MoO$_3$, and HATCN to replace PEDOT:PSS to fabricate perovskite solar cells. Both HTLs were thermally evaporated and they are widely used in OPVs and OLEDs. Fig. 5.10 shows the chemical structures and energy levels of MoO$_3$ and HAT-CN.

![Chemical structures and energy levels of MoO$_3$ and HAT-CN](image)

Fig.5.10. a) Chemical structures of MoO$_3$ and HATCN. b) Energy levels of MoO$_3$, HATCN and perovskite

After employing MoO$_3$ and HATCN as HTL, the solar cell structure becomes
Fig. 5.11 shows the J-V characteristics of perovskite solar cells after employing MoO$_3$ and HATCN as HTLs and Table 5.6 summarizes the devices performances. Devices with MoO$_3$ and HATCN layers have inferior performances relative to the standard cell with PEDOT:PSS layer. Scanning electron microscope was used to investigate the surface of perovskite on MoO$_3$ and on PEDOT:PSS.

Fig. 5.11 J-V characteristics of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solar cell with PEDOT:PSS, MoO$_3$, and HATCN as HTL.
Fig. 5.12 shows the SEM images of perovskite film on MoO$_3$ and on PEDOT:PSS. Under 10000x magnification, the perovskite film on MoO$_3$ has many large voids. Such voids are expected to generate conducting paths between ZnO or PC$_{60}$BM layers on the cathode side and MoO$_3$ on the anode side. The device will be shorted easily. Therefore, device performed poorly when MoO$_3$ was employed as the HTL.

<table>
<thead>
<tr>
<th>HTL</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>12.4</td>
<td>0.9</td>
<td>66</td>
<td>7.1</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>6.2</td>
<td>0.44</td>
<td>37</td>
<td>1.0</td>
</tr>
<tr>
<td>HATCN</td>
<td>3.2</td>
<td>0.3</td>
<td>51</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 5.6 Performances of CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ solar cells with PEDOT:PSS, MoO$_3$, and HATCN as HTL
5.3.3 Importance of ZnO buffer layer

Figure 5.13 shows the J-V curves of our perovskite solar cells with and without ZnO nanoparticles in between CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and PC$_{60}$BM layer. With the ZnO nanoparticle interlayer, a high PCE of 8.6% is obtained. The corresponding short-circuit current, open-circuit voltage, and fill-factor are 15.2mA/cm$^2$, 0.86V, and 65.5%, respectively. Without ZnO nanoparticles, all parameters deteriorate significantly and a very poor PCE of 0.05% was obtained. The performances of perovskite solar cells with or without ZnO are summarized in Table 5.7.
Fig. 5.13 J-V characteristics of perovskite solar cells with or without ZnO

<table>
<thead>
<tr>
<th></th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with ZnO</td>
<td>15.2</td>
<td>0.86</td>
<td>65.5</td>
<td>8.6</td>
</tr>
<tr>
<td>without ZnO</td>
<td>0.39</td>
<td>0.38</td>
<td>34.5</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 5.7 Device performances of the perovskite solar cell with or without ZnO

It is clear that without the ZnO layer, all four parameters, J<sub>sc</sub>, V<sub>oc</sub>, FF, and PCE were greatly decreased. We then investigate the importance of ZnO layer by performing SEM measurement on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> film. Recall from Figure 5.3 which reveals that there are many pinholes in the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> thin film. Without ZnO, PC<sub>60</sub>BM molecules could possibly short the device by making direct contacts between the PEDOT:PSS and the PC<sub>60</sub>BM layers. This phenomenon results in
ultralow $J_{sc}$ in the sample. Therefore, ZnO nanoparticles act as a passivation layer to prevent short circuit.

5.3.4 Future improvements

Although an optimized methodology has been obtained for the preparation of the perovskite layers, the performances of our perovskite solar cell still have a lot of room for improvement. For example, in general, reported perovskite PCEs have been above 13%.\[^{3,12,27}\] There are several ways to improve the PCE in future.

5.3.4.1 Replacing hole transporting layer

Although employing MoO$_3$ and HATCN as HTL have been unsuccessful, other HTLs such as poly-TPD, PCDTBT, NPB, TFB should be explored as long as the HTL can fulfil following conditions: 1) HOMO of the HTL should match the HOMO of perovskite, -5.3eV. 2) the surface energy or morphology has to favor the crystal growth of perovskite, which means the number of holes or voids should be as few as possible. 3) CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite can wet on the underlying HTL surface. If the HTL can fulfil the three conditions above, a device with $V_{oc} > 1V$ should be achievable.
5.3.4.2 Thermal evaporation of CH$_3$NH$_3$PbI$_3$–xCl$_x$ inorganic/organic layer

The crystal growth of CH$_3$NH$_3$PbI$_3$–xCl$_x$ is sensitive to temperature, humidity, or other factors. Although a nitrogen gloves box can provide a well-controlled and consistent fabrication environment, it is more stable to control the fabrication under vacuum. Therefore, it is expected that growth of perovskite films by thermal evaporation should yield less variations in the crystal growth of perovskite films. In addition, there is no wetting problem when CH$_3$NH$_3$PbI$_3$–xCl$_x$ is evaporated on different HTLs.

5.3.4.3 Inverted structure

The first perovskite solar cells employed a dye-sensitized solar cells (DSSC) architecture was employed in perovskite solar cell at the very beginning. Mesoporous TiO$_2$ was a key material in DSSC perovskite solar cell. Using mesoporous TiO$_2$ as electron transporting layer can reduce the short-circuit problem in perovskite solar cell. However, such metal oxide require high temperature processing which can greatly increase the fabrication cost.

5.4 Summary

In this chapter, perovskite solar cell was demonstrated with a reproducible recipe. First, the results show that ZnO is essential in our perovskite solar cell system to passivate CH$_3$NH$_3$PbI$_3$–xCl$_x$ surface layer. Without the ZnO, device performance
dropped from 8.6% PCE to 0.05% PCE.

Secondly, MoO$_3$ and HATCN were employed to replace PEDOT:PSS as HTL. However, many voids were formed when CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ were deposited on MoO$_3$. Therefore, the ETL may be in direct contact with the HTL and form short circuit channels and worsen the cell performance.

Finally, by tuning the following factors: 1) annealing duration, 2) annealing temperature, and 3) perovskite layer spinning speed, a cell with a 9.35% solar cell has been fabricated.
References:


http://www.intechopen.com/books/wide-spectra-of-qualitycontrol/near-infra-red-spectroscopy


123
Chapter 6 Conclusion

In this thesis, we employed organic thin film transistors (OTFT) to probe the bulk mobilities of four different hole transporters (HTs). Polystyrene (PS) was used as the gate dielectric layer. In depth studies of the thickness dependence of NPB devices have been done and the results show that a minimum thickness of 10nm is sufficient for TFT measurements. In contrast, using SiO$_2$ as gate dielectric, the TFT mobilities are 1-2 orders lower. On SiO$_2$ surface, the energetic disorder ($\sigma$) of the HTs increase. Simultaneously, the high temperature limits ($\mu_\infty$) of the carrier mobilities decrease. Both $\sigma$ and $\mu_\infty$ contribute to the reduction of the carrier mobility. The increase in $\sigma$ is related to the presence of randomly oriented polar Si-O bonds.

Initial growth of NPB film has been examined by atomic force microscopy (AFM). The AFM images suggest that NPB molecules undergo island growth (Volmer-Weber growth) on the non-polar gate dielectric, PS. This kind of growth mode occurs when the intermolecular interaction of NPB is stronger than the interaction between NPB and the PS surface. The molecules tend to reduce the surface energy and thus the interfacial (contact) area because the substrate (PS) has weak influence on the orientation of NPB. On the other hand, on SiO$_2$ surface, the interaction between an NPB molecule and the surface would favor a configuration in which the molecule prefers to orient itself parallel (horizontal) to the surface, with
their π-orbitals facing down. Such orientation does not favorable to carrier transport in OTFT measurements.

Apart from OTFT measurements, we examined the optoelectronic properties of perovskite materials. The bandgap and subgap optical absorptions vibrations have been evaluated by photothermal deflection spectroscopy (PDS). An optical bandgap of 1.55eV has been calculated from the experiment which is consistent with the reported value. From the scanning electron microscope, we found that there are many pinholes on the perovskite thin film which may generate conducting path from cathode to anode. The current may be shorted in this case. Furthermore, we optimized our perovskite solar cell to ~9% power conversion efficiency (PCE) by tuning the annealing duration, annealing temperature, and the spin speed of perovskite solar cell. It is found that the processing window of perovskite solar cell is very narrow because the crystallization process is very sensitive to the annealing processes.
Curriculum Vitae

Academic qualifications of the thesis author, Mr. SIT Wai Yu, Jon:

- Received the degree of Bachelor of Science in Applied Physics from the Hong Kong Baptist University, June 2012.

May 2015