Charge Carrier Transport and Injection across Organic Heterojunctions

By

Sai Wing Tsang

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Materials Science and Engineering
University of Toronto

© Copyright by Sai Wing Tsang 2009
Charge Carrier Transport and Injection across Organic Heterojunctions

Sai Wing Tsang

Doctor of Philosophy
Graduate Department of Materials Science and Engineering
University of Toronto
2009

ABSTRACT

The discovery of highly efficient organic light-emitting diodes (OLEDs) in the 1980s has stimulated extensive research on organic semiconductors and devices. Underlying this breakthrough is the realization of the organic heterojunction (OH). Besides OLEDs, the implementation of the OH also significantly improves the power conversion efficiency in organic photovoltaic cells (OPVs). The continued technological advancements in organic electronic devices depend on the accumulation of knowledge of the intrinsic properties of organic materials and related interfaces. Among them, charge-carrier transport and carrier injection are two key factors that govern the performance of a device.

This thesis mainly focuses on the charge carrier injection and transport at organic heterojunctions. The carrier transport properties of different organic materials used in this study are characterized by time-of-flight (TOF) and admittance spectroscopy (AS). An injection model is formulated by considering the carrier distribution at both sides of the interface. Using a steady-state simulation approach, the effect of accumulated charges on energy level alignment at OH is revealed. Instead of a constant injection barrier, it is found that the barrier varies with applied voltage. Moreover, an escape probability function in the injection model is modified by taking into account the total hopping rate and available hopping sites at the interface. The model predicts that the injection current at low temperature can be dramatically modified by an extremely small density of deep trap states. More importantly, the temperature dependence of the
injection current is found to decrease with increasing barrier height. This suggests that extracting the barrier height from the $J$ vs $1/T$ plot, as commonly employed in the literature, is problematic. These theoretical predictions are confirmed by a series of experiments on heterojunction devices with various barrier heights. In addition, the presence of deep trap states is also consistent with carrier mobility measurements at low temperature.

From the point of view of application, an interface chemical doping method is proposed to engineer the carrier injection at an organic heterojunction. It is found that the injection current can be effectively increased or suppressed by introducing a thin (2 nm) doped organic layer at the interface. This technique is further extended to study the impact of an injection barrier at the OH in OLEDs, on device performance. It is shown that a 0.3 eV injection barrier at the OH, that is normally negligible at metal/organic interface, can reduce the device efficiency by 25%. This is explained by the carrier distribution in the density-of-states at the OH.

Furthermore, the carrier transport properties in a bulk heterojunction system are investigated. The bulk heterojunction consists of an interpenetrating network of a polymeric electron donor and a molecular electron acceptor. This material system has been studied in the last few years as an attractive power conversion efficiency (5% under AM 1.5) of OPV cells has been demonstrated. It is found that the electron mobility is greatly dependent on the thermal treatment of the film. Interfacial dipole effect at the heterojunction between the donor and the acceptor is proposed to be the determining factor that alters the carrier mobility in different nano-scale structures.
ACKNOWLEDGEMENTS

First of all, I would like to sincerely thank my supervisor, Prof. Z. H. Lu, who has shared his perspectives on the area of organic electronics and who taught me how to bring out the main theme of a project.

I would also like to thank Dr. Y. Tao for providing me a high quality and freedom environment to conduct the experiments in the National Research Council (NRC) which make this thesis possible. Dr. M. Denhoff has been very inspiration for the understanding of the hopping injection model and semiconductor physics. Dr. N. Drolet has been very helpful in fabricating the solar cell devices, and spending many hours for discussions. Special thanks to Hiroshi, Raluca, and Eric for their technical support.

I should also thank my fellow group members for their friendship and inspiration: Dr. Fenghong Li, Yanyan Yuan, Gordon Yip, Zhibin Wang, Kevin Tsai, Dr. Daniel Grozea, Yiqun Zhao, Michael Helander, Graham Murdoch, and Mark Greiner. Especially Zhibin and Mark for spending time together in the soccer field.

Financial support provided by the Connaguht Scholarship and the National Research Council is greatly appreciated.

Finally, I would like to thank my parents and sister for their support and patience. Last but not least, special thanks to Mingming for her encourage and love in the last 3 years.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. ii

ACKNOWLEDGEMENTS ............................................................................................ iv

TABLE OF CONTENTS ............................................................................................... v

LIST OF FIGURES ....................................................................................................... x

LIST OF TABLES ......................................................................................................... xviii

---

Chapter 1  Introduction............................................................................................ 1

1.1 Abstract ............................................................................................................. 1

1.2 Organic electronics: Development of heterojunction technology ................. 2

1.2.1 Organic light-emitting-diode (OLED) ............................................................ 2

1.2.2 Organic photovoltaic cell (OPV) .................................................................... 7

1.3 Carrier transport and injection in organic semiconductors............................... 9

1.3.1 Electronic properties of organic semiconductor ......................................... 10

1.3.2 Energy/Charge transfer ................................................................................. 12

1.3.3 Formalism of carrier transport in organic semiconductor ......................... 18

1.3.4 Analytical models of carrier transport in organic semiconductor ............. 27

1.4 References ......................................................................................................... 31

Chapter 2  Experiment and material details......................................................... 35

2.1 Abstract ............................................................................................................. 35

2.2 Substrate and thin film preparation .................................................................. 36

2.2.1 Substrate treatment ....................................................................................... 36

2.2.2 Thermal evaporation of organic and metal thin films ............................... 36

2.2.3 Spin coating of polymers ............................................................................. 38
2.3 Characterization techniques and apparatus .................................................. 39
  2.3.1 Time-of-flight (TOF) technique .............................................................. 39
  2.3.2 Admittance Spectroscopy (AS) .............................................................. 41
  2.3.3 Current-voltage-luminance (IVL) measurement ...................................... 43
2.4 Organic electronic materials used for this study ........................................ 44
2.5 References ............................................................................................... 46

Chapter 3 Charge-carrier induced barrier-height reduction at organic heterojunction... 47
  3.1 Abstract .................................................................................................... 47
  3.2 Introduction ........................................................................................... 48
  3.3 Experiment ............................................................................................ 50
  3.4 Results and discussion ............................................................................ 51
    3.4.1 Steady-state simulation: extracting $F_{int}$ and $p_{int}$ ............................ 51
    3.4.2 Modified injection model at OOI ....................................................... 55
    3.4.3 Comparing to experiment .................................................................. 60
  3.5 Conclusion ............................................................................................. 63
  3.6 References ............................................................................................. 64

Chapter 4 Temperature dependence of carrier injection across organic heterojunctions.. 65
  4.1 Abstract ................................................................................................... 65
  4.2 Introduction ............................................................................................ 66
  4.3 Theoretical modeling ............................................................................. 69
    4.3.1 Carrier injection model with proposed $w_{esc}$ .................................... 69
    4.3.2 Impact of deep trap states ................................................................. 74
  4.4 Experiment on heterojunction devices with various injection barriers .......... 82
Chapter 5  Engineering carrier transport across organic heterojunctions by interface doping

5.1 Abstract

5.2 Introduction

5.3 Experiment

5.4 Results and discussion

5.4.1 Injection limited at OOI

5.4.2 Engineering carrier injection by interface doping at OOI

5.4.3 Energy alignment at OOI with doped inter-layer

5.5 Conclusion

5.6 References

Chapter 6  Impact of energy offset at organic heterojunctions on organic light-emitting diodes (OLEDs)

6.1 Abstract

6.2 Introduction to multilayer OLEDs

6.3 Experiment

6.4 Results and discussion

6.4.1 Organic-organic hole injection barrier in Alq3 devices

6.4.2 Organic-organic hole injection barrier in BNPB devices

6.4.3 Organic-organic hole injection barrier in TBADN devices
Appendix B- Publications

B.1 Publications resulting from this thesis
B.2 Other related publications
B.3 Conference presentations

A.5 Disorder parameters extracted by Gaussian-Disorder-Model (GDM)
LIST OF FIGURES

Fig. 1.1 Configuration of eletro-luminescence cell and molecular structures. Adapted from Ref. [5] 3

Fig. 1.2 General structure of OLED with multilayer of organic materials 4

Fig. 1.3 Schematic of singlet (fluorescence) and triplet (phosphorescence) emissions 5

Fig. 1.4 Sony's XEL1 11" OLED (Organic Light Emitting Diode) Digital Television. Adapted from www.sony.com 6

Fig. 1.5 Configuration and current-voltage characteristics of an ITO/CuPc (250 Å)/PV (450 Å) / Ag cell. Adapted from Ref. [27]. 7

Fig. 1.6 Bilayer heterojunction and bulk heterojunction OPV cells. 8

Fig. 1.7 (a) The sp2 orbitals of carbon atom and the 1s orbital of hydrogen atom, (b) the σ-bond of the carbon atom of benzene, and (c) the π-orbital in benzene. 10

Fig. 1.8 Energy splitting of bonding and anti-bonding orbitals 11

Fig. 1.9 (a) Molecular structure of Alq3, (b) HOMO, (c) LUMO. Adapted from Ref. [43] 11

Fig. 1.10 Emission and absorption spectra of donor and acceptor molecules respectively. 12

Fig. 1.11 Schematic diagram of charge transfer from Marcus theory, the red line represent the path of charge transfer in (a) the absent of electric field, (b) resonance, (c) and Marcus inversion. 15

Fig. 1.12 Transport mechanism in solids. Adapted from Ref. [58]. 17

Fig. 1.13 A log(I)-log(t) plot for 1:1 TNF-PVK molecular doped polymer. The slopes of the dashed lines are -0.2 and -1.8 respectively. Adapted from [59]. 21

Fig. 1.14 Temporal evolution of the distribution of carrier energies in a Gaussian DOS of width σ = 2. All profiles are broken at the same carrier density illustrating the different relaxation patterns for mobile and immobile carriers. $\varepsilon_0$ denotes the theoretical mean energy in the long-time limit. Adapted from Ref. [61]. 22
<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>Mobility $\mu$ vs square root of the applied electric field $E^{1/2}$ for a hopping system with fixed energetic disorder ($\sigma = 3$) and variable off-diagonal (positional) disorder. Adapted from Ref. [61].</td>
</tr>
<tr>
<td>1.16</td>
<td>Carrier mobility of a molecularly doped polymer system DESAP:polycarbonate as a function of temperature. Adapted from Ref [62].</td>
</tr>
<tr>
<td>1.17</td>
<td>Field dependent mobility for the CDM for $\delta_d = 5.1$ and two different types of hopping rates, Miller-Abrahams (square) and symmetric (diamond). Adapted from Ref [64].</td>
</tr>
<tr>
<td>1.18</td>
<td>Field dependent mobility for polaron transport in a dipolar solid. Adapted from Ref. [67].</td>
</tr>
<tr>
<td>1.19</td>
<td>Dependence of the equilibrium hopping mobility upon the dopant concentration in a disordered organic semiconductor. Adapted from Ref. [79].</td>
</tr>
<tr>
<td>2.1</td>
<td>(a) 2 inch x 2 inch ITO substrate for fabricating OLED devices; (b) 12 mm x 20 mm ITO substrate for TOF and organic heterojunction devise.</td>
</tr>
<tr>
<td>2.2</td>
<td>General sandwiched structure of device on (a) 2 inch x 2 inch ITO substrate for fabricating OLED devices; (b) 12 mm x 20 mm ITO substrate for TOF and organic heterojunction devise.</td>
</tr>
<tr>
<td>2.3</td>
<td>The cluster tool for fabricating organic electronic devices.</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic diagram of the thermal evaporation process.</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic diagram of spin coating method. The substrate is placed at the center of the platform.</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic diagram of the TOF setup with an organic sample housed inside the cryostat.</td>
</tr>
<tr>
<td>2.7</td>
<td>Typical photocurrent transient measured by TOF technique.</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic diagram of the experiment setup of admittance spectroscopy.</td>
</tr>
<tr>
<td>2.9</td>
<td>(a) The capacitance-frequency relationship can be directly measured by the impedance analyzer. (b) By definition, the negative differential susceptance $-\Delta B = - \omega (C - C_{geo})$. The maximum point in the $-\Delta B$ plot corresponds to $\tau^{-1}$, which is related to the average carrier transit time $\tau_{dc}$ in the TOF experiment by $\tau_{dc} = 0.56 \tau$. [6]</td>
</tr>
</tbody>
</table>
Fig. 2.10 Schematic diagram of the experiment setup of IVL measurement.

Fig. 3.1 Comparison between (line) previous injection model and (symbols) the measured current density of a two-layer device.

Fig. 3.2 Surface topology of 320 nm MTDATA obtained by AFM with surface roughness (rms) equal to 0.9 nm.

Fig. 3.3 Simulation procedure with ATLAS for a two-layer system to extract the electric field and carrier distributions.

Fig. 3.4 Extracted (a) electric field and (b) carrier distribution near the OOI.

Fig. 3.5 Extracted interface electric field $F_{\text{int}}$ with ATLAS at different temperatures.

Fig. 3.6 Extracted carrier density at the injecting (first) layer side of the interface, $p_{\text{int1}}$, and the accepting (second) layer side of the interface, $p_{\text{int2}}$, with ATLAS.

Fig. 3.7 (a) The normalized Gaussian energetic distribution of the carrier density $p_{\text{int1}}(E_{\text{int1}})$ at the injecting layer side of the interface. (b) The normalized factional injection current densities $J(E_{\text{int1}})$ contributed by the carriers at different energy levels. The results are compared with different values of the quasi-Fermi level $E_F$ (from -0.2 eV to -0.4 eV),

Fig. 3.8 Schematic diagrams of energy level alignment at the heterojunction with the boundary condition of (a) vacuum level alignment and (b) Fermi level alignment. The lower graphs are the corresponding alignment of the Gaussian density-of-state (DOS) at both sides of the interface. The shaded region represents those states occupied by electrons.

Fig. 3.9 The field and voltage dependence of the variable barrier $\phi_v$ at 323 K (□), 288 K (○), 266 K (△), 219 K (▽), and 172 K (◇). Assuming thermodynamic equilibrium, $\phi_v$ is calculated by Eq. (4) with $p_{\text{int1}}$ and $p_{\text{int2}}$ obtained by the steady-state simulation. The solid line is a fitting curve to an exponential decay function.

Fig. 3.10 Measured $J - F_{\text{int}}$ characteristics of the ITO / MTDATA(320 nm) / NPB(390 nm) / Ag heterojunction device at 323 K (□), 288 K (○), 266 K (△), 219 K (▽), and 172 K (◇). The corresponding solid symbols are the calculation results based on the modified injection model in Eq. (3) with the variable barriers $\phi_v$ in Fig. (3). The inset is the $J$ vs $1/T$ plot at $F_{\text{int}}$ =
0.5 M V/cm. Fitting the calculation results (solid line) with Eq. (3) to the experiment results (opened symbols) obtains $\phi^* = 0.45 \pm 0.1$ eV, $\sigma_{MTDATA} = 95$ meV and $\sigma_{NPB} = 110$ meV.

Fig. 4.1 Illustration of carrier hopping across a disordered organic heterojunction. The density-of-state (DOS) of the lowest-unoccupied molecular orbital (LUMO) and deep trap energy levels is assumed to be Gaussian.

Fig. 4.2 A schematic diagram of the spatial integration in Eqs. (4.7) and (4.8). An injected carrier at the center of the sphere is localized at a distance $x$ away from the interface. The preferable hopping neighbors are located at a distance $r$ from the injected carrier with a direction $\theta$ between the interface electric field.

Fig. 4.3 Calculated escape probability function $w_{esc}$ using Eq. (4.6) and (4.9) of an injected carrier at a distance $x = 10^{-7}$ cm and an energy $E$ in the second layer. It is parameterized for $\sigma_1 = \sigma_2 = 0.1$ eV, $T = 300$ K, $F_{int} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, and $\gamma = 5 \times 10^{-7}$ cm$^{-1}$. The inset is a linear scale of $w_{esc}$.

Fig. 4.4 Calculated escape probability function $w_{esc}$ with the presence of deep trap states using Eq. (4.6) and (4.9) of an injected carrier at a distance $x = 10^{-7}$ cm and an energy $E$ in the second layer. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1$ eV, $F_{int} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$, $n_t = 10^{10}$ cm$^{-3}$, and $E_t = -1$ eV. The inset is a linear scale of $w_{esc}$.

Fig. 4.5 Calculated $J$ vs $1/T$ characteristics using Eq. (4.4). The solid and dash lines are calculated with the escaped probability function described in Eq. (4.6) and (4.9) respectively. The symbols are the corresponding $J$ vs $1/T$ characteristics with various $w_{esc}$ in the presence of deep trap states. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1$ eV, $F_{int} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$, $n_t = 10^{10}$ cm$^{-3}$, and $E_t = -1.5$ eV.

Fig. 4.6 Calculated fractional current-density $J(E_2, x)$ using Eq. (4.6) and (4.9) at different temperatures. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1$ eV, $F_{int} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$.

Fig. 4.7 Calculated $J$ vs $1/T$ characteristics using Eq. (4.4) and (4.9) as a function of barrier height $\phi$. The lines (symbols) are calculated $J$ without (with) deep trap states. The same parameters as in Fig. 4.5 are used in the calculation.

Fig. 4.8 Calculated $-(slope \ of \ J \ vs \ 1000/T)$ as a function of barrier height $\phi$ for $T > 200$K. The line (symbol) is calculated $J$ without (with) deep trap
states. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1 \text{ eV}$, $F_{\text{int}} = 5 \times 10^5 \text{ V/cm}$, $N = 10^{21} \text{ cm}^{-3}$, $\gamma = 5 \times 10^{-7} \text{ cm}^{-1}$, $n_t = 10^{10} \text{ cm}^{-3}$, and $E_t = -1.5 \text{ eV}$.

Fig. 4.9 Calculated $J$ vs $F_{\text{int}}$ characteristics using Eq. (4.4) and (4.9) as a function of temperature. The lines (symbols) are calculated $J$ without (with) deep trap states. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1 \text{ eV}$, $\phi = 0.5 \text{ eV}$, $N = 10^{21} \text{ cm}^{-3}$, $\gamma = 5 \times 10^{-7} \text{ cm}^{-1}$, $n_t = 10^{10} \text{ cm}^{-3}$, and $E_t = -1.5 \text{ eV}$.

Fig. 4.10 Measured $J$ vs $F_{\text{int}}$ characteristics of different samples at various temperatures. (a) ITO / MTDATA (320 nm) / NPB (390 nm) / Ag, (b) ITO / MTDATA (320 nm) / Alq (430 nm) / Ag, (c) ITO / MTDATA (320 nm) / TCTA (370 nm) / Ag, and (d) ITO / MTDATA (320 nm) / TPBI (490 nm) / Ag.

Fig. 4.11 Measured $J$ vs $1/T$ characteristics of various heterojunction devices at $F_{\text{int}} = 5 \times 10^5 \text{ V/cm}$. The solid lines are guides for eye vision. The inset shows the $-(\text{slope of } J \text{ vs } 1000/T)$ of different samples extracted for $T > 200 \text{K}$.

Fig. 4.12 Measured capacitance vs frequency by admittance spectroscopy (AS) of ITO / MoOx (10 nm) / MTDATA (570 nm) / Ag devices at an applied electric field $F = 7 \times 10^2 \text{ V/cm}$, and at temperature (a) 164 K, (b) 146 K, (c) 123 K, (d) 100 K, and (e) 85 K.

Fig. 4.13 The average hole mobility $\mu_h$ of MTDATA measured by admittance spectroscopy (AS) at various temperatures. The solid lines are the best fits to the Poole-Frenkel expression: $\mu_h = \mu_0 \exp(\beta \sqrt{F})$, where $\mu_0$ is a prefactor, $\beta$ is the electric field dependence coefficient, and $F$ is the applied electric field.

Fig. 4.14 Measured $\mu_h$ vs $1/T^2$ characteristics of MTDATA at $F = 5 \times 10^5 \text{ V/cm}$. The solid symbols are directly measured data. The open symbols are extrapolated from Fig. 4.13. The solid line is the best fit to data using Eq. (4.11), with $\sigma = 0.1 \text{ eV}$, $N = 10^{21} \text{ cm}^{-3}$, $v = 3 \times 10^3 \text{ s}^{-1}$, $\gamma = 5 \times 10^{-7} \text{ cm}^{-1}$, and $p = 2.15 \times 10^{16} \text{ cm}^{-3}$.

Fig. 4.15 Measured photocurrent transient of holes (a) MTDATA, (b) NPB, and (c) TCTA by time-of-flight (TOF) technique.

Fig. 5.1 Schematic diagram of p-type doping of an organic matrix (MTDATA) with a p-type dopant (F4-TCNQ).

Fig. 5.2 Experimental current-density vs voltage ($J$-$V$) characteristics of device E: ITO / MTDATA (236 nm) / Ag (□), and device A: ITO / MTDATA (236 nm) / NPB (82 nm) / Ag (■). The solid line is the SCLC model calculated based on device E. The data (+) are the time-domain
numerically simulated results based on device E. The data (×) are the
time-domain numerically simulated results of the double layer device A,
assuming no transport barrier at the organic-organic interface (OOI).

Fig. 5.3 Current-density voltage (J-V) characteristics of various double layer
devices: device A (■) without an interlayer; device B (●) with an
interlayer NPB:F4-TCNQ (2 nm, 10%); device C (▲) with an interlayer
MTDATA:F4-TCNQ (2 nm, 10%); device D (▼) with an interlayer
MTDATA:F4-TCNQ (2 nm, 15%). The data (×) are the time-domain
numerically simulated results based on device A, assuming no transport
barrier at the organic-organic interface (OOI).

Fig 5.4 Schematic diagrams of energy level alignment at the various organic-
organic interfaces.

Fig. 6.1 Energy diagrams of device A, B and C with HOMO energy levels (eV)
for different organic materials.

Fig. 6.2 (a) Current-density vs voltage (J-V) and (b) luminance vs voltage (L-V)
characteristics of a series of device A. Device A1 without an interlayer;
Device A2 with an interlayer NPB:F4TCNQ (molar ratio 6%, 2 nm); Device A3 with an interlayer NPB:F4TCNQ (molar ratio 18%, 2 nm); Device A4 with interlayer an NPB:F4TCNQ (molar ratio 50%, 2 nm).

Fig. 6.3 Current (open symbols) and power (close symbols) efficiencies of a
series of device A. Device A1 without an interlayer; Device A2 with an
interlayer NPB:F4TCNQ (molar ratio 6%, 2 nm); Device A3 with an interlayer NPB:F4TCNQ (molar ratio 18%, 2 nm); Device A4 with interlayer an NPB:F4TCNQ (molar ratio 50%, 2 nm).

Fig. 6.4 (a) Current-density vs voltage (J-V) and (b) luminance vs voltage (L-V)
characteristics of a series of device B. Device B1 without an interlayer;
Device B2 with an interlayer NPB:F4TCNQ (molar ratio 7%, 2 nm); Device B3 with an interlayer NPB:F4TCNQ (molar ratio 21%, 2 nm); Device B4 with interlayer an NPB:F4TCNQ (molar ratio 50%, 2 nm).

Fig. 6.5 Current (open symbols) and power (close symbols) efficiencies of a
series of device B. Device B1 without an interlayer; Device B2 with an
interlayer NPB:F4TCNQ (molar ratio 7%, 2 nm); Device B3 with an interlayer NPB:F4TCNQ (molar ratio 21%, 2 nm); Device B4 with interlayer an NPB:F4TCNQ (molar ratio 50%, 2 nm).

Fig. 6.6 (a) Current-density vs voltage (J-V) and (b) luminance vs voltage (L-V)
characteristics of a series of device C. Device C1 without an interlayer;
Device C2 with an interlayer NPB:F4TCNQ (molar ratio 10%, 2 nm); Device C3 with an interlayer NPB:F4TCNQ (molar ratio 17%, 2 nm); Device C4 with interlayer an NPB:F4TCNQ (molar ratio 67%, 2 nm).
Fig. 6.7 Current (open symbols) and power (close symbols) efficiencies of a series of device C. Device C1 without an interlayer; Device C2 with an interlayer NPB:F4TCNQ (molar ratio 10%, 2 nm); Device C3 with an interlayer NPB:F4TCNQ (molar ratio 17%, 2 nm); Device C4 with interlayer an NPB:F4TCNQ (molar ratio 67%, 2 nm).

Fig. 6.8 A schematic of energy diagram for holes injection from ITO and transport through MTDATA to NPB. The DOS of HOMO energy levels of the organic materials have a Gaussian distribution. The variances $\sigma$ of the Gaussian DOS are assumed to be 0.1 eV. The open circles are the illustration of hole carriers. They have a mean energy $<E_{hi}>$ away from the centre of the DOS.

Fig. 7.1 J-V characteristics of devices with different growth rates of P3HT:PCBM blend. The power conversion efficiencies for a slow and a fast growth film under AM 1.5G solar irradiation (100 mW/cm$^2$) are 4.6% and 2.6% respectively.

Fig. 7.2 TEM images of P3HT:PCBM film bulk morphology before thermal annealing (a), after thermal annealing at 150°C for 30 minutes (b), and after thermal annealing at 150°C for 2 hrs (c). Adapted from Ref. [1].

Fig. 7.3 Measured capacitance vs frequency characteristics of sample (a) A at T = 263 K and $F = 2.0 \times 10^5$ V/cm; (b) B at T = 263 K and $F = 2.0 \times 10^5$ V/cm; (c) C at T = 263 K and $F = 2.0 \times 10^5$ V/cm; (d) D at T = 270 K and $F = 1.3 \times 10^4$ V/cm. The capacitance $C$ is normalized to the geometrical capacitance $C_{geo}$ of individual sample.

Fig. 7.4 Measured electron mobility $\mu_e$ vs square root of applied electric field $F^{1/2}$ of sample (a) B, (b) C, and (c) D. The solid lines are the best fit of the data to the Pool-Frenkel type of electric field $F$ dependence $\mu_e \propto \exp(\beta F^{1/2})$.

Fig. 7.5 (a) The zero-field mobility $\mu_{0,T}$ extrapolated from the measured $\mu_e$ in Fig. 7.4 vs $1/T^2$ of different samples. (b) The corresponding field dependence coefficient $\beta$ vs $1/T^2$. The solid lines are the best fits to the data at temperature $T > 220$K.

Fig. 7.6 An illustration of the phase segregation of P3HT:PCBM for slow and fast growth rate of the active layer. Interface dipoles are formed at P3HT/PCBM heterojunctions.

Fig. A.1 The field dependent $\mu_{dc}$ of MTDATA extracted by TOF vs the square root of the applied electric field $F^{1/2}$ at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient
current measured by TOF.

Fig. A.2
(a) The zero field mobility \( \mu_{0,T} vs \ 1/T^2 \); (b) the corresponding field dependent \( \beta vs 1/T^2 \). The energetic \( \sigma \) and the positional \( \Sigma \) disorder parameters of MTDATA can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.

Fig. A.3
The field dependent \( \mu_\text{dc} \) of NPB extracted by TOF vs the square root of the applied electric field \( F^{1/2} \) at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.

Fig. A.4
(a) The zero field mobility \( \mu_{0,T} vs \ 1/T^2 \); (b) the corresponding field dependent \( \beta vs 1/T^2 \). The energetic \( \sigma \) and the positional \( \Sigma \) disorder parameters of NPB can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.

Fig. A.5
The field dependent \( \mu_\text{dc} \) of TPD extracted by TOF vs the square root of the applied electric field \( F^{1/2} \) at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.

Fig. A.6
(a) The zero field mobility \( \mu_{0,T} vs \ 1/T^2 \); (b) the corresponding field dependent \( \beta vs 1/T^2 \). The energetic \( \sigma \) and the positional \( \Sigma \) disorder parameters of TPD can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.

Fig. A.7
The field dependent \( \mu_\text{dc} \) of TCTA extracted by TOF vs the square root of the applied electric field \( F^{1/2} \) at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.

Fig. A.8
(a) The zero field mobility \( \mu_{0,T} vs \ 1/T^2 \); (b) the corresponding field dependent \( \beta vs 1/T^2 \). The energetic \( \sigma \) and the positional \( \Sigma \) disorder parameters of TCTA can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.
LIST OF TABLES

Table 1.1  Performance data for a number of white OLEDs over the last few years. The column on the right denotes the emitter type used to create red, green, and blue light (P: phosphorescent emitter; F: fluorescent emitter). Adapted from Ref. [24]. 6

Table 4.1  The heterojunction devices used in this study have a general structure of ITO / first organic layer / second organic layer / Ag. The energy offset at the heterojunction is determined by the energy difference of the highest-occupied molecular orbital (HOMO) of each layer. 84

Table 5.1  Structures of various test devices used in this work. All double layer devices have the same total thickness of organic films (318 nm). For device B, C and D, there is a thin (2 nm) p-doped (10 % or 15 % molar ratio) interlayer. 98

Table 6.1  Structures of various test devices used in this study. In general, the devices consist of ITO / HIL / HTL / EL / HBL / LiF / Al. In some of the devices, there is a 2 nm p-type doped interlayer NPB:F$_4$TCNQ at the HIL / HTL interface. 109

Table 7.1  Summary of preparation condition of the P3HT:PCBM (1:1 wt%) blends. 124

Table 7.2  Extracted GDM parameters of different samples from the measured electron mobility $\mu_e$ in Fig. 7.5. 128

Table A.1  Extracted GDM parameters for MTDATA, NPB, TPD, and TCTA. 145
Chapter 1 Introduction

1.1 Abstract

In this chapter the development of electronic heterojunction devices is introduced. This is followed by a technological review of organic heterojunction devices in the applications of display and lighting, and photovoltaic cells. Afterwards, a fundamental issue that governs the device performance, carrier transport in disordered organic semiconductors, is highlighted with a discussion of recent theoretical developments and experimental discoveries.
1.2 Organic electronics: Development of heterojunction technology

A heterojunction, a junction between two different semiconductors or between a metal and a semiconductor, is a key technology in modern optoelectronics. The famous discovery of the first heterojunction transistor dates back to 1948 by Bardeen and Brattain at Bell Labs.\textsuperscript{[1]} It was then followed by Shockley’s development of a $p$-$n$ junction transistor in 1949.\textsuperscript{[2]} Since then, the development of heterojunction electronic devices has been growing rapidly. Nowadays, THz transistors and semiconductor lasers with different wavelengths can be realized with multilayer hetero-structured or even super-lattice inorganic semiconductors.

In contrast to the successful development of electronic devices based on inorganic semiconductors, application of organic materials in electronics developed slowly until the 1980s. Although the electroluminescence property of organic crystals was discovered in 1964,\textsuperscript{[3]} owing to the extremely high driving voltage $100 \text{ V} - 1 \text{ kV}$, studies on organic semiconducting materials received limited attention. Nevertheless, during the 1950s and 1970s, numerous studies were conducted to investigate the electrical conductivity of organic materials used as the xerographic photoreceptors in the printing industry,\textsuperscript{[4]} which demonstrated the potential application of organic materials in solid-state electronics.

1.2.1 Organic light-emitting-diode (OLED)

The first high efficiency OLED was discovered by Tang and VanSlyke at Kodak in 1987.\textsuperscript{[5]} An attractive efficiency (1% external quantum efficiency, 1.5 lm/W luminous efficiency, $>1000 \text{ cd/m}^2$ brightness) and driving voltage below 10 V were achieved. The device consisted of two layers of organic materials with total thickness less than 150 nm as shown in Fig. 1.1.
The key advantage of Tang’s cell was the implementation of an organic heterojunction. The injected electrons and holes were accumulated at the interface of the two organic materials to provide an emission zone. This effectively increased the probability of electron-hole recombination for light emission. In the last two decades, extensive research has been conducted to optimize the efficiency by engineering the device structure. Generally, a standard OLED includes several organic layers as shown in Fig. 1.2. The hole and electron injection layers (HIL and EIL) have better matching of their carrier transporting energy levels with the electrode work function to improve carrier injection. The hole and electron transport layers (HTL and ETL) have high carrier mobility; the injected carriers can be effectively transported to the emission zone. The injected carriers will accumulate at the interface between the HTL and ETL, and the electron and hole pairs form excitons and release their energy as light.
Recent achievements in OLEDs have put this technology into commercialization. For instance, (i) the introduction of metal fluoride in-between the EIL and aluminum cathode remarkably reduces the driving voltage by enhancing electron injection.\(^6\) (ii) On the anode side, for improving hole injection, it has been demonstrated that a thin layer (3 nm) of C\(_{60}\), a strong electron acceptor, on metal anodes induces a strong interface dipole. Eventually, the dipole reduces the injection barrier and improves hole injection.\(^7,8\) This technology enables the fabrication of OLEDs on a thin layer of transparent metal electrode on flexible substrate. (iii) Besides carrier injection from the electrodes, the organic HTL and ETL have to be highly conductive; any potential energy drop in those layers will increase the driving voltage of the device. Ideally, the driving voltage (eV) is equal to the emitted photon energy. However, intrinsic organic materials normally have relatively wide band gap (> 3 eV) and low carrier mobility (<10\(^{-3}\) cm\(^2\)V\(^{-1}\)s\(^{-1}\)). These are the major causes for the low conductivity. It has been demonstrated that the conductivity of the organic electronic materials and OLED performance can be significantly increased by doping with strong electron donors or acceptors.\(^9\) Eventually, the organic materials can be doped into \(p\)-type or \(n\)-type as in traditional inorganic semiconductors.\(^{10}\) (iv) Another breakthrough is the development of eletro-phosphorescent
Considering the spin statistics of a two-electron system, it can be readily shown that there is only one state with total angular momentum equal to 0, and three states with total angular momentum equal to 1. As shown in Fig. 1.3, light emission from an excited state to a ground state for the former is regarded as singlet emission (fluorescence) with 25% upper limit of the internal quantum efficiency $\eta_{\text{int}}$; the later is regarded as triplet emission (phosphorescence) with 75% upper limit of $\eta_{\text{int}}$. It has been shown that the introduction of host-guest system, doping a (guest) phosphorescence material into a host system, $\eta_{\text{int}}$ can approach 100%.$^{[12]}$ The most commonly used phosphorescence materials are rare earth metal complex; red-emitting PtOEP,$^{[11]}$ green-emitting Ir(ppy)$_3$,$^{[13,14]}$ and blue-emitting FIrpic.$^{[15]}$. These materials facilitate the energy transfer from the host singlet and triplet states to the guest (phosphors) triplet states through intersystem crossing (ISC). This technology also triggered the development of white OLEDs (WOLED) for general lighting applications.

![Fig. 1.3 Schematic of singlet (fluorescence) and triplet (phosphorescence) emissions.](image)

The highly efficient OLED has been commercialized in many portable electronics, e.g. MP3 players, cell phones, and displays used in digital cameras. Another potential application is using WOLED for general lighting. The recent progresses of WOLED reported by companies are summarized in Table 1.1.
### Table 1.1 Performance data for a number of white OLEDs over the last few years. The column on the right denotes the emitter type used to create red, green, and blue light (P: phosphorescent emitter; F: fluorescent emitter). Adapted from Ref. [24].

<table>
<thead>
<tr>
<th>Company/Institution</th>
<th>Year</th>
<th>Power efficiency at 1000 cd/m²</th>
<th>Lifetime at 1000 cd/m²</th>
<th>Emitter type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novaled / Philips[16]</td>
<td>2006</td>
<td>32 lm/W</td>
<td>20 k hrs</td>
<td>R P P F</td>
</tr>
<tr>
<td>Konica-Minolta[17]</td>
<td>2006</td>
<td>64 lw/W</td>
<td>10 k hrs</td>
<td>P P P P</td>
</tr>
<tr>
<td>UDC[18]</td>
<td>2007</td>
<td>25 lm/W</td>
<td>Not announced</td>
<td>P P P F</td>
</tr>
<tr>
<td>Idemitsu Kosan[19]</td>
<td>2007</td>
<td>(17 lm/W) at 10 mA/cm²</td>
<td>30 k hrs</td>
<td>F F F F</td>
</tr>
<tr>
<td>Osram[20]</td>
<td>2008</td>
<td>46 lm/W</td>
<td>5 k hrs</td>
<td>P P P F</td>
</tr>
<tr>
<td>Novaled[21]</td>
<td>2008</td>
<td>35 lm/W</td>
<td>100 k hrs</td>
<td>P P P F</td>
</tr>
<tr>
<td>The OOLA-Project[22]</td>
<td>2008</td>
<td>51 m/W</td>
<td>&gt; 10 k hrs</td>
<td>P P P F</td>
</tr>
<tr>
<td>UDC[23]</td>
<td>2008</td>
<td>102 lm/W</td>
<td>Not announced</td>
<td>P P P P</td>
</tr>
</tbody>
</table>

Although highly efficient and long lifetime OLED displays can be achieved with current technologies, further reducing the production cost is certainly the next challenge for OLEDs. The first commercial OLED TV (11”) has been launched by SONY® in 2008 as shown in Fig. 1.4. However, the retail price USD2,500 is much higher than other competitors in the display market. There are several possible approaches that can further reduce the production cost: using a more cost effective synthesis routine for the organic materials, reducing the number of organic layers, using more robust electrodes for carrier injection, replacing the high vacuum process during device fabrication with other low cost alternatives, e.g. ink-jet printing.

![Fig. 1.4 Sony's XEL1 11" OLED (Organic Light Emitting Diode) Digital Television. Adapted from www.sony.com.](image-url)
1.2.2 Organic photovoltaic cell (OPV)

Organic photovoltaic (OPV) cells have received broad interest in the last 10 years owing to their potential for large area and low cost applications. The study of OPV cells was started in the 1960s; it was discovered that many organic dyes had semiconducting properties and exhibited photovoltaic behavior.\cite{25,26} This was attributed to the excellent absorption properties of the organic dyes. However, the OPV cells formed with only one of those dyes demonstrated very low power conversion efficiency, $\eta_{\text{eff}} < 0.1\%$. Until 1986, Tang announced $\eta_{\text{eff}}$ of 1\% was achieved by forming a heterojunction between two thin layers of dye molecules as shown in Fig. 1.5.\cite{27}

![Fig. 1.5 Configuration and current-voltage characteristics of an ITO/CuPc (250 Å)/PV (450 Å) / Ag cell. Adapted from Ref. \cite{27}.](image)

The advantage of this organic heterojunction over the previous metal/organic PV cells is the high exciton dissociation efficiency at the organic electron donor and acceptor interface. This donor-acceptor heterojunction structure has become the standard platform for small molecular and polymeric OPV cells.
Generally, as shown in Fig. 1.6, the small molecular OPV cells are fabricated using a bilayer structure, and the polymeric OPV cells consist of a layer of mixed donor and acceptor polymers, which form a bulk heterojunction thin film. Briefly, once a photo-excited exciton is generated in the donor or acceptor, it will diffuse to the heterojunction and be dissociated into an electron and hole by the potential difference between the ionization potential of the donor and electron affinity of the acceptor. Those carriers are then collected by the electrodes and generate electricity.

There are several factors that limit the OPV cells performance. (i) Although high carrier mobility (1-10 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) has been reported in organic single crystals,\(^{28,29}\) thin films of the organic materials fabricated in OPV are mostly amorphous with relatively low carrier mobility (\(< 10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\)). Such low mobility restricts the thickness of the organic film that can be used in OPV cells. Higher the mobility, not only the excitons can more readily to diffuse to the heterojunction, but also the dissociated carriers can be more efficiently drifted to the electrode by...
the internal electric field. (ii) The binding energy of excitons is another factor limiting the device efficiency. After an electron is excited into the lowest-unoccupied molecular orbital (LUMO) of the organic materials, it is attracted by a hole in the highest-occupied molecular orbital (HOMO). Therefore, the electron and hole is held together by the coulomb interaction to form an exciton. The binding energy is expected to be $200 - 500$ meV,\cite{30,31} typically one order of magnitude larger than that in silicon. Solely the thermal energy (25 meV) is not sufficient to dissociate the exciton. This attributes to the major difference of the working principle between organic and inorganic solar cells. The later dissociates free carriers readily after the formation of an exciton. (iii) Moreover, the diffusion length of the excitons is a major issue that determines the efficiency. It has been reported that the typical diffusion length of excitons in organic materials used in OPV cells is less then $10$ nm.\cite{32,33} In order to maximize the optical field at the heterojunction, this limits the design of the thicknesses of the donor and acceptor layers in the plenary heterojunction structure as shown in Fig. 1.6. Recently, it has been demonstrated that the bulk heterojunction structure with nano-scale morphology can significantly increase the power conversion efficiency $\eta_{\text{eff}}$ to $5$ % under AM 1.5.\cite{34-36} In such a structure, the donor and acceptor form an interpenetrating network with numerous nano-scale size domains. This effectively reduces the radiative or non-radiative loss of excitons. By modeling the bulk heterojunction, it is predicted that $\eta_{\text{eff}}$ can reach $11$ % by optimizing the energy levels, band gaps, and carrier mobilities.\cite{37} Furthermore, tandem cells are suggested as a feasible approach to achieve $\eta_{\text{eff}}$ over $11$ %.\cite{38-40}.

1.3 Carrier transport and injection in organic semiconductors

The recent technological achievements in organic heterojunction devices are accompanied with the accumulation of the knowledge of the material properties. Among those physical properties, charge-carrier transport in the bulk organic semiconductors and carrier injection at metal/organic interfaces are extensively discussed in the last two decades. Here below, a brief description of a few fundamental physical mechanisms are highlighted as a basis for the following chapters.
1.3.1 **Electronic properties of organic semiconductors**

There is no doubt that the conductivity or carrier transport properties are inherent in the electronic structure of the organic semiconductor. Take the simplest model (benzene) as an example, Fig. 1.7. Each carbon atom has three sp² hybrids orbital, Fig. 1.7a. One orbital binds to a hydrogen atom; the other two bind to the two nearby carbon atoms, forming a σ-bond plane, Fig. 1.7b. The pző orbital is perpendicular to the plane. The weak overlapping between the remaining pзо orbitals of two adjacent carbon atoms forms the π-bond, Fig. 1.7c.

![Fig. 1.7](image)

Fig. 1.7 (a) The sp² orbitals of carbon atom and the 1s orbital of hydrogen atom, (b) the σ-bond of the carbon atom of benzene, and (c) the π-orbital in benzene.

If more carbon atoms are introduced, according to the Pauli exclusion principle, there will be additional splitting of the energy levels that eventually form two semi-continuous “bands”, Fig. 1.8, which consist of the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO). However, unlike the continuous valence and conduction bands in inorganic semiconductors, HOMO and LUMO consist of numerous discrete energy levels.
In organic solids, the molecules are weakly bonded together by Van der Waals forces. There is an absence of long range order as commonly found in inorganic crystals. As a result, the molecular orientation and energetic profile are intrinsically disordered. The localization radius of an electron should be in the order of the magnitude of the molecular geometry (~10 Å), and the wavefunction overlaps between molecules are very limited. It can be readily predicted that the carrier mobility in most organic semiconductors are much smaller than that in their inorganic counterparts. The molecular orbitals play a vital role in determining the carrier transport properties. Fig. 1.9 (a) shows the molecular structure of tris(8-hydroxyquinolinato)aluminum (III) (Alq3), a prototypical green emitter used in OLEDs. The spatial distribution of the HOMO and LUMO in Alq3 are illustrated in Fig. 1.9 (b) and (c) respectively. The HOMO is mainly localized in one of the quinolin group. However, the LUMO is more delocalized which increases the probability of charge transfer of electrons between adjacent molecules. This agrees with the experimental result of two orders of magnitude higher electron mobility than hole mobility in Alq3.[41,42]
1.3.2 Energy/Charge transfer

Beside the localization of the molecular orbitals, the charge transfer mechanism between molecules is another crucial factor that governs the optoelectronic properties in organic semiconductors.

1.3.2.1 Förster resonance energy transfer

Förster transfer is a long range (< 100 Å) energy transfer of excitation energy, through dipole-dipole interaction, from an excited donor molecule to an acceptor molecule. It was originally recognized by T. Förster in 1948.\textsuperscript{[44]} This has been extensively studied in organic materials,\textsuperscript{[45,46]} in semiconducting nano-crystal thin films,\textsuperscript{[47]} and recently applied to explain some biological systems.\textsuperscript{[48]} The energy transfer is facilitated by the overlapping of the emission spectrum of the donor molecule to the absorption spectrum of the acceptor molecule as shown in Fig. 1.10.

![Diagram of Förster resonance energy transfer](image)

Fig. 1.10 Emission and absorption spectra of donor and acceptor molecules respectively.
Different from conventional emission-absorption process, Förster transfer does not involve an emission of photon as a transfer medium. Förster recognized that such process is more efficient through the dipole-dipole interaction. The transfer rate between isolated molecules at a separation $R$ between the donor and acceptor is:

$$k_{D^*\rightarrow A} = \frac{1}{\tau} \left(\frac{R_0}{R}\right)^6$$

(1.1)

where $\tau$ is the luminescence lifetime of the donor in the absence of the acceptor, $R_0$ is the critical distance corresponding to the Förster energy transfer rate equal to other decay rates of the molecules, and is determined by the orientation of the molecules and the overlap between the donor emission spectrum and the acceptor absorption spectrum:

$$R_0^6 = \frac{9000 (\ln 10) \kappa^2 \phi_d}{128 \pi^6 N n^4} \int \frac{f_D(\bar{v}) \varepsilon_A(\bar{v})}{\bar{v}^4} d\bar{v}$$

(1.2)

where $n$ is the refractive index of the medium, $N$ is Avogadro’s number, $\kappa$ is the molecular orientation factor, $\bar{v}$ is the wave number, the integral represents the overlap of the normalized donor emission spectrum $f_D(\bar{v})$, and the acceptor absorption extinction coefficient spectrum $\varepsilon_A(\bar{v})$. Assuming a sufficient overlapping of the spectra, $R_0$ is around 50 Å to 100 Å. This corresponds to a minimum concentration of 0.01 to 0.1% of guest molecules in a host(donor)-guest(acceptor) system. In the application of OLED, Förster energy transfer has been applied to study the bimolecular annihilation. [49-51]

1.3.2.2 Marcus charge transfer

Marcus theory describes a polaronic charge transfer process and has widely been applied in various aspects of chemistry and biology, including photosynthesis, corrosion and chemiluminescence. A
polaron is a quasi-particle consisting of a charge (electron/hole) and its surrounding phonons (phonon cloud). A moving charge inside a dielectric material will interact with the surrounding lattice through long range polarization. The rate of charge transfer depends on the deformation energy and the electronic coupling of polarons. The theory is originally developed for chemical reactions in solvents. A charge will polarize the surrounding solvent molecules and minimizes the energy for charge transfer. In solid state organic materials, the minimum energy can be accompanied by the vibrational relaxation of molecules as pointed out by Marcus.\[52-54\] The charge transfer rate is denoted as:

\[ v_{i \rightarrow j} = \frac{J^2}{h} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left( -\frac{(\Delta E + \lambda)^2}{4 \lambda k_B T} \right) \]  

(1.3)

where \( \Delta E = E_j - E_i \) and \( \lambda \) is the reorganization energy. The transfer integral \( J \) is proportional to the wavefunction overlap:

\[ J \propto \exp\left(-2\gamma r_{ij}\right) \]  

(1.4)

where \( \gamma \) is inverse localization radius, and \( r_{ij} \) is the distance between sites \( i \) and \( j \).

According to the Marcus theory, the rate of charge transfer can be illustrated in Fig. 1.11. The curves on the left and right represent the potential nuclear motion in the starting and destination sites respectively. In the absence of applied electric field with \( \Delta E = 0 \), Fig. 1.11a, the activation energy required to facilitate charge transfer from the starting site to the destination site is \( \lambda/4 \) as depicted in Eq.(1.3). Increasing the applied electric field \( F \) will create a potential difference between the two sites. Eventually if the \( F \) is high enough to lower the nuclear energy of the destination site crosses over the minimum of the starting sites, the charge transfer becomes resonance, Fig. 1.11b. The rate of charge transfer is maximized. In such condition, the carrier mobility is predicted to be temperature independent. However, Fig. 1.11c, if the electric field is further increased, the transfer rate decreases again, it is called the “Marcus inversion”. This striking discovery predicts that the charge transfer decreases at high electric field regime, and has been confirmed in chemical reactions in solvents.\[55\] “Marcus inversion” of carrier mobility has also been report in a molecularly doped polymer system.\[56\]
Fig. 1.11 Schematic diagram of charge transfer from Marcus theory, the red line represent the path of charge transfer in (a) the absence of electric field, (b) resonance, (c) and Marcus inversion.
1.3.2.3 Miller-Abrahams hopping process

In inorganic semiconductors, strong covalent bonds hold atoms together with well ordered configurations. The energy band in this case extends continuously in the bulk and therefore the delocalized carriers can freely move along the band with a relative high mobility, as depicted in Fig. 1.12a. However, for most organic semiconductors, weak intermolecular forces are predominant among molecules or polymers. In this case, discrete energy band structure is dominant in the bulk. The freely propagation wave of charge as usually seen in inorganic semiconductor no longer exists. As a result, carrier transport in organic semiconductors becomes a hopping process that involves thermionic emission and tunneling of carriers between localized sites, Fig. 1.12b. Many of the hopping models for organic semiconductors are based on the Miller-Abrahams formalism that was originally used to describe the hopping process in deep traps in inorganic semiconductors.\[57\] The photon assisted hopping rate between two localized sites is:

\[
v_{i\rightarrow j} = v_0 \exp\left(-2\gamma r_{ij}\right) \begin{cases} \exp\left[-\left(\epsilon_j - \epsilon_i\right)/k_BT\right] & \epsilon_j > \epsilon_i \\ 1 & \epsilon_i > \epsilon_j \end{cases} \quad (1.5)
\]

where \(v_0\) is the attempt-to-jump frequency of the order of the phonon frequency \(10^{12} - 10^{13} \text{ s}^{-1}\), \(\gamma\) is the inverse localization radius, \(r_{ij}\) is the distance between sites \(i\) and \(j\), \(\epsilon_i\) and \(\epsilon_j\) are the site energies. The first exponential in Eq. (1.5) describes the tunneling probability from a localized site \(i\) to another localized site \(j\) separated by a distance \(r_{ij}\). The second exponential depicts the thermally assisted hopping rate. For an energetically upward hop, \(\epsilon_j > \epsilon_i\), the hopping rate follows an exponential function. For an energetically downward hop, \(\epsilon_j < \epsilon_i\), the hopping rate is equal to unity, that is independent of the energy difference of the hopping sites and the temperature. This is the so called “asymmetric Miller-Abrahams rate”.
(a) Band transport – In a perfect crystal, depicted as a straight line, a carrier is delocalized, it moves as a plane wave without scattering. In a real crystal, there is always lattice vibration or phonons that disrupt the crystal symmetry. These phonons scatter the electron and thereby reduce its mobility. Lowering the temperature will therefore increase the mobility.

(b) Hopping transport – If the lattice is irregular, or if the carrier becomes localized on a defect site, lattice vibrations are essential for a carrier to move from one site to another. This is an activated process and the mobility increases with increasing temperature.

Fig. 1.12 Transport mechanism in solids. Adapted from Ref. [58].
1.3.3 Formalism of carrier transport in organic semiconductors

As discussed above, the incentive of investigating the photoconductivity of disordered organic semiconductors started several decades ago when organic materials were recognized as the active materials for photoreceptors in the printing industry. Some general features of carrier transport that were observed experimentally in organic materials were not well understood. It was found that the transient photocurrent exhibited a certain degree of dispersion that depends on the film thickness. Moreover, the carrier mobility generally agreed with an empirical expression:

$$\mu(F, T) = \mu_\infty \exp\left[-\left(\frac{T_0}{T}\right)^2\right] \exp[\beta \sqrt{F}]$$  \hspace{1cm} (1.6)

Where $F$ is the applied electric field, $T$ is the temperature, and $\mu_\infty$, $T_0$ and $\beta$ are some dimensional parameters.

1.3.3.1 The Continuous Time Random Walk (CTRW) formalism

A milestone for the development of the formalism of continuous time random walks (CTRW) in an amorphous network was contributed by Scher and Montroll in the 1970s. \cite{59} Charge transport can be viewed as an accumulated sequence of charge transfer steps from one localized site to the other. In this case, each carrier independently undergoes a random walk, biased into one direction by an applied electric field. The entire character of a propagating packet of carriers depends on a key feature, the hopping time probability distribution $\psi(t)$. In an ordered single crystal, where the hopping rate $W$ is constant, $\psi(t)$ is given by
\[ \psi(t) \propto \exp(-Wt) \quad (1.7) \]

and the charge packet exhibits a normal Gaussian transport. Diffusive spreading of the charge packet causes some broadening of the trailing edge in the case of the photocurrent transient. As long as the field is small and the material is homogeneous, Einstein’s law holds so that

\[ D = \frac{\mu kT}{q}. \quad [60] \]

In this case the spatial width of the charge sheet evolves as:

\[ \left\langle \left( x - x_0 \right)^2 \right\rangle^{1/2} = (2Dt)^{1/2} \quad (1.8) \]

In disordered systems, however, there is a wide distribution of hopping rates, leading to a large range of hopping times that extend well into the experimental time scale. Therefore, the probability distribution becomes:

\[ \psi(t) \propto t^{-(1+\alpha)} , \quad 0 < \alpha < 1 \quad (1.9) \]

proposed by Scher and Montroll,\textsuperscript{[59]} this has been very successful in describing time-of-flight (TOF) experiments in organic and amorphous semiconductors. Such a probability distribution implies an extremely large hopping time dispersion which can result from relatively small variations between the distance and the mutual orientation of the hopping sites. The mean position \( \left\langle l \right\rangle \) of a spatially biased, time-evolving packet of charge carriers that undergoes a random walk with a probability distribution like one described by Eq. (1.9) varies as:

\[ \left\langle l \right\rangle \propto t^\alpha \quad (1.10) \]
The parameter $\alpha$ measures the degree of disorder. When $\alpha \to 1$, the mean position of $\psi(t)$ increases linearly with time, as in the case of Gaussian transport. A smaller $\alpha$ is associated with higher degree of disorder.

In conventional TOF experiments, the current measured before the packet reaches the opposite electrode is governed by:

$$J(t) \propto \frac{d\langle l \rangle}{dt} \propto t^{-(1-\alpha)}$$  \hspace{1cm} (1.11)

and it is no longer constant, but it is decreasing with time. When carriers begin to reach the opposite electrode and become annihilated, a fast drop in the current is observed:

$$J(t) \propto t^{-(1+\alpha)}$$  \hspace{1cm} (1.12)

According to Eqs. (1.11) and (1.12), the shape of the TOF trace is described by only one parameter. When plotted in a double logarithmic scale, it consists of two lines with slopes $-(1-\alpha)$ and $-(1+\alpha)$, crossing at a time that corresponds to the arrival time as shown in Fig. 1.13.
1.3.3.2 Gaussian disorder model (GDM)

The most popular hopping model to describe charge carrier mobility in disordered organic materials is the Gaussian disorder model (GDM). The GDM was proposed by Bässler in 1993 to explain the empirical expression, Eq. (1.6), of charge carrier mobility in disordered solids.\[61\]

There are several assumptions in the GDM:

1. The site energies and site separations are Gaussian type.
2. The intrinsic hopping rate between adjacent molecules follows the Milller-Abrahams(MA) formalism, photon assisted hopping.\[57\]
3. Electron-phonon coupling is sufficiently weak, the polaronic effect is neglected.
4. The process of charge carrier hopping is incoherent.
Bässler used Monte-Carlo (MC) simulation to compute the field and temperature dependence of carrier mobility. The energetic disorder $\sigma$, the positional disorder $\Sigma$, and the applied electric field $F$ were used as the input parameters. The main results of MC simulation are summarized as below:

1. Once the charge carriers undergo hopping across the density-of-states (DOS), they trend to relax toward the tail states. The energetic relaxation has a feature of $\Delta E \propto \ln t$ as shown in Fig. 1.14.

Fig. 1.14 Temporal evolution of the distribution of carrier energies in a Gaussian DOS of width $\hat{\sigma} = 2$. All profiles are broken at the same carrier density illustrating the different relaxation patterns for mobile and immobile carriers. $\epsilon_\infty$ denotes the theoretical mean energy in the long-time limit. Adapted from Ref. [61].

2. At quasi-equilibrium, the occupational DOS is also a Gaussian of width $\sigma$. It offsets from the center of the intrinsic DOS by energy $- \sigma^2/k_B T$. As a result, the activation energy for hopping to another site increases with decreasing temperature.

3. In an intermediate field range the $T$ and $F$ dependences of the charge carrier mobility are predicted to be:

$$
\mu(\hat{\sigma}, \Sigma, F) = \mu_\infty \exp \left\{ 1 \left( \frac{2}{3} \hat{\sigma}^2 \right)^2 \right\} \left\{ \exp \left[ C \left( \hat{\sigma}^2 - \Sigma^2 \right) \sqrt{F} \right] \right\} \begin{cases} 
\exp \left[ C \left( \hat{\sigma}^2 - 2.25 \right) \sqrt{F} \right] & \Sigma \geq 1.5 \\
\exp \left[ C \left( \hat{\sigma}^2 - 2.25 \right) \sqrt{F} \right] & \Sigma < 1.5 
\end{cases} \quad (1.13)
$$
where $C$ is a numerical constant, $\mu_\sigma$ is a prefactor, $\mu_\sigma = \frac{\sigma}{k_B T}$, the Poole-Frankel slope $\beta$ is related to the $\sigma$ and $\Sigma$ by $\beta = C(\hat{\sigma}^2 - \Sigma^2)$, when $\Sigma \geq 1.5$; or $\beta = C(\hat{\sigma}^2 - 1.5^2)$, when $\Sigma < 1.5$.

The GDM provides a method to analyze the electronic structure of disordered materials from their carrier transport properties. A few examples are given in Appendix A for phenylamine-based organic semiconductors. It is worth noting that, although the GDM has been widely used to analyze charge transport in a range of materials, there are several problems with this approach. Most critically, the model only predicts a Poole-Frenkel dependence of mobility for bias fields that are greater than typically $3 \times 10^5$ V/cm as shown in

Fig. 1.15, while experimentally, Poole-Frenkel mobility dependences have been observed at fields down to $8 \times 10^3$ V/cm as shown in Fig. 1.16.[62]

Fig. 1.15 Mobility $\mu$ vs square root of the applied electric field $E^{1/2}$ for a hopping system with fixed energetic disorder ($\hat{\sigma} = 3$) and variable off-diagonal (positional) disorder. Adapted from Ref. [61].

Fig. 1.16 Carrier mobility of a molecularly doped polymer system DESAP:polycarbonate as a function of temperature. Adapted from Ref. [62].
1.3.3.3 Correlated disorder model (CDM): Dipole and polaronic interaction

The discrepancy of field dependence between the GDM and experimental results can be solved by introducing correlation between the energies of spatially close sites as proposed by Gartstein and Conwell. This assumption is physically reasonable because the static fluctuations of the site energies are due to the interaction of a charge carrier with permanent and induced dipoles. Such modification can extend the Pool-Frenkel regime towards lower fields because the field dependence arises from the drop of the electrostatic potential across a relevant length of the hopping system relative to kT. Novikov et al. performed extensive Monte Carlo simulations (50 x 50 x 50 cells) using a three-dimensional (3D) correlated disorder model (CDM), and investigated the carrier mobility in a hopping system with both asymmetric (Miller-Abrahams) and symmetric (small polaron) hopping rates. It was shown that, Fig. 1.17, the Pool-Frenkel dependence of mobility were observed over a wide field range, independent of the specific hopping rate function used.

![Graph](image)

Fig. 1.17 Field dependent mobility for the CDM for $\delta d = 5.1$ and two different types of hopping rates, Miller-Abrahams (square) and symmetric (diamond): Adapted from Ref. [64].
The following empirical expression of temperature and field dependent mobility was proposed by Novikov et al. for the CDM:

\[
\mu(T, F) = \mu_0 \exp \left( -\frac{3\sigma}{5kT} \right)^2 \exp \left[ C_0 \frac{eF}{\sigma_d} \left( \frac{\sigma_d}{kT} \right)^{3/2} \right]
\]  

(1.14)

Comparing to the GDM in Eq. (1.13), both share some similar features. For example, there is a common exponential dependence of the zero-field mobility on \(1/T^2\). However, \(\sigma\) in Eq. (1.14) denotes a total energetic disorder arise both from the Van der Waals contributions, and from the presence of independently and randomly orientated dipoles, i.e. \(\sigma^2 = \sigma_{vdw}^2 + \sigma_d^2\). \(\sigma_{vdw}\) is the contribution from the nondipolar disorder, and \(\sigma_d\) is the dipolar component disorder. It has been extensively studied that the dipolar disorder is also a Gaussian, and is approximately equal to:

\[
\sigma_d = 2.35 \frac{ep}{\varepsilon a^2}
\]

(1.15)

where \(p\) is the dipole moment at each site, \(\varepsilon\) is the dielectric constant of the medium, and \(a\) is the intersite distance.

Another issue with the GDM is that it invokes the Miller-Abrahams hopping rate, which does not take into account the fact that in organic solids, local vibrations and electrons are strongly coupled. The simplest case of nonadiabatic small-polaron hopping, without energetic disorder of the hopping sites, yields an Arrhenius dependence of zero-field mobility with temperature.\(^{[65,66]}\) Recently, Parris et al. modified the correlated disorder model to incorporate a small-polaron transfer rate and found that realistic Poole-Frenkel dependences of carrier mobility with field were observed as shown in Fig. 1.18.\(^{[67]}\)
The following expression was obtained by computer simulation:

\[
\mu(T, F) = \mu_0 \exp \left( - \frac{E_a}{kT} \right) \exp \left( -A_1 \left( \frac{\sigma}{kT} \right)^2 \right) \exp \left[ A_2 \sqrt{\frac{eFR}{\sigma_d}} \left( \frac{\sigma}{kT} \right)^{3/2} - \Gamma \right]
\]

(1.16)

where \( E_a \) denotes the polaronic activation energy which is related to the polaron binding energy \( \Delta \) by \( E_a = \Delta / 2 \).\(^{[66]} \) The values of \( A_1 \) and \( A_2 \) are determined to be 0.31 and 0.79 respectively. A detailed comparison between different disorder models, Eqs. (1.13), (1.14) and (1.16), to a series of carrier mobilities of polymeric systems was conducted by Khan et al.\(^{[68]} \)

All in all, it has been widely discussed that whether the carrier transport in disordered organic solids is dominated by the disorder or by the (small) polaron effects.\(^{[66,69-71]} \) There is no
doubt that a moving charge is always accompanied by a structural distortion. The question is how significant such a distortion will contribute to the carrier transport. Typically, the polaron binding energy $\Delta$ in organic solids is around 100 meV- 200 meV.$^{[72,73]}$ This results in an activation energy $\Delta/4$ of 25meV – 50 meV. However, a typical energetic disorder $\sigma$ is about 100 meV, which results in an activation energy of around 200 meV – 300 meV. Therefore, carrier transport is mainly determined by the disorder effect; and most reported experimental results agree with the GDM and the polaronic effect is rarely observed.

1.3.4 Analytical models of carrier transport in organic semiconductors

The above carrier mobility formalisms are based on simulation, there is no doubt that a proper analytical model gives a more directly insight for the underlying physical mechanism. For carrier transport in disordered organic solids, the most trivial approach is to sum all the possible hopping events with a chosen hopping rate. However, there are numerous hopping events at a given time. This makes simply summing all possible events very difficult or even impossible. There are several alternatives to approach this problem. The difference between theories of carrier hopping in disordered systems essentially originates from different approaches to the averaging scheme.

The first analytical treatment of hopping charge carrier transport in an amorphous solid with Gaussian DOS under the condition of an otherwise empty DOS was carried out by Movaghar et al. using the effective medium approximation (EMA).$^{[74]}$ Recently, Fishchuk et al. further extend the MA theory to describe various aspects of the hopping process in disordered organic solids with Miller-Abrahams and Marcus hopping rates.$^{[75,76]}$ Briefly, the MA theory is based on a set of master equations:

$$\frac{d\rho_t}{dt} = \sum_j v_j \rho_j - \rho_t \sum_j v_{ij}$$

(1.17)
where $\rho_i$ is the occupation density of a site $i$ ($\rho_i \ll 1$), and $v_{ij}$ is the hopping rate between sites $i$ and $j$. An effective medium is then defined as a cubic lattice with spacing $a$, where all the $v_{ij}$ are replaced by an effective hopping rate $v_e$ and all $\rho_i$ by an uniform $\rho_e$. The effective value $v_e$ must be satisfied the condition that the configuration-averaged value of $\delta \rho_i = \rho_i - \rho_0$ vanishes ($\langle \delta \rho_i \rangle = 0$) when any $v_e$ in an effective medium is replaced by the random $v_{ij} \neq v_{ji}$ for any neighboring sites along one of the cubic axes. Such calculations in the two-site approximation yield:

$$
\frac{v_{12} - v_e}{v_{12} + v_{21} + 2v_e} = 0
$$

$$
\frac{v_{21} - v_e}{v_{12} + v_{21} + 2v_e} = 0
$$

(1.18)

Therefore the validity of the EMA can be verified by comparing $v_e$ obtained from the above two equations in Eqs. (1.18), as both equations should give the same value of $v_e$. Using the EMA, Fishchuk et al.\[76\] has successfully formulated the field and temperature dependence of carrier mobility that are comparable to the empirical expression of the CDM as derived from computer simulations.

An analytical model can also be developed by employing the stochastic theory. Arkhipov et al. have extensively employed the concept of effective transport energy $E_\text{tr}$ in carrier transport in disordered organic solids.\[77\] The transport energy effectively simplifies the treatment of the hopping process into a representative energy level, without taking into account all possible jumps in all energy levels, and serves as an analogy of the mobility edge.\[78\] Arkhipov et al. demonstrated that in case of a sufficiently steep density-of-state (DOS) function and a starting site that is sufficiently deep, the most probable value of $E_\text{tr}$ does not depend on the starting site energy. In other words, those carriers which localize in the deep tail region of the DOS distribution will sooner or later jump upward to the shallower states, the effective transport energy $E_\text{tr}$, before hopping into another neighboring site. This assumption yields a transcendental equation as a function of $E_\text{tr}$:\[77\]
where \(g(E)\) is the Gaussian DOS function, and \(\gamma\) is the inverse localization radius. By averaging the rates of carrier jumps to the effective transport level, and estimating the average square jump distance as:

\[
\langle r^2 \rangle = \left[ \int_{-\infty}^{E_{tr}} dE g(E) \right]^{-2/3}
\]

(1.20)

the carrier mobility can be obtained by applying the Einstein relation:

\[
\mu = \frac{e v_0}{kT \rho} \left[ \int_{-\infty}^{E_{tr}} dE g(E) \right]^{-2/3} \int_{-\infty}^{E_{tr}} \frac{dE g(E)}{1 + \exp[(E - E_F)/kT]} \exp \left( \frac{E - E_{tr}}{kT} \right)
\]

(1.21)

where \(\rho\) is the total carrier density, and \(E_F\) the Fermi energy level. Eq. (1.21) has been successfully used to explain the carrier concentration dependent mobility observed in a doped polymer system.\(^{[79]}\)
One questionable issue regarding the derivation of $E_T$ is the assumption that those carriers localized in deep energy levels will jump to shallower states in order to hop into another site. This is reasonable if the carrier gains sufficient thermal energy or the upward hopping rate is much higher than the tunneling probability. Therefore, the assumption may not be applicable at low temperature. As will be discussed in Chapter 4, carrier injection across an organic heterojunction at low temperature is mainly determined by the tunneling of deep trap states at the interface.
1.4 References

Chapter 1 - Introduction


Chapter 2  Experiment and material details

2.1  Abstract

In this chapter, details of device fabrication procedures, both thermal evaporation and spin coating, are given. It is then followed by the introduction of some major characterization techniques, time-of-flight (TOF), admittance spectroscopy (AS), and current-voltage luminance (IVL), that were employed in this thesis. Finally, those organic materials that appear in the following chapters are summarized.
2.2 Substrate and thin film preparation

2.2.1 Substrate treatment

For most of the devices, pre-patterned indium-tin-oxide (ITO) coated glass substrates were used. The thin layer of ITO (120 nm) had a sheet resistance of 20 $\Omega / \square$. For fabricating OLED devices, a 2 x 2 inch pre-patterned ITO (Fig. 2.1a) substrate was used. For carrier mobility measurement and the current-density ($J-V$) measurement of organic heterojunction devices, a smaller 12 mm x 20 mm (Fig. 2.1b) ITO substrate was chosen.

![Fig. 2.1](image_url) (a) 2 inch x 2 inch ITO substrate for fabricating OLED devices; (b) 12 mm x 20 mm ITO substrate for TOF and organic heterojunction devise.

Prior to organic deposition, the ITO substrate was cleaned by a sequence of ultrasonic baths with de-ionized water, isopropyl alcohol, and acetone. Each step lasted for 15 minutes. Afterwards, the ITO substrate was dried with nitrogen ($N_2$) gas. Finally, the substrate was subjected to 10 minutes ultraviolet ozone (UVO) treatment. The UVO treatment can effectively remove the residue organic contaminants on the ITO surface. It is well known that the work function of ITO can be substantially increased from 4.5 eV to around 5.0 eV by the UVO treatment.[1]

2.2.2 Thermal evaporation of organic and metal thin films

The devices used in this study were prepared in a general anode/organic layer(s)/cathode sandwich structure as shown in Fig. 2.2.
For small molecular materials and metals, the thin films were prepared by physical vapor deposition inside a cluster tool from Kurt. J. Lesker, Fig. 2.3.

Since both the organic and metallization chambers were attached together at a base pressure of $10^{-8}$ Torr, possible contamination between layers was minimized. The working principle of the thermal evaporation process is illustrated in Fig. 2.4.
During evaporation, the organic powder was stored inside a crucible. An external control unit adjusted the amount of power supplied to the crucible to reach a desired deposition rate. The thickness and the coating rate of the film were monitored by a crystal microbalance sensor next to the substrate. The coating rate for all the organic layers was controlled at around 0.5 - 1 Å/s, except for the TOF sample where the rate was set at 10 Å/s.

### 2.2.3 Spin coating of polymers

The solution for spin-coating was prepared by mixing a desired amount of polymer and solvent together. Since the film thickness was determined by the concentration of the solution
and the spin rate, the weights of polymer and solvent were carefully controlled. Afterwards, the solution was modestly warmed (below the boiling temperature of the solvent) and stirred for 12 hours to ensure the polymer was completely dissolved. The prepared solution was then dropped on the substrate through a syringe filter to eliminate any large particles. After spin-coating, the film was either heated or let to naturally dry inside a glove box to remove the solvent.

### 2.3 Characterization techniques and apparatus

#### 2.3.1 Time-of-flight (TOF) technique

The application of TOF in organic materials was first introduced by Kepler to investigate an anthracene crystal in 1960.\[2\] Since then, the technique has been widely applied not only to crystalline, but also on many amorphous material systems. The concept of TOF is straightforward. As shown in Fig. 2.6, normally a sample with a thick organic film (> 3 μm) sandwiched by two semi-transparent electrodes is prepared. This ensures the photo-generated carriers are mostly at the interface. In order to prevent a space charge effect, non-injecting (large carrier injection barrier) electrode is normally used. The sample is then housed inside a temperature-regulated cryostat with the transparent electrode facing the laser source. Once it is illuminated by a laser pulse, both free electrons and holes are generated. Depending on the polarity of the external applied electric field (Stanford Research System, PS310), either holes or electrons will drift through the organic layer to the counter electrode. As a result, a transient current can be recorded by a digital oscilloscope (Agilent 54622A) through a sensing resistor.
A typical transient current can be divided into two main regions as shown in Fig. 2.7. The first one is the plateau region, which corresponds to the collective motion of photo-generated carriers, before arriving at the charge-collecting electrode. The second region is the tail region, which arises from diffusion, or detrapping of carriers.\cite{3} This is mostly described as the dispersive tail. The transit time ($\tau$) for either holes or electrons to pass through the sample can be determined by the turning point of the transient current. The drift velocity ($v$) can be calculated by $v = d / \tau$, where $d$ is the sample thickness. According to the definition of mobility $\mu = v / F$, where $F$ represents the external applied electric field, the hole or electron mobility can be calculated. It should be noticed that the turning point in the transient current reflects the transit time of the fastest carrier. For DC measurements, such as current-voltage (IV), an average mobility should be considered. From the TOF transient, the average transit time $\tau_{dc}$ can be roughly taken as the time when the current drops to half of its plateau value.
The experimental results of the TOF measurements on those materials used in this study can be found in Appendix A.

### 2.3.2 Admittance Spectroscopy (AS)

Fig. 2.8 Schematic diagram of the experiment setup of admittance spectroscopy
The first analytical model to describe the space charge effect on device admittance, $Y$, was developed by J. Shao et al. in 1961.\cite{4} They investigated the carrier dynamics in trap-free space-charge-limited cadmium sulphide diodes. It was demonstrated that the carrier transit time is related to the frequency-dependent admittance of the device. In 1999, H. C. F. Martens et al. derived an equivalent admittance model and included both dispersions of carrier mobility and transit time to describe carrier hopping in disorder polymeric solids.\cite{5} Recently, this technique has been proved to be consistent with the mobility measured by TOF technique.\cite{6} Afterwards, it has been widely studied not only on single carrier mobility, but also in the cases of bipolar injection, trapping, dispersive transport, and carrier recombination processes in organic electronic materials.\cite{7-14}

The schematic diagram of the AS setup is shown in Fig. 2.8. A typical AS sample consists of an organic layer sandwiched by two electrodes. One of the electrodes forms an Ohmic contact, while another side should have a large injection barrier to suppress carrier injection. The sample was housed inside a temperature-regulated cryostat. All measurements were conducted in vacuum with a base pressure of $10^{-7}$ Torr. The admittance of the sample was evaluated by an impedance analyzer (HP 4284A). During the measurement, a DC voltage $V_{dc}$ and an AC voltage $v_{ac}$ were superimposed and applied to the sample. The small AC signal $v_{ac}$ is scanned from 20 Hz to 1 MHz with a 50 mV peak-to-peak value, and the $v_{ac}$ has a direct influence on the carrier relaxation processes inside the organic film. The time-scale to build-up the charge carrier is given by the transit time $\tau_{dc}$ of the injected carrier. At low frequency ($\omega < \tau_{dc}^{-1}$), the injected space charges are fast enough to respond to the modulation of $v_{ac}$, resulting to an extra current. Briefly, as $C(\omega) = \text{Im}(Y/\omega) = |Y| \sin \theta / \omega$, at high frequency, the organic layer behaves as a pure capacitor. The phase difference between $v_{ac}$ and $i_{ac}$ is 90\(^\circ\). Once the frequency of $v_{ac}$ drops below the carrier transit time, the contribution of the additional current becomes significant. Eventually, the phase difference between the additional $i_{ac}$ and $v_{ac}$ becomes less than 90\(^\circ\). Therefore, the measured capacitance will be decreased. A typical capacitance vs frequency plot with space-charge effect is shown in Fig. 2.9.
Fig. 2.9 (a) The capacitance-frequency relationship can be directly measured by the impedance analyzer. (b) By definition, the negative differential susceptance $-\Delta B = - \omega (C - C_{geo})$. The maximum point in the $-\Delta B$ plot corresponds to $\tau_r^{-1}$, which is related to the average carrier transit time $\tau_{dc}$ in the TOF experiment by $\tau_{dc} = 0.56 \tau_r$.\[^6\]

The effect mentioned above can be clearly observed by converting the plot of capacitance to the negative differential susceptance $-\Delta B = - \omega (C - C_{geo})$ as shown in Fig. 2.9(b). The maximum frequency ($f_r$ or $\tau_r^{-1}$) in the $-\Delta B$ plot is found to be related to the average carrier transit time ($\tau_{dc}$) by $\tau_{dc} = 0.56 \tau_r$, where $\tau_{dc}$ is the average transit time obtained in the TOF experiment.\[^6\]

### 2.3.3 Current-voltage-luminance (IVL) measurement

The setup shown in Fig. 2.10 is for measuring the I-V and L-I characteristics of OLEDs. These two measurements are conducted simultaneously. The whole setup consists of a programmable parameter analyzer (HP 4140B). It provides a driving voltage and captures the response current from organic samples. Simultaneously, a luminance meter (Minolta LS-110) is used to measure the luminance of the device.
Fig. 2.10 Schematic diagram of the experiment setup of IVL measurement.

### 2.4 Organic electronic materials used for this study

<table>
<thead>
<tr>
<th>Chemical name and abbreviation</th>
<th>Chemical structure</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’,4”-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA)</td>
<td><img src="image1" alt="Chemical structure" /></td>
<td>Hole injecting material used in OLED</td>
</tr>
<tr>
<td>N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’ diamine (NPB)</td>
<td><img src="image2" alt="Chemical structure" /></td>
<td>Hole transporting material used in OLED</td>
</tr>
<tr>
<td>N,N’-diphenyl-N,N’-bis(3-methylphenyl)(1,1’-biphenyl)-4,4’ diamine (TPD)</td>
<td><img src="image3" alt="Chemical structure" /></td>
<td>Hole transporting material used in OLED</td>
</tr>
<tr>
<td>Copper Phthalocyanine (CuPc)</td>
<td><img src="image4" alt="Chemical structure" /></td>
<td>Hole injecting material used in OLED, Electron donor in OPV, p-type material in OFET</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>Structure</td>
<td>Description</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA)</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Hole transporting material Host material for electrophosphorescent OLED</td>
</tr>
<tr>
<td>Mes₂B(p-4,4′-biphenyl-NPh(1-naphthyl)) (BNPB)</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>Blue emitting material used in OLED</td>
</tr>
<tr>
<td>Aluminum tris(8-hydroxyquinoline) (Alq₃)</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>Green emitting material used in OLED</td>
</tr>
<tr>
<td>2,2′,2″-(1,3,5-phenylene) tris(1-phenyl-1H-benzimidazole) (TPBI)</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>Electron transporting and hole blocking material used in OLED</td>
</tr>
<tr>
<td>tetrafluorotetracyanoquinodimethane (F₄-TCNQ)</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>p-type dopant</td>
</tr>
<tr>
<td>Fullerene (C₆₀)</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>Electron acceptor used in OPV n-type material used in OFET</td>
</tr>
<tr>
<td>Poly(3-hexylthiophene) (P3HT)</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>Electron donor used in OPV</td>
</tr>
<tr>
<td>[6,6]-Pentadeuterophenyl C₆₁ butyric acid methyl ester (PCBM)</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>Electron acceptor used in OPV</td>
</tr>
</tbody>
</table>
References

Chapter 3 Charge-carrier induced barrier-height reduction at organic heterojunction

3.1 Abstract

In order to provide an accurate theoretical description of current density – voltage ($J-V$) characteristics of an organic heterojunction device over a wide range of electric fields at various temperatures, it is proposed that an accumulation of charge carriers at the heterojunction will lead to a reduction in the barrier height across the heterojunction. Two well-known hole transporting materials, 4,4’,4”-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA) and N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’diamine (NPB) were used to fabricate an unipolar heterojunction device. It is found that the $J-V$ characteristics depends strongly on applied bias. The simulated $J-V$ characteristics of the heterojunction device, with the modified injection model, are found to be in excellent agreement with the experimental data.
Chapter 3 - Charge-carrier induced barrier-height reduction at organic heterojunction

3.2 Introduction

Heterojunctions formed by two semiconductors have been the foundational technology for many modern electronic devices since 1950s.[1] The first high efficiency organic light-emitting-diode (OLED) structure based on a stack of multi-layer organic materials[2] has become a standard device platform in commercial production. Recently, 5% power conversion efficiency from organic photovoltaic (OPV) cells has been demonstrated in small-molecule heterojunction devices and in polymeric blend structures,[3,4] and thus low cost OPV cells with current printing technology become commercially attractive. Despite those technological achievements with the applications of organic heterojunctions, the studies and understanding of the physics of the charge injection process across organic heterojunction are still very limited.[5-8]

There are two key factors that control the injection current at a heterojunction. One is the energy level alignment which determines the barrier height. According to recently reported photoemission studies, the interface alignment between two undoped organic materials often agrees with the vacuum level alignment rule. However, when one side of the heterojunction has extrinsic carriers, introduced either by chemical doping or electrical doping due to charge carrier accumulation, a considerable re-alignment of energy levels at the interface has been observed.[9-12] We have also reported that the injection current across an organic heterojunction device can be tuned by inserting a thin 2 nm chemically-doped interlayer with different doping concentrations at the interface.[13] The other factor is the nature of the charge injection process. It is generally believed that the charge transport in organic materials is governed by the Miller-Abrahams type hopping process between localized transporting sites.[14]

Recently, Arkhipov et al. have proposed a two step hopping model to describe the charge carrier transport across an interface of disordered organic dielectric.[5] The injection model considers the jump rate of a carrier from the center of the Gaussian density-of-state (DOS) in the injecting layer into the DOS of the accepting layer. However, the model does not include the energy distribution and occupation of carriers at the interface. Moreover, the calculated field dependence of the injection current is much smaller than those observed experimentally, as depicted in Fig. 3.1. Woudenbergh et al. found that measurements of a polymeric heterojunction
device do not match the injection model.[6] They modified the model to account for the charge filling effect of holes in the injecting layer by assuming the carriers are injected from the quasi-Fermi level rather than from the center of the highest-occupied-molecular orbital (HOMO).

![Comparison between (line) previous injection model and (symbols) the measured current density of a two-layer device.](image)

**Fig. 3.1** Comparison between (line) previous injection model and (symbols) the measured current density of a two-layer device.

In this chapter, systematic experimental current density – voltage \((J-V)\) characteristics of organic heterojunction devices made from relatively well-understood organic molecules were studied. In order to describe the experimental results, we found that it is essential to include two critical parameters to the existing theory: a) energy distribution of carriers at the injecting layer interface, and b) dynamic barrier height, \(\phi\), associated with quasi-Fermi level shifting.
3.3 Experiment

The approach in this experiment is to use a unipolar device where the current is mainly determined by the charge injection process at the organic heterojunction. This requires that the contact resistance at the metal-organic (MO) interface for charge injection and the number of trap states in the bulk organic material are negligible. This can be achieved by using 4,4’,4’’-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA) and N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’-diamine (NPB) to fabricate the heterojunction device. MTDATA and NPB are prototypical hole-injecting and hole-transporting materials used in OLED technology. The amorphous films formed with MTDATA and NPB provide a smooth surface that can effectively prevent any effect of non-homogeneous electric field at the OOI from a rough surface. The surface topology of MTDATA on ITO obtained by AFM is shown in Fig. 3.2.

![AFM image of MTDATA surface topology](image)

Fig. 3.2 Surface topology of 320 nm MTDATA obtained by AFM with surface roughness (rms) equal to 0.9 nm.

Due to the difference in HOMO levels of MTDATA (5.0-5.1 eV) and NPB (5.4-5.6 eV),\[^{10,11,15}\] there exists an energy barrier of around 0.5 eV for hole injection at the MTDATA / NPB interface. It has also been demonstrated that an quasi-Ohmic contact is formed at the indium tin
oxide (ITO) and MTDATA interface. Moreover, the trap-free space-charge-limited conduction behavior in single layer devices supports that there are a negligible number of trap states in both materials.

A hole-only heterojunction device with a structure of anode / injecting layer / accepting layer / cathode was fabricated for this study. Pre-patterned ITO coated glass substrate was used as the anode. The substrate was cleaned by a sequence of ultrasonic solvent baths and followed by UV-ozone treatment. A 320 nm layer of MTDATA was thermally evaporated on top of ITO as the injecting layer. It was then covered by 390 nm of thermally evaporated NPB as the accepting layer. Finally, silver was evaporated on top of NPB to form the cathode. The organic and metal layers were fabricated in a single vacuum system with a base pressure of $10^{-8}$ Torr. On the cathode side, a large energy difference between the lowest unoccupied molecular orbital (LUMO) of NPB (2.5 eV) and the work function of Ag (4.3 eV) effectively restricts electron injection into the device. The field and temperature dependent hole mobilities of individual organic material were characterized by the time-of-flight (TOF) technique. Details of TOF measurement has been described in the Experimental section. The measured mobilities were fitted to the Gaussian-disordered model (GDM), the extracted parameters are listed in Appendix A.

3.4 Results and discussion

3.4.1 Steady-state simulation: extracting $F_{\text{int}}$ and $p_{\text{int}}$

In order to compare the injection model to the measured $J-V$ characteristics of an heterojunction device, the electric field at the interface, $F_{\text{int}}$, and the charge carrier densities at both sides of the interface region, the injecting layer side, $p_{\text{int1}}$, and the accepting layer side, $p_{\text{int2}}$, have to be determined. The complete two layer organic system including contacts was modeled using ATLAS, to solve the standard electric field, drift, and diffusion equations used in semiconductor modeling. The iteration method was similar to the method used in Ref. [6]. The
applied voltages and measured current densities were used as the input parameters to a steady-state model of the device. The field and temperature dependent mobilities measured by TOF were used in the simulation. The hole-injecting electrode was modeled using a Schottky contact with the barrier height chosen to give a density of holes equal to $10^{21}$ cm$^{-3}$ at the anode / injecting layer interface. The cathode / accepting layer interface was specified as Ohmic (i.e. the hole concentration is pinned to the equilibrium value at this contact). ATLAS does not contain the hopping injection model. Instead, we used a thermal injection model at the organic heterojunction and adjusted the parameters to give our measured current for each applied voltage. This is equivalent to modeling the two layers separately and using the current and electric field as boundary conditions at the interface. The simulation procedure is illustrated in Fig. 3.3.

![Diagram](image)

Fig. 3.3 Simulation procedure with ATLAS for a two-layer system to extract the electric field and carrier distributions.
As shown in Fig. 3.4, the results of the simulation show that the holes pile up at the injecting layer side of the interface creating a large electric field, which remains constant across the accepting layer. In the range of applied voltage considered here, there is a low and constant concentration of holes throughout the accepting layer. The current in the accepting layer is simply given by $J \approx \varepsilon \mu \rho_{\text{int}} F_{\text{int}}$.

Re-plotting Fig. 3.4, the interface electric field and carrier density can be obtained as shown in Fig. 3.5 and Fig. 3.6 respectively. $F_{\text{int}}$ is linearly proportional to the applied voltage. Since the energy offset at the MTDATA / NPB interface effectively suppresses hole injection, the hole density in MTDATA is much higher than that in NPB as depicted in Fig. 3.6. As a result, most of the applied voltage drops across the NPB film. The electric fields at the OOI and across the TPD film are only slightly less than directly calculated from $V / d_{\text{NPB}}$. Moreover, both $F_{\text{int}}$ and $\rho_{\text{int}}$ are
independent of temperature, as mentioned in Ref.[6], the charge distribution in the injecting layer MTDATA is governed by electrostatics. Even though the injection current at the OOI is smaller at lower temperature, a much higher carrier density in the injecting layer makes the electric field mostly distributed in the accepting layer.

**Fig. 3.5** Extracted interface electric field $F_{\text{int}}$ with ATLAS at different temperatures.
Fig. 3.6 Extracted carrier density at the injecting (first) layer side of the interface, $p_{\text{int1}}$, and the accepting (second) layer side of the interface, $p_{\text{int2}}$, with ATLAS.

3.4.2 Modified injection model at OOI

We have modified the injection model to account for the hole occupation by summing the contribution to the current of all the occupied hole states, $p_{\text{int1}}(E)$, at the injecting layer side of the interface:
\[
J = \int_{-\infty}^{\infty} dE_{\text{int}1} \frac{P_{\text{int}1}(E_{\text{int}1})}{N_f} \left[ e v_0 \int_{a}^{\infty} dx \exp(-2\gamma x) \right] dE_{\text{int}2} \text{Bol}(\phi - E_{\text{int}1} + E_{\text{int}2} - eF_{\text{int}}x) 
\times g(E_{\text{int}2}) w_{\text{esc}} \right] 
\]  

(3.1)

where \(N_f\) is the total DOS, \(e\) is the electron charge, \(v_0\) is the attempt-to-jump frequency of the order of the phonon frequency, \(E_{\text{int}1}\) is the energy of carriers at the injecting layer side of the interface, \(a\) is the nearest-neighbor distance, \(\gamma\) is the inverse localization radius, and \(x\) is the hopping distance into the accepting layer. \(E_{\text{int}2}\) is the energy of the first site on the accepting side, \(\phi\) is the barrier height, \(F_{\text{int}}\) is the interface electric field, \(g(E) = N_f / \sqrt{2\pi \sigma} \exp(-E^2 / 2\sigma^2)\) is the Gaussian DOS in the accepting layer, and \(\text{Bol}(E)\) is the energy dependence of the jump rate:

\[
\text{Bol}(E) = \begin{cases} 
1 & E < 0 \\
\exp(-E / kT) & E > 0 
\end{cases} 
\]  

(3.2)

The expression inside the square bracket in Eq. (3.1), without the term \(E_{\text{int}1}\), was derived by Arkhipov et al. [5]. It calculates the thermally assisted hopping rate for a hole at the interface of the injecting layer to a site over a distance, \(x\), into the accepting layer. This is multiplied by the escape probability, \(w_{\text{esc}}\), of the hole continuing into the bulk of the accepting layer (as opposed to hopping back down the barrier). The expression from Ref. [5] assumes that there is a hole, at the HOMO level of the interface of the injecting layer, for every receiving site in the accepting layer. Our modification accounts for the occupancy and the energy distribution of holes at the injecting layer side of the interface. In order to do this, the expression in the square bracket is multiplied by the probability that an injecting site is occupied, \(P_{\text{int}1}(E)/N_f\), and everything is integrated over \(E_{\text{int}1}\). The argument of \(\text{Bol}(E)\) was modified from \((\phi + E_{\text{int}2} - eF_{\text{int}}x)\) in Ref. [5] to \((\phi - E_{\text{int}1} + E_{\text{int}2} - eF_{\text{int}}x)\) to account for the energy distribution in the injecting layer.
Using the ATLAS simulation results for $p_{\text{int}}$, the quasi-Fermi level $E_F$ and the hole occupation probability $p_{\text{int}}(E)$ can be obtained using:

$$p_{\text{int}} = \int_{-\infty}^{\infty} dE p_{\text{int}}(E) = \frac{N_t}{\sqrt{2\pi\sigma}} \int_{-\infty}^{\infty} dE \frac{\exp\left(-1/2 \left(\frac{E}{\sigma}\right)^2\right)}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

(3.3)

where $\sigma$ is the width of the Gaussian DOS in the injecting layer. $p_{\text{int}}(E_{\text{int}})$ and the integrand of Eq. (3.1), $J(E_{\text{int}})$, are plotted as a function of $E_{\text{int}}$ in Fig. 3.7 for different values of $E_F$.

![Diagram](image_url)

Fig. 3.7 (a) The normalized Gaussian energetic distribution of the carrier density $p_{\text{int}}(E_{\text{int}})$ at the injecting layer side of the interface. (b) The normalized factional injection current densities $J(E_{\text{int}})$ contributed by the carriers at different energy levels. The results are compared with different values of the quasi-Fermi level $E_F$ (from -0.2 eV to -0.4 eV).
Remarkably, the current contributed by those carriers at $E_F$ is almost negligible. The main contribution is due to the carriers at the energy of the maximum of the DOS, even though the Fermi level and the majority of the carriers lie below this level. This demonstrates that the assumption made in Ref. [6] that the carriers are injected from the Fermi level is incorrect. Mathematically, this peak is due to the exponentially falling factor of the Fermi function in $p_{\text{int}}(E)$ in Eq. (3.3) canceling the exponentially rising factor in $Bol(E)$ in Eq. (3.2), leaving the Gaussian in $p_{\text{int}}(E)$ as the predominant energy dependent factor.

The model described above assumes a constant energy level alignment at the organic heterojunction which is determined by imposing vacuum level alignment. However, the existence of an interface dipole would shift the vacuum level and change the alignment.[20] As discussed earlier in this letter, there is recent experimental and theoretical support for the existence of an interface dipole in, at least, some organic systems. Considering this, we propose a model where the energy level alignment is determined by the changes in Fermi levels in the two organic layers. The result of this is that a change in carrier concentrations will cause a change in the barrier height. The simplest assumption is to assume thermodynamic equilibrium across the interface which implies that the Fermi level is continuous at the interface.

This model is illustrated in Fig. 3.8, which shows the energy levels in the case with an applied voltage and a current in the device. The energy level bending in the injecting layer is due to the holes piling up at the interface. Fig. 3.8(a) shows the case where the vacuum levels of the two layers are matched at the interface. In this case the Fermi level will be discontinuous. The barrier height, which is the difference between the HOMO levels at the interface, is constant. Fig. 3.8(b) represents our model, where an interface dipole has formed which aligns the two Fermi levels. This will shift the vacuum levels and now the difference between the HOMO levels has shifted resulting in a smaller barrier height. Changing the current will change the hole concentrations, hence changing the Fermi levels. Evidently, this model features a variable barrier height $\phi_v$. 

58
Fig. 3.8 Schematic diagrams of energy level alignment at the heterojunction with the boundary condition of (a) vacuum level alignment and (b) Fermi level alignment. The lower graphs are the corresponding alignment of the Gaussian density-of-state (DOS) at both sides of the interface. The shaded region represents those states occupied by electrons.
3.4.3 Comparison with experiment

Using Eq. (3.3) and the simulated interface hole densities $p_{\text{int}}$ and $p_{\text{int}}$ of the ITO / MTDATA (320 nm) / NPB (390 nm) / Ag heterojunction device, the variable barrier $\phi_v$ can be obtained by adjusting the energy alignment so that the Fermi levels $E_F$ match at the MTDATA/NPB interface. Our choice of the values of $\sigma_{\text{MTDATA}}$ and $\sigma_{\text{NPB}}$ used in the calculation will be discussed later. Fig. 3.9 shows the calculated $\phi_v$ as a function of applied voltage at different temperatures. $\phi_v$ varies little with temperature, but it decreases exponentially when the applied voltage increases. This can be explained by the occupancy of holes in the interface DOSs. According to the simulation results, with increasing voltage, $p_{\text{int}}$ increases from $10^{17}$ cm$^{-3}$ to $10^{19}$ cm$^{-3}$ and $p_{\text{int}}$ increases from $10^{9}$ cm$^{-3}$ to $10^{13}$ cm$^{-3}$. The amount of change of the Fermi levels depends on the changes in $p_{\text{int}}$ and $p_{\text{int}}$ and on the DOS (at the position of the Fermi levels). In this device the Fermi level in the accepting layer changes more rapidly than that in the injecting layer, leading to a decreasing barrier as voltage increases. It can be deduced that, besides the energy difference of the HOMO levels, the energy profile is significant in controlling carrier injection across organic heterojunction.
Fig. 3.9 The field and voltage dependence of the variable barrier $\phi_v$ at 323 K (□), 288 K (○), 266 K (△), 219 K (▽), and 172 K (◇). Assuming thermodynamic equilibrium, $\phi_v$ is calculated by Eq. (4) with $p_{\text{int}}^{1}$ and $p_{\text{int}}^{2}$ obtained by the steady-state simulation. The solid line is a fitting curve to an exponential decay function.

The inset in Fig. 3.10 illustrates the first step in our calculation for the ITO / MTDATA / NPB / Ag heterojunction device. An inverse localization radius $\gamma = 5 \times 10^7 \text{ cm}^{-1}$ has been used.\(^{[21]}\) The nearest-neighbor distance $a = 1 \text{ nm}$ is taken as the size of a NPB molecule. By assuming only one net charge is carried by a molecule at a given time, the total number of DOS $N_t \approx 1 \times 10^{21} \text{ cm}^{-3}$. For a fixed interface electric field ($F_{\text{int}} = 0.5 \text{ M V/cm}$), the disorder parameters $\sigma_{\text{MTDATA}}$ and $\sigma_{\text{NPB}}$, and the attempt-to-jump frequency, $\nu_0$ are varied to obtain the best fit to the temperature dependent data. Using the values $\nu_0 = 7.88 \times 10^{13} \text{ s}^{-1}$, $\phi_v = 0.45 \pm 0.1 \text{ eV}$, $\sigma_{\text{MTDATA}} = 95 \text{ meV}$ and $\sigma_{\text{NPB}} = 110 \text{ meV}$, the theory agrees with the observed thermally activated current. The values for the disorder are slightly larger than those obtained from TOF
measurement. A broadening would be expected in the presence of an interface dipole.\textsuperscript{[22]} The above values are used in Eq. (3.1) with the introduction of the variable barrier, $\phi$, to calculate the $J$ vs $F_{\text{int}}$ characteristics in Fig. 3.10. The calculated electric field and temperature dependent injection current densities are in excellent agreement with the experimental results. The good agreement between two sweeping directions of the applied voltage at all temperatures also suggests that the trap charging effect is negligible. It is worthwhile noting that ignoring the contribution of the variable barrier $\phi$ will vastly underestimate the field dependence of the injection current across the heterojunction.

![Fig. 3.10 Measured $J - F_{\text{int}}$ characteristics of the ITO / MTDATA(320 nm) / NPB(390 nm) / Ag heterojunction device at 323 K (□), 288 K (○), 266 K (△), 219 K (▽), and 172 K (○). The corresponding solid symbols are the calculation results based on the modified injection model in Eq. (3) with the variable barriers $\phi$, in Fig. (3). The inset is the $J$ vs 1/T plot at $F_{\text{int}} = 0.5$ M V/cm.](image-url)
Fitting the calculation results (solid line) with Eq. (3) to the experiment results (opened symbols) obtains $\phi_e = 0.45 \pm 0.1 \text{ eV}$, $\sigma_{MDATA} = 95 \text{ meV}$ and $\sigma_{NPB} = 110 \text{ meV}$.

### 3.5 Conclusion

In conclusion, an injection model for an organic heterojunction which includes the distribution of carriers at the injecting side of the interface has been proposed. This model shows that the main contribution to the injection current is from carriers at the peak of the Gaussian density-of-state (DOS) rather than at the Fermi level. In addition, we have proposed a variable injection barrier height $\phi_e$ which arises from the energy level re-alignment triggered by the relative Fermi level shifting caused by charge carrier accumulation at the interface. The model is verified by the excellent agreement with the experimental results of the current density – voltage ($J-V$) characteristics of an organic heterojunction device for various temperatures over a wide range of electrical field. The results show that a dynamic change in carrier concentration and DOS energy alignment at the heterojunction plays a significant role in the performance of organic heterojunction devices.
3.6 References

Chapter 4 Temperature dependence of carrier injection across organic heterojunctions

4.1 Abstract

Theoretical and experimental study of carrier injection across organic heterojunctions of various barrier heights (0.4 eV – 1.0 eV) over a wide range of temperatures is presented in this chapter. An injection model with proposed escape probability function $w_{\text{esc}}$ is formulated to include the total hopping frequency at both sides of the heterojunction. The model predicts that the injection current at low temperature can be dramatically modified by an extremely small amount of deep trap states. Moreover, the temperature dependence of the injection current is found to decrease with increasing barrier height. This suggests that extracting the barrier height from the $J$ vs $1/T$ plot, as commonly employed in literature, is problematic. Experimentally, heterojunction devices with injection barrier from 0.4 eV to 1.0 eV are fabricated from various organic materials. The measured temperature dependence of the injection current is in good agreement with the calculated results. By measuring the carrier mobility of a single layer device at low temperature, a temperature dependence similar to the heterojunction devices suggests that the small density of deep trap states originates in the bulk of the material.
4.2 Introduction

As discussed in Chapter 3, owing to the weak coherence of electronic states in disordered organic materials, the carrier injection across organic heterojunctions is treated as a hopping or thermally assisted tunneling process. The hopping rate $\nu$ of a carrier being injected from a starting site to a target site, separated by a distance $x$ and with energy difference $E$, can be simply described by the Miller-Abrahams expression:\[^{[1]}\]

$$
\nu = \nu_0 \exp(-2\gamma x) \text{Bol}(E)
$$

(4.1)

$$
\text{Bol}(E) = \begin{cases} 
1 & E < 0 \\
\exp(-E/kT) & E > 0 
\end{cases}
$$

(4.2)

where $\nu_0$ is the attempt-to-jump frequency having a value close to the phonon frequency, $\gamma$ is the inverse localization radius, and $\text{Bol}(E)$ accounts for the energy independent downward ($E < 0$) and energy dependent upward ($E > 0$) jumps.

Fig. 4.1 illustrates the injection of carriers across an organic heterojunction. The injection process can be basically divided into two steps: 1) In order to overcome the energy barrier $\phi$, carrier injection into the density-of-state (DOS) of the second layer is accomplished by an upward jump. 2) After a carrier is injected into the second layer, it will either jump back into the first layer or further advance to the bulk of the second layer. This process is described by the escape probability $w_{\text{esc}}$ of the injected carrier. Due to the exponential dependence of the thermionic process, it can be easily deduced that the injection current is largely depended on the shape of the DOS at both sides of the interface. Under thermodynamic equilibrium condition, those carriers that accumulate at the first layer side of the interface will fill up the lower energy
states. As a result, a broader DOS in the first layer will eventually reduce the injection current. On the other hand, a broader DOS in the second layer has more low energy states that facilitates the injection. The impact of accumulated charges at organic-organic interface (OOI) on carrier injection has been discussed in Chapter 3. Moreover, since the downward jump is energetically favorable as indicated in Eq. (4.2), any deep trap states in the second layer, with energy close to or lower than the accumulated carriers in the first layer, will significantly increase the injection current. Intuitively, the escape probability $w_{\text{esc}}$ of an injected charge, hopping into the bulk of the second layer, depends on the hopping rate and the number of available sites at both sides of the interface. This process is crucial as it determines the net injection current across the interface.
Chapter 4 - Temperature dependence of carrier injection across organic heterojunctions

Fig. 4.1 Illustration of carrier hopping across a disordered organic heterojunction. The density-of-state (DOS) of the lowest-unoccupied molecular orbital (LUMO) and deep trap energy levels is assumed to be Gaussian.

This chapter is organized as follow: Sec. 4.3 gives a formalism of an injection model with a proposed $w_{esc}$. Using the modified model, we calculate the impact of deep trap states on the temperature and field dependence of the injection current. In Sec. 4.4, experiment results of a series of heterojunction devices with barrier heights from 0.4 eV to 1.0 eV are given. The reduced temperature dependence of injection current for larger barrier is compared to the proposed model with deep trap states. In Sec. 4.5 we demonstrate the temperature dependence of carrier mobility in a single layer device. The results support that the deep traps originate in the bulk of the material with a density comparable to the model prediction. It is then followed by the discussion and conclusion.
4.3 Theoretical modeling

4.3.1 Carrier injection model with proposed \( w_{esc} \)

In disordered organic materials, it is commonly assumed that the DOS has a Gaussian distribution:

\[
g(E) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right)
\]  

(4.3)

where \( E \) is the site energy reference to the center of the Gaussian DOS, \( N \) is the total DOS, and \( \sigma \) is the Gaussian width. In the absence of polaronic effects, the hopping rate across the heterojunction can be described by Eqs. (4.1) and (4.2). As discussed in Chapter 3, taking into account the distribution of carriers \( p_1(E) \) at the first layer side of the interface, the injection current \( J \) can be formulated as:

\[
J = e v_0 \int_{-\infty}^{\infty} dE_1 \frac{p_1(E_1)}{N_1} \int_a^\infty dx \exp(-2\gamma x) \int_{-\infty}^{\infty} dE_2 \Box l(\phi - E_1 + E_2 - eF_{int}x) \\
\times g(E_2) w_{esc}(x, E_2)
\]

(4.4)

where \( e \) is the electron charge, \( a \) is the nearest-hopping distance, \( x \) is the hopping distance into the second layer, \( \phi \) is the barrier height, and \( F_{int} \) is the interface electric field. The first integral in Eq. (3) describes the probability that an injecting site in the first layer is occupied. The second and third integrals account for the hopping rate over a distance, \( x \), of a carrier in \( E_1 \) in the first
layer into $E_2$ in the second layer. The hopping rate is then multiplied by the DOS, $g(E)$, in the second layer and the escape probability, $w_{esc}(x,E)$, of the carrier continuing into the bulk.

Arkhipov et al. suggest that $w_{esc}$ can be determined by the average number of injection-facilitating neighbors, $n_i(x,E)$, in the second layer.$^{[3]}$ The backward jump into the first layer is assumed energetically downward. By considering the argument inside the exponential function in Eq. (1), the backward hopping parameter is simply equal to $2\gamma x$ for a carrier localized in a site with energy $E$ at a distance $x$ from the interface in the second layer. Therefore, one can calculate $n_i(x,E)$ by counting the hopping sites in the second layer with hopping parameter less than $2\gamma x$:

$$n_i(x,E) = 2\pi \int_0^r dr \int_0^1 dz \int_{-\infty}^{E+2kT(x-r)+eF_{int}z} dE_2 g(E_2)$$  \hspace{1cm} \text{(4.5)}

where $r$ is the distance away from the injected carrier in the second layer, $z = \cos \theta$, and $\theta$ is the angle between the $F_{int}$ and the hopping direction. The escape probability $w_{esc}$ is defined as the probability that the carrier in the second layer has at least one injection-facilitating neighbor, which is determined by the Poisson distribution:

$$w_{esc}(x,E) = 1 - \exp\left[-n_i(x,E)\right]$$ \hspace{1cm} \text{(4.6)}$$

It is worth noting that Eq. (4.5) is formulated by assuming all the backward jumps into the first layer are energetically downward. Therefore, the probability in Eq. (4.6) is independent of the barrier height $\phi$, and is solely dependent on the number of injection-facilitating neighbors in the second layer. Fig. 3 shows the energy dependence of $w_{esc}(a,E)$ of a carrier localized at $a = 10^{-7}$
cm from the interface with $F_{\text{int}} = 5 \times 10^5$ V/cm. For an injected carrier localized well above $E = 0$, the center of the Gaussian DOS, $w_{\text{exc}}(a,E)$ saturates at 1. Because of the dramatic decreases of the DOS in the Gaussian tail, $w_{\text{exc}}(a,E)$ decreases rapidly for those carriers localized in lower energy states. However, if the carrier is localized well below $E = 0$, the backward jump into the first layer is not necessarily downward, and the number of available backward hopping sites is also reduced. Therefore, assuming all backward jumps are downward will underestimate the escape probability of those carriers localized in lower energy states.

We formulate the escape probability by comparing the total hopping frequency at both sides of the interface. For an injected carrier in the second layer, a successful hop into the neighboring site depends on both the hopping frequency, Eqs. (4.1) and (4.2), and the number of available sites, Eq. (4.3). The escape probability is determined by the ratio of the total forward to the overall hopping frequencies at both sides of the interface. Considering a carrier localized at a site in the second layer with energy $E$ and a distance $x$ away from the interface, the total forward hopping frequency $\nu_{fw}$ is:

$$\nu_{fw}(x,E) = 2\pi \int_0^\infty dr \int_{-\infty}^{\infty} dE_2 \text{Bol}(E_2 - eF_{\text{int}}rz - E)g(E_2)$$  \hspace{1cm} (4.7)$$

and total backward hopping frequency $\nu_{bw}$ becomes:

$$\nu_{bw}(x,E) = 2\pi \int_{x}^{\infty} dr \int_{-\infty}^{\infty} dE_1 \text{Bol}(E_1 - \phi + eF_{\text{int}}xz - E)g(E_1)$$  \hspace{1cm} (4.8)$$

The spatial integrations of Eqs. (4.7) and (4.8) are illustrated in Fig. 4.2.
Fig. 4.2 A schematic diagram of the spatial integration in Eqs. (4.7) and (4.8). An injected carrier at the center of the sphere is localized at a distance $x$ away from the interface. The preferable hopping neighbors are located at a distance $r$ from the injected carrier with a direction $\theta$ between the interface electric field.

Since most of the electric field is distributed in the second layer, the contribution of the electric field on the potential landscape in the first layer is neglected. Using Eqs. (4.7) and (4.8), the escape probability $w_{esc}(x,E)$ is obtained:
Chapter 4 - Temperature dependence of carrier injection across organic heterojunctions

\[ w_{\text{esc}}(x, E) = \frac{v_{fw}}{v_{fw} + v_{bw}} \quad (4.9) \]

As shown in Fig. 4.3, the calculated \( w_{\text{esc}}(x, E) \) using Eq. (4.9) approaches 1 when \( E \) is close to -0.25 eV. Although, backward jumps for carriers localized in higher energy states are mostly downward, the number of available sites in the second layer with a smaller hopping distance is higher than that in the first layer. Consequently, \( v_{fw} \) is higher than \( v_{bw} \) even for a carrier localized slightly below the maximum of the Gaussian DOS. On the other hand, at lower energy, \( w_{\text{esc}}(x, E) \) calculated with Eq. (4.9) is much larger than the one calculated with Eq. (4.6), and it saturates to a constant value \( w_{\text{esc}} \approx \exp(2\gamma x - \phi / kT) \). Despite the hopping rate is higher for downward jump, the steep increase of the Gaussian DOS from the tail to the maximum region overwhelms the exponential decrease of the upward hopping rate. Therefore, for an injected carrier localized well below the DOS, an upward jump into both sides of the interface is favorable. The ratio of the forward and backward hopping rates is determined by the position of the injected carrier, \( x \), and the energy difference of the DOS, \( \phi \), of the first and the second layers.
Chapter 4 - Temperature dependence of carrier injection across organic heterojunctions

Fig. 4.3 Calculated escape probability function $w_{\text{esc}}$ using Eq. (4.6) and (4.9) of an injected carrier at a distance $x = 10^{-7}$ cm and an energy $E$ in the second layer. It is parameterized for $\sigma_1 = \sigma_2 = 0.1$ eV, $T = 300$ K, $F_{\text{int}} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, and $\gamma = 5 \times 10^{-7}$ cm$^{-1}$. The inset is a linear scale of $w_{\text{esc}}$.

4.3.2 Impact of deep trap states

The influence of trap states on the injection current can be included by simply modifying Eq. (4.3) with the DOS of traps which is also assumed to be Gaussian:
\[
g(E) = \frac{N}{\sqrt{2\pi\sigma_t}} \exp\left(-\frac{E^2}{2\sigma_t^2}\right) + \frac{n_t}{\sqrt{2\pi\sigma_t}} \exp\left(-\frac{(E - E_t)^2}{2\sigma_t^2}\right)
\]  \tag{4.10}

where \(n_t\) is the total DOS of the traps, \(\sigma_t\) is the Gaussian width, \(E_t\) is the depth of the traps relative to the center of the DOS of the transporting sites. Fig. 4.4 shows the influence of deep trap states, \(n_t = 10^{10} \text{ cm}^{-3}\), \(E_t = -1 \text{ eV}\), and \(\sigma_t = 0.1 \text{ eV}\), at both sides of the interface, on the escape probability functions \(w_{\text{esc}}(x,E)\). The probability calculated with Eqs. (4.6) and (4.7) are significantly increased by a few orders of magnitude for energies near the trap states. Although the trap density is extremely small compared to the total DOS of the transporting sites \(N = 10^{21} \text{ cm}^{-3}\), comparing to the density of the transporting sites at the lower tail of the Gaussian DOS, the additional deep trap states introduce a large number of available hopping-neighbors at the tail region. Since the hopping distance from the injected carriers to the traps states in the second layer is smaller than those in the first layer, \(\nu_{\text{fw}}\) is higher than \(\nu_{\text{bw}}\) and \(w_{\text{esc}}(x,E)\) calculated with Eq. (4.9) approaches 1. On the other hand, as mentioned above, \(w_{\text{esc}}(x,E)\) in Eq. (4.6) assumes a constant backward hopping rate and ignores the variation of the number of the downward hopping sites in the first layer, the calculated probability is much smaller than the one calculated with Eq. (4.9).
Fig. 4.4 Calculated escape probability function $w_{\text{esc}}$ with the presence of deep trap states using Eq. (4.6) and (4.9) of an injected carrier at a distance $x = 10^{-7}$ cm and an energy $E$ in the second layer. It is parameterized for $\sigma_1 = \sigma_2 = 0.1$ eV, $T = 300$ K, $F_{\text{int}} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$, $n_t = 10^{10}$ cm$^{-3}$, and $E_t = -1$ eV. The inset is a linear scale of $w_{\text{esc}}$.

The calculated temperature dependence of injection current using Eq. (4.4) and different escape probability functions $w_{\text{esc}}(x, E)$ is shown in Fig. 4.5. In the absence of traps, the temperature dependence for $T > 100$ K, calculated with $w_{\text{esc}}(x, E)$ in Eq. (4.6) and (4.9), are comparable with each other. In this temperature range, the injection current is dominated by the thermionic process; carriers are injected into the higher energy states in the second layer. However, at lower temperature, the injection current calculated with $w_{\text{esc}}(x, E)$ in Eq. (4.9) is a few orders of magnitude higher than the one calculated using Eq. (4.6). As the temperature decreases, the current becomes dominated by the carrier injection into the lower tail of the DOS in the second layer. On the one hand, a higher current obtained with $w_{\text{esc}}(x, E)$ in Eq. (4.9) is a
consequence of the higher escape probability of the injected carriers at lower energy levels which has been discussed above. Such deviation at low temperature is more significant even with a small density of deep trap states, $10^{10}$ cm$^{-3}$, as shown in Fig. 4.5. The injection current calculated with $w_{\text{esc}}(x,E)$ in Eq. (4.9) is dramatically increased and pinned at a constant value. On the other hand, due to the extremely small value of $w_{\text{esc}}(x,E)$ in Eq. (4.6) at low energy level, the contribution of the additional trap states to the injection current is negligible, unless a much higher trap density, $10^{16}$ cm$^{-3}$, is used. However, such a large trap density is unrealistic in the material systems used for this study, which will be discussed in Sec. 4.5.

Fig. 4.5 Calculated $J$ vs $1/T$ characteristics using Eq. (4.4). The solid and dash lines are calculated with the escaped probability function described in Eq. (4.6) and (4.9) respectively. The symbols are the corresponding $J$ vs $1/T$ characteristics with various $w_{\text{esc}}$ in the presence of deep trap states. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1$ eV, $F_{\text{int}} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$, $n_t = 10^{10}$ cm$^{-3}$, and $E_t = -1.5$ eV.
The hopping injection model which discussed above includes both thermionic emission and tunneling contributions. The fractional injection current-density \( J(E_2, x) \), injection current from the first layer into a localized site in the second layer with energy \( E_2 \) and distance \( x \) away from the interface, is shown in Fig. 4.6. At higher temperature, the injection current mainly contributed by those carriers injected into higher energy states in the second layer. At lower temperature, thermally activated upward hopping becomes unfavorable, most carriers tunnel through the barrier into the second layer. Consequently, carrier injection into those energy sites which deeper in the bulk of the second layer becomes dominant.
Fig. 4.6 Calculated fractional current-density $J(E_2, x)$ using Eq. (4.6) and (4.9) at different temperatures. It is parameterized for $\sigma_1 = \sigma_2 = 0.1$ eV, $F_{\text{int}} = 5 \times 10^5$ V/cm, $\phi = 0.5$ eV, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$. 

79
Using Eq. (4.4) and \( w_{\text{esc}}(x,E) \) in Eq. (4.9), the temperature dependence of the injection current with different injection barriers is shown in Fig. 4.7.

![Figure 4.7](image_url)

Fig. 4.7 Calculated \( J \) vs 1/T characteristics using Eq. (4.4) and (4.9) as a function of barrier height \( \phi \). The lines (symbols) are calculated \( J \) without (with) deep trap states. The same parameters as in Fig. 4.5 are used in the calculation.

In the absence of traps, the temperature dependence at \( T > 100K \) increases with increasing barrier height. This agrees with the general observation of the thermionic emission process, and is commonly employed as the rule-of-thumb to determine the injection barrier. Interestingly, the trend is opposite to the trend with the presence of deep trap states. The temperature dependence decreases with increasing barrier height. It is worth noting that, for sufficiently large barriers, the injection current becomes temperature and barrier height
independent, over a wide range of temperature. In that case, the injection current is mainly contributed by the non-energetic downward hopping into the deep trap states in the second layer. By re-plotting Fig. 4.7, the slope of $J$ vs $1/T$ between 300 K and 200 K can be obtained as shown in Fig. 4.8. It is clearly shown that, even with an extremely small density of deep trap states, simply using the Arrhenius plot to determine the activation energy is inappropriate.

![Graph showing -(slope of $J$ vs 1000/T) as a function of barrier height $\phi$ for $T > 200$K. The line (symbol) is calculated $J$ without (with) deep trap states. It is parameterized for $\sigma_1 = \sigma_2 = \sigma_t = 0.1$ eV, $F_{int} = 5 \times 10^5$ V/cm, $N = 10^{21}$ cm$^{-3}$, $\gamma = 5 \times 10^{-7}$ cm$^{-1}$, $n_t = 10^{10}$ cm$^{-3}$, and $E_t = -1.5$ eV.]

In addition, the electric field dependence on the injection current at low temperature is also altered by the introduction of deep trap states as shown in Fig. 8. On the one hand, without the deep traps, the field dependence increases with decreasing temperature. Since the applied electric field reduces the potential energy of the hopping sites in the second layer, the carriers
have higher probability to be injected into those states closer to the centre of the Gaussian DOS. This is attributed to the field dependence of the injection current. On the other hand, with the addition of deep trap states, the injection current at low temperature is not only significantly increased, but also becomes independent of the electric field. In this case, downward hopping into the trap states becomes dominant, which is independent of the applied electric field. The field dependence increases, unless a large electric field is applied to lower the potential energy that hopping into the Gaussian DOS becomes significant.

![Graph showing calculated J vs F_int characteristics using Eq. (4.4) and (4.9) as a function of temperature. The lines (symbols) are calculated J without (with) deep trap states. It is parameterized for \( \sigma_1 = \sigma_2 = \sigma_i = 0.1 \text{ eV}, \phi = 0.5 \text{ eV}, N = 10^{21} \text{ cm}^{-3}, \gamma = 5 \times 10^{-7} \text{ cm}^{-1}, n_i = 10^{10} \text{ cm}^{-3}, \) and \( E_i = -1.5 \text{ eV}.\)]
4.4 Experiment on heterojunction devices with various injection barriers

A series of hole-only heterojunction devices with a general structure of anode / first organic layer / second organic layer / cathode were fabricated for this study. The hole injection barrier is determined by the difference of the highest-occupied molecular orbital (HOMO) energy levels at the heterojunction. The interface dipole effect on the injection barrier is ignored; as the injection current measured at high temperature agree with trend of the HOMO energy level offset. Pre-patterned indium tin oxide (ITO) coated on glass substrate was used as the anode. The substrate was cleaned by a sequence of ultrasonic solvent baths and followed by UV-ozone treatment. A 320 nm layer of 4,4’,4”-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA) was thermally evaporated on top of the ITO as the first organic layer for all of the devices. The MTDATA layer was then covered by another thermally evaporated organic layer; 390 nm of N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’ diamine (NPB), 430 nm of tris(8-hydroxyquinoline) aluminum (Alq), 370 nm of 4,4’,4’’-tris(N-carbazolyl)-triphenylamine (TCTA), or 490 nm of 2,2’,2”-(1,3,5-phenylene) tris(1-phenyl-1H-benzimidazole) (TPBI). Finally, Ag was evaporated on top of the second layer to form the cathode with an active area of 0.16 cm². The device structures are summarized in Table 4.1. The organic and metal layers were fabricated in a single vacuum with a base pressure of 10⁻⁸ Torr. Thicknesses of the organic films were measured by a stylus profilometer. The J-V characteristics of the devices were characterized using a Keithley 236 Source-Measure unit. The carrier mobility measurement on a single layer device with MTDATA was done by admittance spectroscopy (AS) with a HP 4284A LRC meter. The J-V and carrier mobility measurements were performed in a temperature regulated cryostat with a base pressure of about 10⁻⁶ Torr. During the measurement, a silicon diode temperature sensor was attached on the glass substrate next to the test device. The temperature was controlled and monitored by a Lakeshore 331 temperature controller. For every 20 K temperature step, 45 minutes of idle period were taken to ensure a stabilized temperature.
First organic layer / second organic layer | HOMO energy of the 1st layer (eV) | HOMO energy of the 2nd layer (eV) | Energy offset at the heterojunction (eV) |
--- | --- | --- | --- |
MTDATA (320 nm) / NPB (390 nm) | 5.1 \cite{4,5} | 5.5 \cite{4-8} | 0.4 ± 0.1 |
MTDATA (320 nm) / Alq (430 nm) | 5.7 \cite{8-10} | 0.6 ± 0.1 |
MTDATA (320 nm) / TCTA (370 nm) | 5.1 \cite{4,5} | 5.9 \cite{8} | 0.8 ± 0.1 |
MTDATA (320 nm) / TPBI (490 nm) | 6.1 \cite{11} | 1.0 ± 0.1 |

Table 4.1 The heterojunction devices used in this study have a general structure of ITO / first organic layer / second organic layer / Ag. The energy offset at the heterojunction is determined by the energy difference of the highest-occupied molecular orbital (HOMO) of each layer.

Fig. 4.10 shows the $J-F_{\text{int}}$ characteristics of the heterojunction devices at different temperatures. For all the devices, the injection current becomes nearly temperature independent below 150 K. In order to ensure that the pinned current is not due to the leakage current from the measurement system, we have directly measured the current on the glass substrate. The leakage current density, with correction for the device active layer, is around $10^{-11}$ A/cm$^2$. It is two orders of magnitude lower than the measured current density of the device. It is worth noting that, for the MTDATA/TCTA and MTDATA/TPBI devices, the hysteresis of the injection current measured with different ramping directions of applied electric field becomes larger at lower temperature. This suggests that there is some trap charging effects in the devices.
Fig. 4.10 Measured $J$ vs $F_{\text{int}}$ characteristics of different samples at various temperatures. (a) ITO / MTDATA (320 nm) / NPB (390 nm) / Ag, (b) ITO / MTDATA (320 nm) / Alq (430 nm) / Ag, (c) ITO / MTDATA (320 nm) / TCTA (370 nm) / Ag, and (d) ITO / MTDATA (320 nm) / TPBI (490 nm) / Ag.

Re-plotting

Fig. 4.10 at a constant $F_{\text{int}} = 5 \times 10^5$ V/cm, the temperature dependence of the injection current for different devices is shown in Fig. 4.11. At $T > 200$ K, the carrier injection across the heterojunction is still thermally activated; the injection current is higher for devices with a smaller injection barrier. However, if one determines the activation energies from the slopes in Fig. 4.11 at the temperature between 300 K and 200 K, as shown in the inset, it gives a contradictory result, namely that the device with a larger injection barrier has smaller activation energy. Moreover, at low temperature the measured currents for different devices are pinned at a
similar value, $10^{-8} - 10^{-9} \text{A/cm}^2$. The measured electric field and temperature dependences are in good agreement with the calculation results with deep trap states as shown in Fig. 4.7, Fig. 4.8, and Fig. 4.9.

![Graph showing J vs 1/T characteristics](image)

Fig. 4.11 Measured $J$ vs $1/T$ characteristics of various heterojunction devices at $F_{\text{int}} = 5 \times 10^5 \text{V/cm}$. The solid lines are guides for eye vision. The inset shows the $-(slope \ of \ J \ vs \ 1000/T)$ of different samples extracted for $T > 200\text{K}$.

### 4.5 Experiment on carrier mobility in single layer device

The calculation and experiment results discussed above suggest that the carrier injection across the heterojunction at low temperature is dominated by an extremely small density of deep trap states, $10^{10} \text{cm}^{-3}$, in the material. It is interesting to determine whether the traps originate at the interface or in the bulk of the material. Since both the carrier transport and injection in
disordered organic materials are hopping processes, a similar electric field and temperature dependence of the transport properties are expected if there are any bulk trap states in the material.

We have measured the hole mobility, \( \mu_h \), of MTDATA over a wide range of temperature. Due to the weak photocurrent signal of MTDATA obtained by the time-of-flight (TOF) technique at low temperature, AS is employed for this study.\(^{12}\) In order to form a quasi-Ohmic contact to supply enough space charges for the thin film, a thin layer of molybdenum oxide (MoO\(_x\)) has been evaporated on top of the ITO to form the injection anode.\(^{13}\) The device has a structure of ITO / MoO\(_x\) (10 nm) / MTDATA (570 nm) / Ag. Fig. 4.12 shows the measured frequency dependent capacitance at a constant applied electric field, \( F = 7 \times 10^5 \) V/cm, at different temperatures. The position of the drop in capacitance is correlated with the carrier transit time. At lower temperature, the minimum of capacitance shifts to lower frequency, which indicates a larger carrier transit time and therefore a smaller carrier mobility.
Fig. 4.12 Measured capacitance vs frequency by admittance spectroscopy (AS) of ITO / MoOx (10 nm) / MTDATA (570 nm) / Ag devices at an applied electric field $F = 7 \times 10^5$ V/cm, and at temperature (a) 164 K, (b) 146 K, (c) 123 K, (d) 100 K, and (e) 85 K.
The field and temperature dependent mobilities measured by AS are summarized in Fig. 4.13.

Fig. 4.13 The average hole mobility $\mu_h$ of MTDATA measured by admittance spectroscopy (AS) at various temperatures. The solid lines are the best fits to the Poole-Frenkel expression:

$$\mu_h = \mu_0 \exp (\beta \sqrt{F})$$

where $\mu_0$ is a prefactor, $\beta$ is the electric field dependence coefficient, and $F$ is the applied electric field.

By re-plotting Fig. 4.13, the temperature dependence of the mobility at $F = 5 \times 10^5$ V/cm is shown in Fig. 4.14. The temperature dependence is similar to those observed in the heterojunction devices; the mobility is pinned at a constant value at low temperature. It has been proposed that the carrier mobility can be formulated with the consideration of carrier concentration $p$ as: $^{[14]}$
\[
\mu_h = \frac{eV_0}{kT\rho}\left[\int_{-\infty}^{E_F} dE \cdot g(E)\right]^{2/3} \int_{-\infty}^{E_F} \frac{dE \cdot g(E)}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \exp\left(\frac{E - E_{tr}}{kT}\right)
\]
(4.11)

where \(E_{tr}\) is the effective transport level of energy, \(E_F\) is the Fermi level. In a space-charge limited (SCL) regime, the average value of \(\rho\) is equal to \(3/2(\varepsilon, \varepsilon_0 V/ed)^2\), where \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_r\) is the relative dielectric constant, and \(d\) is the thickness of the organic film. For \(F = 5 \times 10^5\) V/cm, \(d = 570\) nm and \(\varepsilon_r = 3\), we get \(\rho = 2.15 \times 10^{16}\) cm\(^{-3}\). The solid line in Fig. 4.14 is calculated using Eq. (4.11) with \(\nu = 3 \times 10^{13}\) s\(^{-1}\), \(\gamma = 3 \times 10^7\) cm\(^{-1}\), \(N = 10^{21}\) cm\(^{-3}\) and \(\sigma = 0.1\) eV. Those parameters are comparable to values previously reported.\(^2\) At \(T > 180\) K, there is good agreement between the calculation and experimental results. However, the measured mobility is a few orders of magnitude higher below 100 K.

Fig. 4.14 Measured \(\mu_h\) vs \(1/T^2\) characteristics of MTDATA at \(F = 5 \times 10^5\) V/cm. The solid symbols are directly measured data. The open symbols are extrapolated from Fig. 4.13. The solid line is the best fit to data using Eq. (4.11), with \(\sigma = 0.1\) eV, \(N = 10^{21}\) cm\(^{-3}\), \(\nu = 3 \times 10^{13}\) s\(^{-1}\), \(\gamma = 5 \times 10^7\) cm\(^{-1}\), and \(\rho = 2.15 \times 10^{16}\) cm\(^{-3}\).
From the results of the carrier mobility measurement in the single layer device, it suggests that the deep traps originate at in the bulk of the material. The carriers transport through the non-energetic tunneling process at low temperature. In addition, the well defined plateau regions obtained in TOF measurements, Fig. 4.15, also suggest that the trap density should be much smaller than the number of accommodated space charges $10^{13}-10^{14}$ cm$^{-3}$. This agrees with the proposed model that predicts an extremely small density of deep trap states can significantly increase and pin the injection current across the heterojunction at low temperature.

Fig. 4.15 Measured photocurrent transient of holes (a) MTDATA, (b) NPB, and (c) TCTA by time-of-flight (TOF) technique.
4.6 Discussion

We have considered adding trap states, Eq. (4.10), into the analytical mobility model in Eq. (4.11). However, in order to reduce the temperature dependence, one has to choose a density of trap states close to that of the space charge $10^{16}$ cm$^{-3}$. This can be understood by the fact that Eq. (4.11) is based on carrier transport at the transport energy level $E_{tr}$. It will be changed only if the number of additional trap states is large enough to redistribute the carriers in the DOS. Nevertheless, the calculated mobility with $10^{16}$ cm$^{-3}$ trap states still has a higher temperature dependence than the experimental results. Such a trap density is also much higher than the number of photo-excited carriers in TOF measurements. Moreover, an unrealistic value of phonon frequency $\nu_0 = 10^{16}$ s$^{-1}$ has to be used in Eq. (4.11) to fit the data. We have measured the temperature dependence of injection current for various single layer devices with different injection barriers at the metal/organic interfaces.\cite{16} It is found that the temperature dependence has also decreased with a larger injection barrier. Similar temperature dependence has also been reported by Baldo et al. on electron injection from metals into Alq.\cite{17} Therefore, it is believed that carrier transport and injection pinned at low temperature by the presence of an extremely small density of deep trap states is a general feature in disordered organic materials. As such small number of trap states exists even in high-purity inorganic crystal, such as silicon.

4.7 Conclusion

An injection model with a proposed escape probability function $w_{esc}$ based on the total hopping frequencies at both sides of the organic heterojunction is formulated. It has been shown that the injection current at low temperature is greatly increased and pinned by an extremely small density of deep trap states $10^{10}$ cm$^{-3}$. As a result, the injection current across a heterojunction with a larger injection barrier has a smaller temperature dependence. The calculation results are in good agreement with the experimental results of heterojunction devices.
with barrier heights ranging from 0.4 eV – 1.0 eV. We have also demonstrated that the carrier mobility in a single layer device shows similar temperature dependence. This strongly supports that the small number of deep trap states originate from the bulk of the material instead of only from the interface. This study also suggests that, in the presence of the deep trap states, simply extracting the barrier height from the Arrhenius plot is inappropriate.
4.8 References


5.1 Abstract

In this Chapter, it will be shown that injection current at an organic heterojunction can be effectively engineered by introducing a thin (2 nm) $p$-doped interlayer at the junction. Two common hole transporting materials, $4,4',4''$-Tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (MTDATA) and $N,N'$-diphenyl-$N,N'$-bis(1-naphthyl)(1,1'-biphenyl)-4,4'diamine (NPB), and $p$-type dopant tetra-fluorotetracyanoquinodimethane (F$_4$-TCNQ), were used to build various test devices. For a hole-only heterojunction device, ITO / MTDATA / NPB / Ag, both experimental measurement and theoretical modeling showed that the current flow in the device is limited by the heterojunction potential barrier or band-offset at the MTDATA/NPB interface. It is found that the device current flow can be modulated dramatically to increase or decrease by introducing a 2 nm $p$-doped NPB:F$_4$-TCNQ or MTDATA:F$_4$-TCNQ interlayer, respectively. Quasi-Fermi energy level realignment at the doped/undoped organic-organic interface is proposed as the working principle for the observed phenomena.
5.2 Introduction

Organic light-emitting diode (OLED) is a key technology for flat-panel displays and has huge potential for future lighting applications. The current high research activities in OLED was triggered by the first seminal report of constructing the device using organic-organic heterojunction,[1] which is now the standard device platform in commercial production. Heterojunctions provide a practical engineering method to modulate carrier (electrons or holes) concentration in the device thus leading to much improved stability and efficiency. For multilayered structures with no intrinsic free carriers inside the device, charge carriers (electrons/holes) have to be injected from two opposite electrodes (cathode/anode). These injected carriers have to pass through different organic layers before they form excitons in the emission layer. In the past decade, there were numerous studies on the metal/organic (MO) interface. It has been successfully demonstrated that the injection can be improved by modification at the MO interface. In some case, true Ohmic contact at MO interface has been demonstrated.[2] As a result, operating voltage in OLEDs has been improved steadily over the last decade. One of the current challenges in OLED device physics is to understand and control of charge transport across organic-organic interface (OOI). It is well-known that energy offset exists at any heterojunctions. In conventional inorganic semiconductor devices, e.g. laser diode, heterojunction plays a critical role in device performance. In organic electronic materials, such energy offset has been shown to be the major factor limiting the injection current at the organic-organic interface OOI.[3-5] This is therefore important to understand and to control the carrier transport across the OOI. The current approach to this problem is mostly chemistry-type, i.e. synthesizing and matching various classes of organic derivatives. Due to many restrictions such as optical path, molecular stability, carrier mobility etc., the choice of practical materials and even thickness for each layer are quite often limited. In this letter, we report an alternative physical method which involves inserting a thin $p$-doped interlayer at the OOI to effectively modulate the carrier transport across the heterojunction. Controlling the injection current with the doped-interlayer at OOI can be applied to balance the electron and hole currents in the device. Balancing electron and hole currents has been proved to be a determining factor for the device efficiency in OLED. The doping mechanism is illustrated in Fig. 5.1. F$_4$-TCNQ is a strong electron acceptor which has the LUMO energy level closes to the HOMO energy level of...
NPB. The occupied electron states in NPB can be readily transferred to the F_4-TCNQ that increases the hole concentration in NPB molecules and forms a $p$-doped layer. Furthermore, theoretical modeling was used to explain the current-voltage characteristics using these materials’ physical parameters independently extracted by time-of-flight (TOF) technique using method reported in Ref. [6].

Fig. 5.1 Schematic diagram of $p$-type doping of an organic matrix (MTDATA) with a $p$-type dopant (F_4-TCNQ).

5.3 Experiment

Simple double layer hole-only devices were used for this study. The devices have a general structure: substrate/anode/organic layer-I /organic layer-II /cathode. Pre-patterned indium tin oxide (ITO) on glass was used as the anode. The ITO substrate was cleaned by acetone then methanol in ultra-sonic baths followed by uv-ozone treatment. Two hole transporting materials 4,4’,4’’-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine
Chapter 5 - Engineering carrier transport across organic heterojunctions by interface doping

(MTDATA, from Syntec GmbH) and N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’diamine (NPB, from H. W. Sands) were used to form the various types of organic heterojunctions. The highest-occupied molecular orbital (HOMO) of MTDATA and NPB are 5.1 eV and 5.4 eV, respectively.\textsuperscript{[7,8]} Therefore there exists a hole injection barrier of 0.3 eV from MTDATA to NPB. The organic films were thermally evaporated on top of the ITO substrate in vacuum with a base pressure of \(10^{-7}\) Torr. It was then followed by evaporating silver (Ag) as the top contacting cathode. Due to a large energy difference between the work function of Ag (4.3 eV) and the lowest unoccupied molecular orbital (LUMO) (< 2.5 eV) of the organic materials, Ag cathode is restricted from injecting electrons into these devices. In some devices, a \(p\)-doped interlayer was inserted at the OOI. The \(p\)-doped interlayer was achieved by co-evaporation of host (MTDATA or NPB) and \(p\)-type dopant, tetra-fluorotetracyanoquinodimethane (F\(_4\)-TCNQ, 99.9% purity, from Lumtec. Co. Ltd). The doping ratio (in molar %) was controlled by independently monitoring the evaporation rates of the host and the dopant. The device structures used for this study are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Device</th>
<th>Organic layer I</th>
<th>Interlayer</th>
<th>Organic layer II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MTDATA (236 nm) /</td>
<td>-----</td>
<td>/ NPB (82 nm)</td>
</tr>
<tr>
<td>B</td>
<td>MTDATA (236 nm) /</td>
<td>NPB:F(_4)-TCNQ (2 nm, 10%)</td>
<td>/ NPB (80 nm)</td>
</tr>
<tr>
<td>C</td>
<td>MTDATA (234 nm) /</td>
<td>MTDATA:F(_4)-TCNQ (2 nm, 10%)</td>
<td>/ NPB (82 nm)</td>
</tr>
<tr>
<td>D</td>
<td>MTDATA (234 nm) /</td>
<td>MTDATA:F(_4)-TCNQ (2 nm, 15%)</td>
<td>/ NPB (82 nm)</td>
</tr>
<tr>
<td>E</td>
<td>MTDATA (236 nm) /</td>
<td>-----</td>
<td>/ -----</td>
</tr>
</tbody>
</table>

Table 5.1 Structures of various test devices used in this work. All double layer devices have the same total thickness of organic films (318 nm). For device B, C and D, there is a thin (2 nm) \(p\)-doped (10 \% or 15 \% molar ratio) interlayer.

For time-of-flight (TOF) measurements, thick film (3-4 \(\mu\)m) of MTDATA or NPB was thermally evaporated onto ITO coated glass substrate. Semitransparent aluminum (Al) electrode was used as the positively bias electrode. The organic film was photoexcited by a frequency-tripled Nd:YAG pulsed laser (\(\lambda \approx 355\) nm, pulsed width = 6 ns). A dc power supply (Stanford PS310) was used to provide an external voltage to extract photogenerated holes. The
photocurrent was monitored by a digital oscilloscope (Agilent 54622A) through a sensing resistor in series contact with the sample. Current density-voltage ($J-V$) measurements were carried out using a KEITHLEY 236 meter. The active area for all samples was 0.16 cm$^2$. The thicknesses of the organic films were measured by a profilometer. For all measurements, $J-V$ and TOF, the samples were mounted inside a cryostat in vacuum with a base pressure of $10^{-6}$ Torr at 300 K.

5.4 Results and discussion

5.4.1 Injection limited at OOI

To demonstrate the effect of energy barrier on carrier injection at an organic heterojunction, Fig. 5.2 shows $J-V$ characteristics (open squares) measured from a single layer hole-only device ITO/MTDATA (236 nm)/Ag, or device E.

Fig. 5.2 Experimental current-density vs voltage ($J-V$) characteristics of device E: ITO / MTDATA (236 nm) /Ag (□), and device A: ITO / MTDATA (236 nm) / NPB (82 nm)/ Ag (■). The solid line is the SCLC model calculated based on device E. The data (+) are the time-domain numerically simulated results based on device E. The data (×) are the time-domain numerically simulated results of the double layer device A, assuming no transport barrier at the organic-organic interface (OOI).
Chapter 5 - Engineering carrier transport across organic heterojunctions by interface doping

The solid line is a theoretical $J$-$V$ curve calculated based on the trap-free space-charge-limited current (SCLC) model with field dependent mobility\[9\]

$$J_{SCLC} = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \exp(0.89 \beta \sqrt{E} \frac{V^2}{L^2})$$

where $\varepsilon_r = 3$ is the relatively permittivity and is obtained by measuring the device capacitance, $\varepsilon_0$ is the absolute permittivity, $E$ is the applied electric field, $V$ is the applied voltage bias and $L$ is the organic film thickness. The zero field hole mobility $\mu_0 = 1.28 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ and field dependent coefficient $\beta = 1.88 \times 10^{-3}$ (V/cm)$^{-1/2}$ were obtained independently by TOF technique. The excellent agreement between the measured and calculated current densities proves that the conduction is dominated by the bulk organic film and contact resistance between ITO and MTDATA is negligible.\[7,10\] The results have been further verified with differential time-domain numerical simulation using a method reported by Ref. [11]. Thus zero contact resistance was used as the boundary condition. The simulated steady current densities were obtained at different bias voltages (symbols (+)). The measured, calculated and simulated results are all in excellent agreement with each other.

The measured $J$-$V$ characteristics of a double layer device ITO / MTDATA (236 nm) / NPB (82 nm) / Ag (filled square), device A, is also shown in Fig. 5.2. By using TOF technique, $\mu_0$ and $\beta$ of NPB were found to be $5.27 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ and $1.80 \times 10^{-3}$ (V/cm)$^{-1/2}$, respectively. Although the hole mobility of NPB is more than one order of magnitude higher than that of MTDATA, the measured $J$ of the double layer device is much lower than that of the single layer device. This is attributed to a hole transport barrier (0.3 eV) at the MTDATA / NPB interface. In order to illustrate the effect of transport barrier at the OOI, the maximum attainable current in the double layer device was simulated (shown in cross $\times$ in Fig. 5.2) using time-domain simulation method (Ref. [11]) by assuming no barrier at the OOI. Briefly in the simulation, the holes were injected at the anode with no resistance, and then drifted along the applied electric field moving through MTDATA then through NPB. In this case, the current is only limited by the space charges inside the organic layers. By comparing the simulation results with the measured $J$,
especially at low field region, it is clear that the current in the double layer device is significantly limited by the presence of a potential barrier at the OOI.

### 5.4.2 Engineering carrier injection by interface doping at OOI

Fig. 5.3 shows $J-V$ characteristics of double layer devices with inclusion of various types of $p$-doped interlayers. In device B, a thin layer of NPB:F$_4$-TCNQ (2 nm) is placed between MTDATA and NPB. It is found that the measured $J$ (filled circles) is significantly increased upon the insertion of the NPB:F$_4$-TCNQ interlayer. However, when the interlayer is replaced by MTDATA:F$_4$-TCNQ (2 nm) as in device C, the measured $J$ (filled upward triangles) is dramatically reduced. In device D, the measured $J$ (filled downward triangles) is found to be further suppressed by increasing the doping ratio to 15%.

![Fig. 5.3 Current-density voltage ($J-V$) characteristics of various double layer devices: device A (■) without an interlayer; device B (●) with an interlayer NPB:F$_4$-TCNQ (2 nm, 10%); device C (▲) with an interlayer MTDATA:F$_4$-TCNQ (2 nm, 10%); device D (▼) with an interlayer MTDATA:F$_4$-TCNQ (2 nm, 15%). The data (×) are the time-domain numerically simulated results based on device A, assuming no transport barrier at the organic-organic interface (OOI).](image-url)
5.4.3 Energy alignment at OOI with doped inter-layer

It is well known that doping can effectively increase the charge-carrier concentration in organic semiconductors.\textsuperscript{[12,13]} Furthermore, it has also been demonstrated that doping can induce energy level realignment at the OOI.\textsuperscript{[14,15]} Devices B, C and D all contain a heavily $p$-doped interlayer at the junction. Despite the fact that the hole concentration in the $p$-doped interlayer is much higher than those in the undoped matrix, the measured current densities of devices C and D are much lower than the undoped device A. Therefore, it is reasonable to assume that the effective injection barrier is increased by the energy level realignment at the OOI due to doping. The schematic energy diagrams of the double layer devices are depicted in Fig 5.4. In device A, the hole injection barrier is attributed to the HOMO energy levels difference (0.3 eV) between MTDATA and NPB, and the device hole current mainly determined by the efficiency of hole injection across MTDATA/NPB heterojunction. In the following discussion, effective p-type doping of NPB and MTDATA has been assumed. The p-type doping induced change in the Fermi level and carrier concentration have been reported.\textsuperscript{[12,13,16]} In device B, the $p$-type-doping reduces the energy gap between Fermi level and HOMO of NPB inside the interlayer. As a result, the HOMO offset at the NPB/NPB:F$_4$-TCNQ interlayer is effectively reduced and consequently transport barrier at the MTDATA/NPB is now reduced. In this case, the interlayer functions as an intermediate energy level that facilitates hole injection into NPB. In device C or D, similarly, the energy gap between Fermi level and HOMO of the MTDATA:F$_4$-TCNQ interlayer is reduced by $p$-doping. In this case, however, this uplifting in the HOMO energy level leads to an increase in the hole injection barrier. The injected holes from the MTDATA will be initially trapped inside the interlayer, and then these carriers will have to overcome a larger energy barrier in order to be injected from the interlayer into NPB. As a result, the current density in device C and D is much reduced when compared with undoped device A.
Fig 5.4 Schematic diagrams of energy level alignment at the various organic-organic interfaces.
5.5 Conclusion

In conclusion, we have shown, in both experiment and theoretical simulation, that charge transport in double layer device is limited by a potential barrier at the organic-organic heterojunction. We have demonstrated that this transport barrier at the organic heterojunction can be effectively modulated by introducing a thin (2 nm) $p$-doped interlayer at the heterojunction. It is found that charge transport across MTDATA/NPB heterojunction can be easily modulated by inclusion of a doped interlayer at the junction; NPB:F$_4$-TCNQ interlayer for increasing hole current or MTDATA:F$_4$-TCNQ interlayer for decreasing hole current. A change in the quasi Fermi level upon doping together with energy level alignment at the heterojunctions were proposed as the underlying physics principle to explain the observed phenomena. The junction doping technique provides an promising alternative process pathway to module electron or hole current in organic electronic devices using commonly available organic semiconductor molecules.
5.6 References


Chapter 6  Impact of energy offset at organic heterojunctions on organic light-emitting diodes (OLEDs)

6.1  Abstract

The impact of energy offset at organic heterojunctions on organic light-emitting diodes (OLEDs) is investigated by interface doping. This technique provides a means to modulate the charge carrier transport across an organic heterojunction without interfering with the bulk transport properties. It is shown that a thin (2 nm) $p$-type doped interlayer at the hole injection layer (HTL) / hole transporting layer (HTL) interface can effectively increase the device current. As a consequence, the power efficiency of a device is increased by up to 24%. It is found that unlike charge carrier injection at metal-organic (MO) interfaces, an energy barrier height of 0.3 eV will still limit the charge carrier transport across organic-organic interfaces (OOIs). This is explained by the charge carrier distribution in a Gaussian density-of-state (DOS) in disordered electronic materials. The charge carriers mean energy in donor molecules are localized away from the centre of Gaussian DOS and this makes charge carrier injection less efficient at OOI.
6.2 Introduction to multilayer OLEDs

Since the discovery of the first highly efficient organic heterojunction light-emitting diode (OLED) by Tang et al in the 1980s,[1] extensive research has been conducted on organic semiconductors and devices. Although the OLED is now a contender in flat-panel display market, higher device efficiency is desired, especially for lighting applications. The general structure of an OLED consists of multi-layers of organic thin films sandwiched by two electrodes, which include the anode / hole injection layer (HIL) / hole transporting layer (HTL) / electro-luminescence layer (EL) / electron transporting layer or hole blocking layer (ETL or HBL) / cathode. In the past few decades, extensive research has been reported on the electronic properties of metal-organic (MO) interfaces. In order to have higher injection efficiency, the transporting site energy of organic materials must match the work function of electrodes. It has been shown that modifying the MO interfaces has a large impact on both device efficiency and stability.[2,3] Furthermore it has also been analytically and experimentally demonstrated that quasi-Ohmic contacts can be achieved when the energy barrier at MO interfaces is less than 0.3 eV.[4]

Compared to a MO interface, the issue of charge carrier transport at organic-organic interfaces (OOIs) has been overlooked. Arkhipov et al. has proposed an analytical model to describe charge carrier hopping at the interface separating two disorderd organic materials.[5] It was shown that the majority of interfacial jumps are roundtrip ones and only very few jumps lead to true charge injection. As a result, carrier recombination at OOI is much higher than that predicted by conventional Langevin theory.[6,7] The OOI model is further justified by Woudenbergh et al with experimental results of a polymeric heterojunction, poly-phenylene vinylene derivative (PPV) / poly(9,9-dioctylfluorene) (PFO).[8] It has been demonstrated that the polymeric heterojunction strongly limits the hole current due to an interface energy barrier. The current densities at a high electric field (>10^6 V/cm) are in agreement with the OOI model. However, the strong field dependence of the current densities in the lower field region must take into account the effect of charge carrier distribution in a Gaussian density-of-state (DOS) of PPV. Details of carrier injection at OOI have been discussed in Chapters 3 and 4.
In the present study, the impact of energy offset at organic heterojunctions on OLEDs is investigated by interface doping. The interface doping technique provides a means to modulate charge carrier transport at the OOI without changing its bulk properties.\cite{9} It will be shown that energy offsets at OOIs play an important role by limiting the current and lowering the power efficiency of OLEDs. Unlike the case of MO interface, where a quasi-Ohmic contact is formed when the energy barrier is less than 0.3 eV, it is found that such an energy barrier can still suppress carrier injection at an OOI. This issue will be discussed with the concept of carrier distribution in ordered organic materials.

### 6.3 Experiment

The OLEDs used for this study have a general structure of glass substrate / indium tin oxide (ITO) / hole injection layer (HIL) / hole transporting layer (HTL) / electro-luminance layer (EL) / hole blocking layer (HBL) / Lithium fluoride (LiF) / Aluminium (Al). 4,4’,4’’-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (MTDATA) was used as the HIL. N,N’-diphenyl-N,N’-bis(1-naphthyl)(1,1’-biphenyl)-4,4’ diamine (NPB) was used as the HTL. In order to investigate the impact of energy level offset at the organic heterojunctions on device performance, three different electro-luminance materials were chosen to fabricate the ELs. Their highest occupied molecular orbital (HOMO) energy levels vary from 5.4 eV to 5.8 eV. Aluminum tris(8-hydroxyquinoline) (Alq3) with a HOMO energy level equal to 5.7 eV was used in device A.\cite{10} Mes_{2}B(p-4,4’-biphenyl-NPh(1-naphthyl)) (BNPB) with a HOMO energy level equal to 5.4 eV was used in device B.\cite{11} 2,6-di(t-butyl)-9,10-di-(2-naphthyl)anthracene (TBADN) with a HOMO energy level equal to 5.8 eV was used in device C.\cite{12} In device B and C, there was a HBL 2,2’,2”-(1,3,5-phenylene) tris(1-phenyl-1H-benzimidazole) (TPBI). The pre-patterned ITO anode was cleaned by a series of ultrasonic baths with deionized water, methanol and acetone, and followed by uv-ozone treatment. The organic layers were sequentially deposited on top of the ITO in a vacuum chamber with a base pressure of $10^{-8}$ Torr. It was then followed by depositing of LiF (1 nm) and Al (100nm) to form the cathode contact. In some of the devices, a thin $p$-doped interlayer (2 nm) was inserted at the MTDATA/NPB interface. The $p$-doped interlayer was achieved by coevaporation of NPB and a $p$-type dopant, tetra-

108
fluorotetracyanoquinodimethane (F_{4}-TCNQ). Details of the device structures are summarized in Table 6.1.

The devices were encapsulated before being removed from the vacuum chamber. The device characteristics were measured by a HP 4140B picoammeter and a Minolta LS-110 luminance meter.

<table>
<thead>
<tr>
<th>Devices</th>
<th>HIL (nm)</th>
<th>Interlayer (molar %, nm)</th>
<th>HTL (nm)</th>
<th>EL (nm)</th>
<th>HBL (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>------</td>
<td>----</td>
<td>A2</td>
<td>MTDATA  (40)</td>
<td>NPB:F_{4}TCNQ (6%, 2)</td>
</tr>
<tr>
<td>A3</td>
<td>MTDATA  (40)</td>
<td>NPB:F_{4}TCNQ (18%, 2)</td>
<td>A4</td>
<td>MTDATA  (40)</td>
<td>NPB:F_{4}TCNQ (50%, 2)</td>
</tr>
<tr>
<td>B1</td>
<td>------</td>
<td>----</td>
<td>B2</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (7%, 2)</td>
</tr>
<tr>
<td>B3</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (21%, 2)</td>
<td>B4</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (50%, 2)</td>
</tr>
<tr>
<td>C1</td>
<td>------</td>
<td>----</td>
<td>C2</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (10%, 2)</td>
</tr>
<tr>
<td>C3</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (17%, 2)</td>
<td>C4</td>
<td>MTDATA  (25)</td>
<td>NPB:F_{4}TCNQ (67%, 2)</td>
</tr>
</tbody>
</table>

Table 6.1 Structures of various test devices used in this study. In general, the devices consist of ITO / HIL / HTL / EL / HBL / LiF / Al. In some of the devices, there is a 2 nm p-type doped interlayer NPB:F_{4}TCNQ at the HIL / HTL interface.

### 6.4 Results and discussion

As shown in Fig. 6.1 the energy diagrams of the devices, the injected holes from the anode to the EL encounter energy barriers at the MTDATA/NPB and NPB/EL interfaces. Interface doping with different doping concentrations has been employed to modify the hole transport across the MTDATA/NPB interface. [9]
6.4.1 Organic-organic hole injection barrier in Alq3 devices

In device A, there is a 0.3 eV energy barrier for hole transport across both the MTDATA/NPB and NPB/Alq3 interfaces. As shown in Fig. 6.2(a), for devices A2, A3, and A4, the current densities are increased with a 2 nm NPB:F$_4$TCNQ interlayer at the MTDATA/NPB interface. At low and high electric field regions, the current densities can be increased by 3 and half orders of magnitude, respectively. This is consistent with the double layer device as reported earlier.$^{[9]}$ As depicted in Fig. 6.2(b), the luminance of the device is also increased by a half order of magnitude. As a result, the operating voltage is reduced by 2 V.
Fig. 6.2 (a) Current-density vs voltage ($J-V$) and (b) luminance vs voltage ($L-V$) characteristics of a series of device A. Device A1 without an interlayer; Device A2 with an interlayer NPB:F$_4$TCNQ (molar ratio 6%, 2 nm); Device A3 with an interlayer NPB:F$_4$TCNQ (molar ratio 18%, 2 nm); Device A4 with interlayer an NPB:F$_4$TCNQ (molar ratio 50%, 2 nm).

However, in Fig. 6.3, there is no change in the current efficiencies for all devices both with and without the interlayer. This can be attributed to the equal improvements of the current density and luminance as discussed before. It also indicates that the electron and hole densities in EL have equal improvement; otherwise the current efficiency will drop due to unbalance of carriers. On the other hand, as the operating voltage is reduced, the power efficiency is increased by approximately 22 % at 20 mA/cm$^2$. In device A, the energy barriers at the MTDATA/NPB and NPB/Alq3 interfaces are comparable. Therefore, reducing the contact resistance at the MTDATA/NPB interface has a notable effect on device performance. In this case, the potential drop across other MO or OO interfaces will be increased. Consequently, the number of carriers injected into Alq3 and therefore the efficiency are increased.
6.4.2 Organic-organic hole injection barrier in BNPB devices

In device B, a blue emitter BNPB was used to fabricate the EL. As shown in Fig. 6.1, the LUMO and HOMO energy levels of BNPB are comparable with those of NPB.\textsuperscript{111} Compared to device A that has two energy barriers for injected hole to EL, the number of holes at the BNPB layer in device B is only limited by the energy barrier at MTDATA/NPB interface. The $J$-$V$ and $L$-$V$ characteristics of the device are shown in Fig. 6.4(a) and (b), respectively. Both current and luminance are increased in devices B2, B3 and B4 with an NPB:F$_4$TCNQ interlayer.
Fig. 6.4 (a) Current-density vs voltage ($J-V$) and (b) luminance vs voltage ($L-V$) characteristics of a series of device B. Device B1 without an interlayer; Device B2 with an interlayer NPB:F4TCNQ (molar ratio 7%, 2 nm); Device B3 with an interlayer NPB:F4TCNQ (molar ratio 21%, 2 nm); Device B4 with interlayer an NPB:F4TCNQ (molar ratio 50%, 2 nm).

As shown in Fig. 6.5, the current and power efficiencies are increased by 15 % and 24 % at 20 mA/cm$^2$, respectively, in device B3. However, by further increasing the doping concentration, the current and power efficiencies are reduced as shown in device B4. This is mainly attributed to excess number of holes in the EL. Since the hole current in device B is only limited by the energy barrier at the MTDATA/NPB interface, applying an interface technique has more notable effect on device performance than device A.
Chapter 6 - Impact of energy offset at organic heterojunctions on organic light-emitting diodes (OLEDs)

Fig. 6.5 Current (open symbols) and power (close symbols) efficiencies of a series of device B. Device B1 without an interlayer; Device B2 with an interlayer NPB:F$_4$TCNQ (molar ratio 7%, 2 nm); Device B3 with an interlayer NPB:F$_4$TCNQ (molar ratio 21%, 2 nm); Device B4 with interlayer an NPB:F$_4$TCNQ (molar ratio 50%, 2 nm).

6.4.3 Organic-organic hole injection barrier in TBADN devices

In device C, the EL is fabricated with another blue emitter TBADN. The HOMO energy level of TBADN is about 5.8 eV, as shown in Fig. 6.1. The energy barrier for hole transport across the NPB/TBADN interface is 0.4 eV, which is 0.1 eV larger than that at the MTDATA/NPB interface. Fig. 6.6(a) and (b) show the $J$-$V$ and $L$-$V$ characteristics of the devices, respectively. Both current density and luminance are the same for the devices with and without the NPB:F$_4$TCNQ interlayer at MTDATA/NPB interface.
Fig. 6.6 (a) Current-density vs voltage ($J$-$V$) and (b) luminance vs voltage ($L$-$V$) characteristics of a series of device C. Device C1 without an interlayer; Device C2 with an interlayer NPB:F$_4$TCNQ (molar ratio 10%, 2 nm); Device C3 with an interlayer NPB:F$_4$TCNQ (molar ratio 17%, 2 nm); Device C4 with interlayer an NPB:F$_4$TCNQ (molar ratio 67%, 2 nm).

All devices have the same efficiencies as shown in Fig. 6.7. Although the contact resistance at the MTDATA/NPB interface is reduced in devices C2, C3 and C4, same device performance obtained in all devices indicates that the hole current is greatly limited by the 0.4 eV energy barrier at the NPB/TBADN interface.
We discuss the effect of the HOMO energy level distribution and alignment on hole transport at OOI. Unlike charge carrier injection at MO interfaces where carriers are injected from a well defined Fermi-surface, carriers being injected at OOI have an energy distribution due to the disordered nature of organic materials.\textsuperscript{[13]} Fig. 6.8 shows the energy diagrams for holes transport from ITO to MTDATA and to NPB, where the organic materials have a Gaussian DOS distribution for their HOMO energy levels. The variances $\sigma$ of the DOS are assumed to be 0.1 eV as commonly found in amorphous organic electronic materials.\textsuperscript{[13-16]} The energy barrier at the MO interface is generally the energy difference between the metal work function and the center of the organic DOS. At OOI, the energy barrier is the energy difference between their centers of the DOS. In this case, there is 0.3 eV energy barrier at both ITO/MTDATA and MTDATA/NPB interfaces. It has been proved that such a value of the energy barrier at ITO/MTDATA interface is negligible, consequently replacing a higher work function anode does not further increase the
device current. At this interface, due to the distribution of HOMO energy level in MTDATA, the tail of the DOS overlaps with the ITO work function. The holes in the ITO Fermi surface can effectively be injected into MTDATA. After the injection, the holes will through MTDATA and relax to a mean energy $<E_h>$. It has demonstrated by Monte Carlo simulation that in disordered semiconductors, $<E_h>$ is found to be $\sigma^2 / kT$ away from the centre of Gaussian DOS for low concentrations, and it moves closer to the centre at higher concentrations. As a result, compared to hole injection at ITO/MTDATA interface, holes transport from MTDATA to NPB have to overcome an additional energy barrier $<E_h>$. In our devices, it is believed that the NPB:F$_4$TCNQ interlayer provides an intermediate energy level to increase the overlapping of DOSs.

Fig. 6.8 A schematic of energy diagram for holes injection from ITO and transport through MTDATA to NPB. The DOS of HOMO energy levels of the organic materials have a Gaussian distribution. The variances $\sigma$ of the Gaussian DOS are assumed to be 0.1 eV. The open circles are the illustration of hole carriers. They have a mean energy $<E_h>$ away from the centre of the DOS.
6.5 Conclusion

In summary, it has been demonstrated that the interface doping technique can improve charge carrier transport across organic heterojunctions in OLEDs. The power efficiency of the BNPB blue OLED is increased by 24%. Unlike charge carrier injection at ITO/MTDATA interface, it is found that a 0.3 eV energy offset at MTDATA/NPB still limits the charge carrier transport. This is explained by considering a Gaussian distribution of the DOS in disordered semiconductors. The holes in ITO can effectively be injected into the tail of the DOS of MTDATA. As the injected holes in MTDATA relax to a mean energy $<E_h>$ that situated away from the centre of Gaussian DOS, the holes in MTDATA have to overcome $<E_h>$ in order to transport to NPB. This makes charge carrier injection at OOI less efficient than that in MO interface. Matching energy levels in organic electronic devices is significant for optimizing device efficiency.
6.6 References

Chapter 7 Charge-carrier transport in polymeric bulk-heterojunction device

7.1 Abstract

The electron transport properties in various poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) bulk heterojunction blend films, prepared by various process conditions, are investigated by admittance spectroscopy (AS) at various temperatures. It is found that the electron mobility and the dispersive transport behavior show a strong dependence on the blend microstructure; less organized blends have orders of magnitude reduction in the mobility and a much more dispersive transport. Using the Gaussian disordered model (GDM), it is found that the difference of the energetic disorder of the density-of-states (DOS) between blends plays a significant role in the observed phenomena. It is proposed that the difference in the energetic disorder is due to different effective area of interfacial dipole at the P3HT/PCBM heterojunctions in the various blend films.
### 7.2 Introduction

The electron donor poly(3-hexylthiophene) (P3HT) and the electron acceptor [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) are the most promising materials in making low-cost organic photovoltaic cells by various solution processing technologies. More importantly, they are the template for the design of new materials. Using P3HT:PCBM blend, reproducible power conversion efficiencies of about 5% have been reported recently.\(^1\)\(^-\)\(^3\) This blend consists of an inter-penetrating network of donors and acceptors, forming bulk heterojunctions that effectively dissociate the photo-induced excitons. In order to further increase the efficiency with these solution-processible bulk-heterojunction solar cells, much effort is required to understand the corresponding impact of the interactions between the polymer donor and the fullerene derivative acceptor in such blends.

![J-V characteristics of devices with different growth rates of P3HT:PCBM blend. The power conversion efficiencies for a slow and a fast growth film under AM 1.5G solar irradiation (100 mW/cm²) are 4.6% and 2.6% respectively.](image)

It is well-known that the efficiency of the bulk-heterojunction solar cells is highly sensitive to the nanoscale organization of the bulk-heterojunction active layer, as shown in Fig. 7.1.\(^2\)\(^,\)\(^4\)\(^,\)\(^5\) Therefore, the strategy used to cast the active layer is critical. During the casting of the
active layer, the transition from liquid to solid is first accompanied by the self-organization of the polymer followed by the phase segregation of the individual materials in the blend. As shown in , the degree of phase segregation is sensitive to the thermal treating after casting the active layer. By controlling the growth rate of the active layer, one can control the domain size of the individual material and the resulting nanoscale organization of the active layer. A high degree of ordering obtained from a slow growth of the active layer is necessarily the main contribution to the observed high charge-carrier mobility in bulk-heterojunction systems.\[^{6-8}\]

![Fig. 7.2 TEM images of P3HT:PCBM film bulk morphology before thermal annealing (a), after thermal annealing at 150\(^\circ\)C for 30 minutes (b), and after thermal annealing at 150\(^\circ\)C for 2 hrs (c). Adapted from Ref. [1].](image)

Recently, it has been observed that a spontaneous transfer of a negative charge from P3HT to C\(_{60}\) in bilayer structure forms an interface dipole.\[^{9}\] Similarly, in P3HT:PCBM bulk-heterojunctions, there are numerous interfaces between the individual materials. It can be deduced that the presence of possible dipoles at these numerous interfaces will alter the charge-carrier transport properties in the blend film.

In this Chapter, the electron transport properties in various P3HT:PCBM blends as a function of the film microstructure will be discussed. Admittance spectroscopy (AS), a powerful tool for probing the charge carrier dynamics, is employed to extract the electron mobility at
various temperatures and to understand the physical mechanism for electron transport in the bulk-heterojunction thin films.

### 7.3 Experiment

The samples fabricated in this study consist of a single active layer of P3HT:PCBM (1:1, wt %) sandwiched between an anode (Al, 70nm) and a cathode (Mg:Ag, 10:1, 50 nm) on glass substrates. The cathode was further covered by 50 nm of Ag used as capping layer. The metal electrodes were thermally evaporated in vacuum at a base pressure of $10^{-7}$ Torr. The active layers were prepared by spin-coating the blend solution in dichlorobenzene onto the Al electrode. The organization in the active layer was controlled by varying the growth rate of the active layer. Control of the growth rate was achieved by controlling the solution concentration, spinning speed and thermal treatment of the active layer after spin-coating. Details of the active layer preparation conditions are summarized in TABLE I. Samples A, B and C had the same solution concentration and spinning condition, but different thermal treatments. The growth rate of the active layer was decreased from sample A to sample C. In order to further decrease the growth rate in sample D while maintaining similar film thickness, a diluted solution was used with a smaller spinning speed. As a result, the growth rate in the different samples was in the order of sample A > B > C > D. The thicknesses of the active layer were measured by a profilometer. The electron mobility in P3HT:PCBM thin films was characterized by AS with an HP 4284A LRC meter. For AS measurement, negative biases were applied at the Mg:Ag electrode. Details of the principle and the experiment setup of AS have been discussed in Chapter 2. Although electron injection from Mg:Ag into P3HT is possible, the injected electrons will be rapidly transferred to the PCBM molecules which has a lower lowest-unoccupied molecular orbital (LUMO) energy level. Prior to the charge carrier mobility measurements, any absorbed ambient effect during sample transfer or residual solvent was eliminated by moderately heating the sample at 50 °C for 24 hours inside a temperature regulated cryostat with a base pressure of $10^{-6}$ Torr.
Table 7.1 Summary of preparation condition of the P3HT:PCBM (1:1 wt%) blends

<table>
<thead>
<tr>
<th>sample</th>
<th>soln concentration</th>
<th>spinning condition</th>
<th>thermal treatment</th>
<th>thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>112 mg / mL</td>
<td>1000 rpm (60s)</td>
<td>baked 200°C (30mins)</td>
<td>1.20 μm</td>
</tr>
<tr>
<td>B</td>
<td>112 mg / mL</td>
<td>1000 rpm (60s)</td>
<td>baked 100°C (30mins)</td>
<td>1.16 μm</td>
</tr>
<tr>
<td>C</td>
<td>112 mg / mL</td>
<td>1000 rpm (60s)</td>
<td>naturally dried for 24 hrs</td>
<td>1.16 μm</td>
</tr>
<tr>
<td>D</td>
<td>42.5 mg / mL</td>
<td>300 rpm (60s)</td>
<td>naturally dried for 24 hrs</td>
<td>1.50 μm</td>
</tr>
</tbody>
</table>

7.4 Results and discussion

7.4.1 Electron mobility measured by admittance spectroscopy

Fig. 7.3 shows the typical capacitance vs frequency characteristics of the different samples measured by AS. A minimum capacitance $C_{\text{min}}$ at a certain frequency is found in samples B, C, and D. This feature corresponds to the space charge effect in the bulk of the material.\cite{10,11} It also proves that a quasi-Ohmic contact is formed at the Mg:Ag/PCBM interface.\cite{12} The electron mobility $\mu_e$ can be effectively extracted from the measured capacitance. Briefly, if $C_{\text{min}}$ occurs at higher frequency it indicates a higher charge carrier mobility. Therefore, $\mu_e$ increases from sample B to sample D, corresponding to a fast and a slow growth rate respectively. Moreover, the degree of charge carrier mobility dispersion can be revealed by considering the ratio of $C_{\text{min}}/C_{\text{geo}}$, where $C_{\text{geo}}$ is the geometrical capacitance of the sample. In the case of non-dispersive transport, $C_{\text{min}}/C_{\text{geo}} = 0.75$. \cite{10,11} The value of $C_{\text{min}}/C_{\text{geo}}$ increases for more dispersive transport. For highly dispersive transport the capacitance minimum vanishes. As shown in Fig. 7.3, there is no capacitance minimum observed in sample A. The value of $C_{\text{min}}/C_{\text{geo}}$ deceases from 0.98 in sample B to 0.92 in sample D, which suggests that the electron transport becomes less dispersive as the growth rate of the active layer decreases. It is worth considering that the dispersive transport behavior can originate from the presence of trap states, or from the disordered properties of the transporting sites, both positional and energetic. However, since the samples are prepared with the same batch of materials, the variation of bulk trap states in different samples is safely excluded. Furthermore, it has been demonstrated that a slower growth rate of the active layer leads to a more ordered P3HT:PCBM film.\cite{3,5} Therefore,
the difference of the disordered properties between samples is attributed to the variation of the observed electron transport behavior.

Fig. 7.3 Measured capacitance vs frequency characteristics of sample (a) A at $T = 263$ K and $F = 2.0 \times 10^5$ V/cm; (b) B at $T = 263$ K and $F = 2.0 \times 10^7$ V/cm; (c) C at $T = 263$ K and $F = 2.0 \times 10^5$ V/cm; (d) D at $T = 270$ K and $F = 1.3 \times 10^4$ V/cm. The capacitance $C$ is normalized to the geometrical capacitance $C_{\text{geo}}$ of individual sample.
7.4.2 Analysis with the Gaussian disordered model (GDM)

The electron mobilities of sample B, C, and D measured by AS at various temperatures are shown in Fig. 7.4. In general, the mobilities follow the Poole-Frenkel type of electric field $F$ dependence $\mu_e \propto \exp(\beta F^{1/2})$, where $\beta$ is the field dependence coefficient.

Fig. 7.4 Measured electron mobility $\mu_e$ vs square root of applied electric field $F^{1/2}$ of sample (a) B, (b) C, and (c) D. The solid lines are the best fit of the data to the Poole-Frenkel type of electric field $F$ dependence $\mu_e \propto \exp(\beta F^{1/2})$.

It is found that $\mu_e$ in sample B, which has the fastest growth rate among all samples, has the highest temperature and electric field dependence. From the measured $\mu_e$, the disordered properties of the electron transporting site in PCBM can be revealed by analyzing the data with the Gaussian disordered model (GDM):$^{[13]}$
where $\mu_{\text{inf}}$ is a prefactor, $\sigma$ is the energetic disorder parameter that can be understood as the width of the Gaussian density-of-state (DOS), $\Sigma$ is the positional disorder parameter, and $C$ is a constant. By extrapolating the measured $\mu_e$ to zero field, $\sigma$ can be obtained from the plot of the zero field mobility $\mu_{0,T}$ vs $1/T^2$ as shown in Fig. 7.5a. On the other hand, $\Sigma$ can be extracted by plotting $\beta$ vs $1/T^2$ as shown in Fig. 7.5b. The extracted disorder parameters for different samples are summarized in Table 7.2.

Fig. 7.5 (a) The zero-field mobility $\mu_{0,T}$ extrapolated from the measured $\mu_e$ in Fig. 7.4 vs $1 / T^2$ of different samples. (b) The corresponding field dependence coefficient $\beta$ vs $1 / T^2$. The solid lines are the best fits to the data at temperature $T > 220K$. 
Table 7.2 Extracted GDM parameters of different samples from the measured electron mobility $\mu_e$ in Fig. 7.5.

As expected, the largest positional disorder parameter $\Sigma$ is found in sample B and the smallest in sample D. A more organized film of P3HT:PCBM blend can be formed from a slower growth rate of the active layer. Although it is generally believed that such improved ordering is only a result of the increase of crystalline packing of P3HT, there is no doubt that more PCBM will also pack together to retain a constant effective volume. This has been proved by the observed phase segregation between P3HT and PCBM measured by AFM.[4] Surprisingly, there is a large difference in the energetic disorder parameter $\sigma$ between different samples. As depicted in Eq. (7.1), the low field mobility is mainly determined by the $\mu_{\text{inf}}$ and $\sigma$. Taking sample B and D as an example, $\mu_{\text{inf}}$ in sample B is about one order of magnitude lower than that in sample D. However, a large value of $\sigma$ in sample B attributes to more than two orders of magnitude reduction in mobility. Extensive experimental studies on carrier transport properties in polymers doped with hole-transporting molecules have been reported by Borsenberger and co-workers, with detailed discussion of $\mu_{\text{inf}}$ and $\sigma$ in different polymer hosts.[14,15] The prefactor $\mu_{\text{inf}}$ depends on the inter-site distance $R$ and wave-function decay constant $\alpha$ as:

$$\mu_{\text{inf}} \propto R^2 \exp\left( -2\alpha R \right)$$

(7.2)

Owning to the energy difference of the transporting sites in P3HT and PCBM, the wave-function overlap is larger between PCBM molecules. Moreover, in a less organized blend that with smaller degree of phase segregation, more PCBM molecules are mixed with the P3HT polymers which increases the inter-molecular distance. As a result, a smaller $\alpha$ and a larger $R$ in less organized blend attribute to a smaller $\mu_{\text{inf}}$. Despite this spatial effect, it is found that the increased
energetic disorder of PCBM in the less organized blend plays an important role for the reduction in electron mobility.

### 7.4.3 Impact of dipole at P3HT/PCBM interface on electron transport

The variation of $\sigma$ in different blend films can be explained by considering the presence of interface dipoles between P3HT and PCBM. The dipolar effect on the energy profile of the DOS and the charge-carrier transport in a disordered media was originally proposed by Dieckmann and Young under the framework of the GDM.\textsuperscript{[16,17]} The energetic disorder parameter takes into account both the dipole-induced disorder $\sigma_d$ and the van der Waals interactions between molecules $\sigma_{vdw}$, i.e.:

$$\sigma^2 = \sigma_d^2 + \sigma_{vdw}^2$$  \hspace{1cm} (7.3)

The additional $\sigma_d$ broadens the Gaussian DOS which depends on the amount and the orientation of the dipole moments in the system.\textsuperscript{[17]} It has been recently reported that there exists an interface dipole between P3HT and C\textsubscript{60} by photoemission study.\textsuperscript{[9]} Assuming the magnitude of the dipole at the P3HT/PCBM interface in different blend films are comparable, it is proposed that the origin of the difference of $\sigma_d$ between samples with slower and faster growth rate of the active layer is due to the variation of the interfacial area of the heterojunctions as illustrated Fig. 4.
Fig. 7.6 An illustration of the phase segregation of P3HT:PCBM for slow and fast growth rate of the active layer. Interface dipoles are formed at P3HT/PCBM heterojunctions.

Less phase segregation between P3HT and PCBM is expected for the film grown faster. The area of the P3HT/PCBM interface, and therefore the number of interface dipoles are larger inside this blend. Moreover, as the PCBM phase is smaller, the injected electrons have higher probability to experience the interface dipole effect during the multi-directional hopping process. This attributes to a larger overall energetic disorder $\sigma$ for the sample having a faster growth rate of the active layer. A larger $\sigma$ reduces the electron mobility and results in much more dispersive transport behavior. In other words, in the absence of dipoles at the P3HT/PCBM interface, the difference in charge carrier mobility between samples are mainly determined by the prefactor $\mu_{inf}$ and the positional disorder parameter $\Sigma$, which depends on the degree of the self-organization of samples. However, the presence of dipoles at the P3HT/PCBM interface additionally increases the energetic disorder parameter $\sigma$ which further reduces the charge carrier mobility. The contribution of the dipole disorder $\sigma_d$ also depends on the degree of the self-organization of the samples; a larger $\sigma_d$ is expected in less organized blends that have larger P3HT/PCBM interface area.
7.5 Conclusion

In conclusion, the electron transport properties in P3HT:PCBM (1:1) blend films have been studied by admittance spectroscopy at various temperatures. It is found that both the electron mobility and the dispersive transport behavior depend strongly on the growth rate of the active layer. According to the results of the measured electron mobility of different samples at various temperatures, the electron mobility is mainly determined by the variation of the energetic disorder, rather than by the spatial distribution of the transporting sites in PCBM. This is proposed to be a result of the variation of the induced-dipole disorder at the P3HT/PCBM interfaces within the blend films. A faster growth rate with less phase segregation between P3HT and PCBM leads to larger effective area of interfacial dipole at the P3HT/PCBM heterojunctions which impede electron transport in the blend films by increasing the energetic disorder of the density-of-states.
7.6 References

Chapter 8  Conclusions and Future Work

8.1  Conclusions

This thesis reports on research progress in carrier injection and transport across organic heterojunctions (OHs). A theoretical model of carrier injection across an OH has been proposed to explain several new experimental findings. The model has been validated against measurements of a series of single carrier OH devices at various applied electric field and temperatures. The impact OH on OLED performance is also demonstrated. The major conclusions of the thesis are summarized as follow:

In Chapter 3, an injection model for OHs which includes the distribution of carriers at the injecting side of the interface is presented. This model shows that the main contribution to the injection current is from carriers at the peak of the Gaussian density-of-states (DOS) rather than at the Fermi level. In addition, charge carrier dependent barrier height, $\phi$, is proposed based on energy level re-alignment of the Fermi level. The model is verified by the excellent agreement with the experimental results of the current density – voltage ($J-V$) characteristics of an OH device for various temperatures over a wide range of electrical field. The results show that dynamic change in carrier concentration and DOS energy alignment at the OH play significant roles in the performance of organic heterojunction devices.

In Chapter 4, an escape probability function, $w_{esc}$, based on the total hopping frequencies at both sides of the organic heterojunction is formulated. It is shown that the injection current at low temperature is greatly increased and pinned by an extremely low density ($10^{10}$ cm$^{-3}$) of deep trap states. As a result, the injection current across a heterojunction with a larger injection barrier has a smaller temperature dependence. The calculation results are in good agreement with the experimental results of heterojunction devices with barrier heights ranging from 0.4 eV – 1.0 eV.
It is also demonstrated that the carrier mobility in a single layer device shows similar temperature dependence. This strongly supports the view that the small number of deep trap states originate from the bulk material instead of only from the interface. This study also suggests that, in the presence of the deep trap states, simply extracting the barrier height from the Arrhenius plot is inappropriate.

In Chapter 5, both experiment and theoretical simulation, show that charge transport in a double layer device is limited by a potential barrier at the organic-organic heterojunction. It is demonstrated that the injection barrier at the OH can be effectively modulated by introducing a thin (2 nm) $p$-doped interlayer at the heterojunction. Carrier injection across MTDATA/NPB heterojunction can be easily modulated by inclusion of a doped interlayer at the junction: a NPB:F$_4$-TCNQ interlayer for increasing hole current or a MTDATA:F$_4$-TCNQ interlayer for decreasing hole current. A change in the quasi Fermi level upon doping together with energy level alignment at the heterojunctions were proposed as the underlying physics principles to explain the observed phenomena. The junction doping technique provides a promising alternative pathway to modulate electron or hole current in organic electronic devices using commonly available organic semiconductor molecules.

In Chapter 6, interface doping is demonstrated as an alternative engineering way to enhance charge carrier injection across organic heterojunctions in OLEDs. The power efficiency of the BNPB blue OLED is increased by 24% through interface doping to eliminate the heterojunction barrier. Unlike charge carrier injection at ITO/MTDATA interface, it is found that a 0.3 eV energy offset at MTDATA/NPB still limits the charge carrier transport. This is explained by considering a Gaussian distribution of the DOS in disordered semiconductors. The holes in ITO can effectively be injected into the tail of the DOS of MTDATA. As the injected holes in MTDATA relax to a mean energy $<E_h>$ that is situated away from the centre of the Gaussian DOS, the holes in MTDATA have to overcome $<E_h>$ in order to transport to NPB. This makes charge carrier injection at an OOI less efficient than that at a MO interface. Matching energy levels in organic electronic devices is significant for optimizing device efficiency.
In Chapter 7, the electron transport properties in P3HT:PCBM (1:1) blend films are studied by using admittance spectroscopy at various temperatures. It is found that the electron mobility and the dispersive transport behavior depend strongly on the growth rate of the blend films. According to the results of the measured electron mobility of different samples at various temperatures, the electron mobility is mainly determined by the variation of the energetic disorder, rather than by the spatial distribution of the transporting sites in PCBM. This is explained as a result of the variation of the induced-dipole disorder at the P3HT/PCBM interfaces within the blend films. A faster growth rate with less phase segregation between P3HT and PCBM leads to larger effective area of interfacial dipoles at the P3HT/PCBM heterojunctions, and thus the electron transport in the blend films is decreased by the increased energetic disorder of the density-of-states.

8.2 Future Work

Chapter 3 shows that the carrier concentration at the organic heterojunction can be extracted by a steady state simulation. Ultimately, the carrier concentration can be obtained experimentally by the capacitance-voltage method as developed for the heterojunctions in inorganic semiconductors.\cite{1} Therefore, extracting barrier height and calculating the injection current at the organic heterojunctions can be done without the need of knowing the carrier mobility of each material.

In Chapter 4, the measured carrier mobility of a single carrier device is shown (Fig. 4.14) to have a large discrepancy with the model proposed by Arkhipov \textit{et al.} at low temperature. It is believed that the measured temperature dependence of the carrier mobility is a common feature in organic semiconductors as has been reported by several groups.\cite{2,3} The most critical reason for the discrepancy is the formulation of the effective transport energy \( E_{tr} \) which is assumed that the most possible jumps are energetically upward.\cite{4} However, downward jumps may be dominated, especially the thermal energy is not enough for upward jump or there is a large energy barrier. This is already demonstrated by considering the total hopping frequency and
available hopping sites at both sides of the interface in the studies in Chapter 4. This suggests that the formulation of the effective transport energy $E_{tr}$ has to be revised.

In addition, shown in Chapter 7, the effect of heterojunction dipoles on electron transport in a bulk heterojunction (P3HT:PCBM) film is presented. More detailed study on such effect can be conducted by replacing P3HT with another “inert” polymer (e.g. polycarbonate (PC)). Therefore, there should be an absence of dipole effect in the PC:PCBM system, and the dipole effect on carrier transport can be more clearly differentiated. Furthermore, it is also interesting to investigate the hole transporting properties of the P3HT:PCBM blend. This information should be useful for understanding the improved performance of the OPV cells.

### 8.3 References

Appendix A-  Experimental results of carrier mobility measured by time-of-flight (TOF) technique

A.1  Average hole mobility of MTDATA

Device structure: ITO / MTDATA (3.00 μm) /Al (30 nm)

![Graph showing field dependent μ dc of MTDATA extracted by TOF vs the square root of the applied electric field F^1/2 at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.]

Fig. A.1 The field dependent $\mu_{dc}$ of MTDATA extracted by TOF vs the square root of the applied electric field $F^{1/2}$ at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.
Fig. A.2 (a) The zero field mobility $\mu_{0,T}$ vs $1/T^2$; (b) the corresponding field dependent $\beta$ vs $1/T^2$. The energetic $\sigma$ and the positional $\Sigma$ disorder parameters of MTDATA can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.
A.2 Average hole mobility of NPB

Device Structure: ITO / NPB (3.5 \( \mu \)m) /Al (30nm)

![Graph showing the field-dependent \( \mu_{dc} \) of NPB extracted by TOF vs the square root of the applied electric field \( F^{1/2} \) at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.]

Fig. A.3 The field dependent \( \mu_{dc} \) of NPB extracted by TOF vs the square root of the applied electric field \( F^{1/2} \) at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.
Fig. A.4 (a) The zero field mobility $\mu_{0,T}$ vs $1/T^2$; (b) the corresponding field dependent $\beta$ vs $1/T^2$. The energetic $\sigma$ and the positional $\Sigma$ disorder parameters of NPB can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.
A.3 Average hole mobility of TPD

Device Structure: ITO / TPD (4.2 μm) /Al (30nm)

\[ \mu_{dc} (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) \]

\[ F^{1/2} (\text{V/cm})^{1/2} \]

\[ T = 278 \text{ K} \]

\[ F = 1.43 \times 10^5 \text{ V/cm} \]

Fig. A.5 The field dependent $\mu_{dc}$ of TPD extracted by TOF vs the square root of the applied electric field $F^{1/2}$ at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.
Fig. A.6 (a) The zero field mobility $\mu_{0,T}$ vs $1/T^2$; (b) the corresponding field dependent $\beta$ vs $1/T^2$. The energetic $\sigma$ and the positional $\Sigma$ disorder parameters of TPD can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.
A.4 Average hole mobility of TCTA

Device Structure: ITO / TCTA (4.5 μm) / Al (30nm)

Fig. A.7 The field dependent $\mu_{dc}$ of TCTA extracted by TOF vs the square root of the applied electric field $F^{1/2}$ at different temperatures. The solid lines are the best line fits to the data. The inset shows the typical transient current measured by TOF.
Fig. A.8 (a) The zero field mobility $\mu_{0,T}$ vs $1/T^2$; (b) the corresponding field dependent $\beta$ vs $1/T^2$. The energetic $\sigma$ and the positional $\Sigma$ disorder parameters of TCTA can be extracted from these plots as listed in Table A.1. The solid lines are the best line fits to the data.
A.5 Disorder parameters extracted by Gaussian-Disorder-Model (GDM)

<table>
<thead>
<tr>
<th></th>
<th>$\sigma$ (eV)</th>
<th>$\Sigma$</th>
<th>$C$</th>
<th>$\mu_{inf}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTDATA</td>
<td>0.093</td>
<td>2.15</td>
<td>$2.30 \times 10^{-4}$</td>
<td>3.95 x 10$^{-3}$</td>
</tr>
<tr>
<td>NPB</td>
<td>0.090</td>
<td>2.08</td>
<td>$2.27 \times 10^{-4}$</td>
<td>4.73 x 10$^{-2}$</td>
</tr>
<tr>
<td>TPD</td>
<td>0.080</td>
<td>2.57</td>
<td>$3.15 \times 10^{-4}$</td>
<td>7.42 x 10$^{-2}$</td>
</tr>
<tr>
<td>TCTA</td>
<td>0.112</td>
<td>3.70</td>
<td>$1.74 \times 10^{-4}$</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Table A.1 Extracted GDM parameters for MTDATA, NPB, TPD, and TCTA.
Appendix B - Publications

B.1 Publications resulting from this thesis:


B.2 Other related publications:


### B.3 Conference presentations

**Invited talk:**


2. S. K. So, S. C. Tse, **S. W. Tsang**, “Using PEDOT:PSS to Form Nearly Ohmic Hole Injection Contact to Small-molecule Organic Charge Transporters”, MRS 2006 Fall meeting, Boston, United States, Symposium S14.1

**Poster presentation:**


4. S. C. Tse, S. W. Tsang, and S. K. So, "Nearly ohmic injection contacts from PEDOT:PSS to phenylamine compounds with high ionization potentials", SPIE Optics and Photonics 2006, San Diego, **6333-63**

