

DOCTORAL THESIS

Charge transport and injection in amorphous organic electronic materials

Tse, Shing Chi

Date of Award:
2007

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

Charge Transport and Injection
in
Amorphous Organic Electronic Materials

TSE Shing Chi

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

Principal Supervisor: Dr. SO Shu Kong

Hong Kong Baptist University

August 2007

Abstract

This thesis presents how we use various measuring techniques to study the charge transport and injection in organic electronic materials. Understanding charge transport and injection properties in organic solids is of vital importance for improving performance characteristics of organic electronic devices, including organic-light-emitting diodes (OLEDs), photovoltaic cells (OPVs), and field effect transistors (OFETs).

The charge transport properties of amorphous organic materials, commonly used in organic electronic devices, are investigated by the means of carrier mobility measurements. Transient electroluminescence (EL) technique was used to evaluate the electron mobility of an electron transporting material - *tris*(8-hydroxyquinoline) aluminum (Alq₃). The results are in excellent agreement with independent time-of-flight (TOF) measurements. Then, the effect of dopants on electron transport was also examined.

TOF technique was also used to examine the effects of tertiary-butyl (*t*-Bu) substitutions on anthracene derivatives (ADN). All ADN compounds were found to be ambipolar. As the degree of *t*-Bu substitution increases, the carrier mobilities decrease progressively. The reduction of carrier mobilities with increasing *t*-butylation can be attributed to a decrease in the charge-transfer integral or the wavefunction overlap.

In addition, from TOF measurements, two naphthylamine-based hole transporters, namely, *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine (NPB) and 4,4',4''-tris(*n*-(2-naphthyl)-*n*-phenyl-amino)-triphenylamine (2TNATA) were found to possess electron-transporting (ET) abilities. An organic light-emitting diode that employed NPB as the ET material was demonstrated. The electron conducting mechanism of NPB and 2TNATA in relation to the hopping model will be discussed. Furthermore, the ET property of NPB applied in OLEDs will also be examined.

Besides transient EL and TOF techniques, we also use dark-injection space-charge-limited current (DISCLC) to study the charge injection properties of three phenylamine-based (PA) compounds, MTDATA (4,4',4''-Tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine), NPB, and TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl) (1,1'-biphenyl)-4,4' diamine). Poly(3,4-ethylenedioxythiophene) doped with polystyrenesulphonic acid (PEDOT:PSS) was used as a hole-injecting anode in current-voltage (*JV*) and DISCLC. Clear DISCLC transient peaks were observed over a wide range of electric fields in all cases. For MTDATA and NPB, hole mobilities evaluated by DI experiments are in excellent agreement with mobilities deduced from TOF technique. It can be concluded that, for the purpose of *JV* and DI experiments, PEDOT:PSS forms an Ohmic contact with MTDATA and a quasi-Ohmic contact with NPB despite the relatively low-lying highest occupied molecular orbital of the later. In the case of TPD, hole injection from PEDOT:PSS deviates substantially from Ohmic injection, leading to a lower than expected DI-extracted hole mobility. Finally, a composite anode will be demonstrated to improve the hole injection efficiency.

Table of Contents

| | |
|---|----------|
| Declaration | i |
| Abstract | ii |
| Acknowledgements | iv |
| Table of Contents | vi |
| List of Figures | x |
| List of Tables | xiv |
| | |
| Chapter 1 Introduction | 1 |
| | |
| Chapter 2 Basic Principles of Organic Semiconductors | |
| I. Structure and Electronic Properties | 11 |
| II. Charge Transport Mechanism | 13 |
| A. Microscopic Charge Transport Mechanism | 13 |
| 1. Electronic Band and Hopping Transportation | 13 |
| 2. Hopping Model | 16 |
| B. Macroscopic Charge Transport Mechanism | 20 |
| 1. Poole Frenkel (PF) Model | 20 |
| 2. Gaussian Disorder Model (GDM) | 21 |
| III. Charge Injection Mechanism | 23 |
| A. Electronic Properties of Interfaces | 23 |
| B. Thermionic Emission | 28 |
| C. Tunneling Injection | 29 |
| D. Thermo-activated Hopping Injection | 30 |
| IV. Current-voltage Characteristics of Organic Solids | 32 |
| A. Space-charge-limited Current (SCLC) | 32 |
| B. Dark-injection Space-charge-limited Current (DISCLC) Transient | 35 |
| V. Working Principle of Organic Light-emitting Diodes (OLEDs) | 39 |

Chapter 3 Experimental details

| | | |
|------|--|----|
| I. | Materials Purification | 43 |
| II. | Sample Preparation | 45 |
| | A. Substrate Pre-treatment | 45 |
| | B. PEDOT:PSS Deposition | 47 |
| | C. Organic and Metallic Layer Deposition | 48 |
| | D. Liquid Nitrogen Cryostats with Intelligent Temperature Controller (ITC) | 49 |
| | E. Sample Encapsulation | 50 |
| III. | Experimental Methods | 51 |
| | A. Current-voltage (<i>JV</i>) and Luminance-current (<i>LJ</i>) Characteristics | 51 |
| | B. Electroluminescence (EL) Measurement | 52 |
| | C. Time-of-flight (TOF) Measurement | 53 |
| | D. Transient Electroluminescence (EL) Measurement | 56 |
| | E. Dark-injection Space-charge-limited Current (DISCLC) Measurement | 58 |

Chapter 4 Electron Transport Properties of Undoped and Doped *Tris*(8-hydroxyquinoline) Aluminum (Alq_3)

| | | |
|------|--|----|
| I. | Introduction | 62 |
| II. | Experimental Details | 64 |
| | A. Chemical Structures of Alq_3 and the Dopants | 64 |
| | B. Structures of Undoped and Doped Devices | 65 |
| III. | Results and Discussions | 66 |
| | A. Intrinsic Alq_3 Mobility | 66 |
| | B. Information Obtainable from Transient EL Measurements | 74 |
| | C. Doped Alq_3 Mobility Evaluated from Transient EL Technique | 75 |
| IV. | Summary | 77 |

Chapter 5 Microscopic Charge Transport Mechanism of Anthracene Derivatives

| | | |
|------|---|----|
| I. | Introduction | 79 |
| II. | Experimental Details | 80 |
| | A. Chemical Structures of Anthracene Derivatives | 80 |
| | B. TOF Sample Structure | 81 |
| III. | Results and Discussions | 82 |
| | A. Mobility Results of ADN Derivatives by TOF | 82 |
| | B. Molecular Orbital of ADN Derivatives | 85 |
| | C. Microscopic View on Ambipolar Transport of ADN Derivatives | 87 |
| | D. Effects of Tertiary-butyl (<i>t</i> -Bu) Substitution on Anthracene Derivative | 90 |
| | E. Microscopic Charge Transport Studies: Reorganization Energy and Charge-transfer Integral | 92 |
| IV. | Summary | 95 |

Chapter 6 Bipolar Transport in Naphthylamine-based Compounds and their Applications

| | | |
|------|--|-----|
| I. | Introduction | 97 |
| II. | Experimental Details | 98 |
| | A. Chemical Structures of NPB, 2TNATA and the Dopants | 98 |
| | B. TOF Sample Structure | 98 |
| | C. Devices Fabrication | 99 |
| III. | Results and Discussions | 101 |
| | A. Mobilities of NPB and 2TNATA by TOF | 101 |
| | B. Electron-only Device | 104 |
| | C. Application of NPB as an Electron Transporting Layer in OLEDs | 106 |
| | D. Microscopic Explanation on Bipolar Transport in Naphthylamine-based Compounds | 109 |
| | E. Color Tunable Homojunction NPB Devices | 112 |
| IV. | Summary | 121 |

Chapter 7 Nearly Ohmic Hole Injection and Macroscopic Charge-transport Phenomena in Phenylamine-based Compounds

| | | |
|------|--|-----|
| I. | Introduction | 124 |
| II. | Experimental Details | 126 |
| | A. Measurement Techniques | 126 |
| | B. Phenylamine-based Compounds and their Energy Levels | 129 |
| | C. Sample Structures | 129 |
| III. | Results and Discussions | 131 |
| | A. Mobility Result of MTDATA, NPB and TPD by TOF | 131 |
| | B. Different Anodes with NPB | 133 |
| | C. Using PEDOT:PSS as Hole-injecting Anode for Phenylamine-based Compounds | 135 |
| | D. Mobility Results of MTDATA, NPB and TPD by DISCLC | 136 |
| | E. Mechanisms of Hole Injection Using PEDOT:PSS Anode | 138 |
| | F. Hole Injection Using Composite Anode | 142 |
| IV. | Summary | 146 |

Chapter 8 Conclusions

149

| | |
|------------------|-----|
| Curriculum Vitae | 154 |
|------------------|-----|