Optimizing electro-luminescence processes in organic light-emitting diodes

Divayana, Yoga

2008

Divayana, Y. (2008). Optimizing electro-luminescence processes in organic light-emitting diodes. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13162>

<https://doi.org/10.32657/10356/13162>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**OPTIMIZING ELECTRO-LUMINESCENCE PROCESSES
IN ORGANIC LIGHT-EMITTING DIODES**

**YOGA DIVAYANA
SCHOOL OF ELECTRICAL & ELECTRONIC
ENGINEERING**

2008

OPTIMIZING ELECTRO- LUMINESCENCE PROCESSES IN ORGANIC LIGHT-EMITTING DIODES

YOGA DIVAYANA

**SCHOOL OF ELECTRICAL & ELECTRONIC
ENGINEERING**

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the Degree of
Doctor of Philosophy

2008

© Copyright by Yoga Divayana, 2008. All right reserved.

*This work is dedicated to Leni,
my wife, my best friend,
and to my Parents,
for their constant encouragement and support*

Abstract

Organic electronic and photonic devices have attracted great attention in recent years due to their unique properties. From electronic point of view, organic materials show capability similar to their inorganic counterpart of transporting charges, producing light and even magnetism. Mechanically, organic is a soft material which can be processed at low temperature.

This thesis focuses on the photonic side of the technology – the organic light-emitting diode (OLED). OLED makes use of organic material to produce light by injecting both holes and electrons from two different terminals, respectively. Before emission of light, the electron and hole recombine to form a quasi-particle called the excitons. During this process, not all the carriers contribute to the recombination. The reason for this is the imbalance of carrier injection and transportation within the device. Firstly, we investigate the controversial role of copper-phthalocyanines which is commonly used to balance the carriers. We also introduce two different methods to solve the electron-hole imbalance problem: (1) by adding a thin layer of hole blocking layer to truly block hole-carrier within the device, (2) by using an electron transporting layer to also block the hole-carrier to balance the carrier.

Recombination of electron and hole is occurred in the area called the emission layer. The exciton, however, are readily to diffuse to various adjacent layers. If the adjacent layer has lower band gap than the exciton, it will transfer the energy the adjacent layer. To prevent the exciton diffusion, we introduce an exciton-confining structure which confines the exciton within the emission layer.

White OLED (WOLED) has a potential in display and general illumination due to its low cost processes and high efficiency. We introduce two designs of WOLEDs which utilize two exciton sources as emission layer to produce two different colors. The devices are capable of reaching a good white with moderate performance in efficiency.

In normal circumstances, only a quarter of the excitons contribute to light production via fluorescence. This is because among every four excitons, only one forms singlet while the other three form triplets. The triplet excitons are lost since their transitions to the ground state are forbidden. To harvest the triplet, molecule with heavy-metal ligand (phosphorescent) is introduced by means of host-guest system, where the phosphorescent material acts as guest. In host-guest system, doping concentration is crucial to optimize the device's performances. We investigate why such precision in concentration in doping is required. Our finding can lead development to a better phosphorescent material.

In some extreme cases, the doping concentration required is as low as 0.1% guest/host ratio. For this application, conventional co-doping method can be a problem especially considering repeatability. We solve this problem by introducing a sequential doping, where instead of co-evaporation, the guest and host layers are sequentially evaporated to form the emission layer. The device fabricated with sequential doping show similar, or even better, performances than that with co-doping method. Furthermore, sequential doping has more variables to vary than the conventional co-doping method. We show that sequential doping is capable to achieve OLED with tunable emission spectrum without scarifying the efficiency.

Acknowledgement

I would like to first thank and acknowledge my supervisor, Prof. Sun Xiaowei, who introduced me into the field of organic electronic and research in general. His guidance and support have been magnificent during my three years of study.

I am grateful to Dr. Chen Baijun who has patiently trained me with the experiment and to who I discussed most of the experimental problems we had during our early work.

I would like to thank all other graduate students, Tan Swee Tiam, Liu Yanjun, Alagappan Gandhi, Ji Xiaohong, Eunice Leong Sok Ping, Yang Yi, Heng Tun Seng, Edwin Teo, and everyone in Nanoelectronic Lab, or previously called the Ion Beam Processing lab, to provide a fun and enjoyable environment in the lab. We have the best team of the school in this lab.

Many of my experiments would not be possible without the help of the lab technicians. My thanks go to Mr. Hasman Bin Hassan, Mdm. Neo Bee Geok and Miss Teh Hsieh Foong, Janet for the help during my past years.

I would like to thank Agus Putu Abiyasa, the best friend I have ever had. We have more than ten years of friendship where he has always been there to listen to all the problems I had. I would like to thank Abi for the discussions and many hours of “winning eleven”.

I am blessed to know many inspiring people that influence the course of my life, Prof. Yohannes Surya, Oki Gunawan, PhD., members of the Indonesian Physics Olympiad team year 2000 and my high school teachers (SMUN 4 Denpasar, Bali, Indonesia). I would like to thank them for all their wise advices.

To my brother and sister, Novandika Dwipayana and Novitri Mahawidyani, I wish to thank them for the support and all the funny jokes.

I would like to thank my parents, Ketut Wija and Titik Wahyani who always believe in me. This thesis would not be here without their constant support and encouragement during my period of study far from home.

Finally, to my wife, Ni Wayan Leni Redani, thank you for your love, your patient and your enthusiasm. You have sacrificed much in helping me through tough time. Half of this thesis is her hard work. She is the backbone of this thesis. This thesis is dedicated to Leni and my parents.

Yoga Divayana

Singapore

November, 2007

Table of contents

Abstract.....	iv
Acknowledgement.....	vi
Table of contents.....	viii
List of tables.....	xiv
List of figures.....	xv

Chapter 1

Introduction.....	1
1.1 Introduction.....	1
1.2 What is OLED?.....	1
1.3 Brief history of OLED.....	3
1.4 Thesis outline.....	12

Chapter 2

Physics of organic semiconductor.....	14
2.1 Organic semiconductor.....	14
2.2 The excitons.....	19
2.2.1 Formation of excitons.....	19
2.2.2 Multiplicity of excitons (Singlet and Triplet).....	19
2.3 The dimers.....	20
2.4 The excimers.....	23
2.5 The exciplexes.....	23

2.6 Photophysical processes in organic.....	24
2.6.1 Jablonski diagram.....	24
2.6.2 Phosphorescence and fluorescence.....	25
2.6.3 Internal conversion.....	26
2.6.4 Intersystem crossing	27
2.6.5 Inter-molecular energy transfer (Dexter and Förster transfer)....	27
2.7 Current dependent losses.....	30
2.7.1 The singlet-singlet annihilation.....	30
2.7.2 The singlet-triplet annihilation.....	31
2.7.3 The singlet-polaron annihilation.....	31
2.7.4 The singlet-heat annihilation.....	32
2.7.5 The triplet-triplet annihilation.....	35
2.8 Energy levels and alignments at organic molecular interfaces.....	35
2.8.1 Transport versus optical bandgaps.....	36
2.8.2 Metal-organic interfaces.....	36
2.8.3 Organic-organic heterojunctions interfaces.....	39
2.9 Carrier injection and transportation.....	39
2.9.1 Charge injection from metal to semiconductor (interface-limited)	40
2.9.1.1 Fowler-Nordheim tunneling.....	40
2.9.1.2 Richardson-Schottky thermionic emission.....	41
2.9.1.3 Emtage and O'Dwyer thermionic effect in insulator...	42
2.9.1.4 Work of Scott and Malliaras.....	43
2.9.1.5 Phonon-assisted charge hopping.....	43

2.9.1.6 Gaussian disorder hopping model.....	46
2.9.1.7 Interface-limited injection from broaden interface state to bulk state.....	47
2.9.2 Bulk-limited transport.....	49
2.9.2.1 Space charge limited.....	49
2.9.2.2 Trap-filled limited.....	50

Chapter 3

Materials and characterization of OLED.....	51
3.1 Organic materials for OLED.....	51
3.2 Fabrication of OLED.....	57
3.3 Characterization of OLED.....	60

Chapter 4

Balancing the electron-hole current.....	68
4.1 Introduction.....	68
4.2 Role of CuPc and oxygen treatment in balancing current injection.....	69
4.2.1 Introduction.....	69
4.2.2 Theory of carrier injection and transportation.....	70
4.2.3 Experimental.....	73
4.2.4 Results and discussion.....	75
4.3 Balancing the electron-hole current with a BCP inserted between the hole- injection layer and hole-transporting layer.....	80
4.3.1 Introduction.....	80

4.3.2 Experimental.....	81
4.3.3 Results and discussion.....	81
4.4 Balancing the electron-hole current with an Alq ₃ inserted between the hole-injection layer and hole-transporting layer.....	87
4.4.1 Introduction.....	87
4.4.2 Experimental.....	87
4.4.3 Results and discussion.....	88
4.5 Summary	95

Chapter 5

Improved blue organic light-emitting diode with an exciton confinement structure.....	97
5.1 Introduction.....	97
5.2 Experimental.....	98
5.3 Results and discussion.....	98
5.4 Summary.....	105

Chapter 6

Multilayer approach for multicolor emission.....	107
6.1 Introduction.....	107
6.2 Experimental.....	108
6.3 Results and discussion.....	108
6.4 Summary	119

Chapter 7

Observation of excitonic quenching by long-range dipole-dipole interaction in sequentially doped organic phosphorescent host-guest system	120
7.1 Introduction.....	120
7.2 Experimental.....	121
7.3 Results and discussion.....	123
7.4 Summary.....	135

Chapter 8

Sequential doping approach for fluorescent device.....	136
8.1 Introduction.....	136
8.2 Highly efficient red fluorescent.....	137
8.2.1 Introduction.....	137
8.2.2 Experimental.....	137
8.2.3 Results and discussion.....	138
8.3 Highly efficient blue fluorescent	153
8.3.1 Introduction.....	153
8.3.2 Experimental.....	154
8.3.3 Results and discussion.....	154
8.4 Summary	164

Chapter 9

Conclusions and recommendation for future works.....	166
9.1 Conclusions.....	166

9.2 Recommendation for future works.....	169
Refereed journal publications.....	172
Conference presentations.....	174
Bibliography.....	175

List of tables

Table 3.1

Various types of organic materials used for OLED categorized by their functionality	53
---	----

Table 3.2

Basic radiometry units.....	61
-----------------------------	----

Table 3.3

Basic photometry units.....	62
-----------------------------	----

Table 4.1

Operating voltage and current efficiency for devices with various blocking-Alq ₃ thicknesses at a fixed current density of 100 mA/cm ²	88
--	----

Table 8.1

Summary of performances for devices with various BCzVBi thicknesses...	158
--	-----

List of figures

Figure 1.1

Three dimensional illustration of OLED structure.2

Figure 1.2

The first OLED structure employed by Tang *et al*.....4

Figure 1.3

Electrophosphorescence and combined fluo-phosphorescence structures reported by Baldo *et al*.....7

Figure 1.4

The singlet and triplet excitons are harvested in two different channels (top).
Electroluminescence spectrum at various different current densities shows an insignificant spectrum shift (below) as reported by Sun *et al*.....11

Figure 2.1

Illustration of the π electrons in anthracene molecule.....15

Figure 2.2

Splitting of the π and σ electrons energy levels due to wavefunctions overlap.
The HOMO and LUMO are formed by the $\pi - \pi^*$ levels, respectively.....16

Figure 2.3

Bandgap for various molecules as a function of number of rings.....16

Figure 2.4

Illustration of the Frank-Condon principle (Stoke's shift) in molecular structure.....18

Figure 2.5

Different orientation of molecule alignment determines whether dimer state has larger or lower (or both) bandgap than the monomer.....22

Figure 2.6

Potential diagrams of excimer and monomer.23

Figure 2.7

Jablonski diagram of a single molecule.....24

Figure 2.8

Illustration of the Förster and Dexter transfer mechanism.....29

Figure 2.9

Normalized quantum efficiency (η_{SH}) vs current density (J) characteristics of OLED, based on SSA (star) and SHA model with rate of $k_{th}JV$ (triangular) and $k_{th}[^1M^*]JV$ (square).....34

Figure 2.10

Illustration of carrier injection from the metal to the Gaussian state of the organic molecule.....47

Figure 2.11

Illustration of carrier injection from the interface state (metal-organic) to the bulk state from.....48

Figure 3.1

A schematic diagram of the clustered fabrication facilities.....59

Figure 3.2

Illustration of explanatory notes in Table 3.2 and 3.3.....63

Figure 3.3

Photopic and scotopic human eye response.....64

Figure 3.4

Color matching function of CIE.....66

Figure 3.5

CIE Coordinate.....66

Figure 4.1

(a) Calculated current density versus electric field when return-flow is included (solid line) and when return-flow is excluded (dash line). (b) Calculated current injection for non-zero CuPc DOS width as a function of electric field.....74

Figure 4.2

(a) Current density versus applied voltage for the devices with various CuPc thicknesses of 0, 10, 20, 30 nm, respectively. (b) Current efficiency as a function of current density for devices in (a).....77

Figure 4.3

(a) Current density versus applied voltage for the devices with various CuPc thicknesses of 0, 5, 15, 20 nm, respectively. For all devices the ITO is treated with O₂ plasma treatment at P=15 Pa for 3.5 minutes; (b) Current efficiency as a function of current density for devices in (a).....79

Figure 4.4

Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of BCP. The insets in (a) and (b) show the

band diagram of an OLED with a HBL inserted between HIL and HTL, and the current efficiency versus current density curves, respectively.....83

Figure 4.5

The operating voltage as a function of BCP thickness at a current density of 100 mA/cm² for all four devices in Figure 4.4. The insert shows the electroluminescence spectrum for all devices.85

Figure 4.6

Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of NPB. The device without BCP layer is also shown for comparison (represented by star). The inserts in (a) and (b) show the operating voltage as a function of NPB thickness at a current density of 100 mA/cm², and the current efficiency versus current density curves, respectively.86

Figure 4.7

Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of blocking-Alq₃. The inserts in (a) and (b) show the electroluminescence spectra and current efficiency versus current density curves, respectively.97

Figure 4.8

Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of NPB. The inset in (b) show the current efficiency versus current density curves.....92

Figure 4.9

Electroluminescence spectra for devices with various NPB thicknesses. Broadened and red-shifted spectra clearly indicate exciplex formation, as the NPB thickness decreases (indicated by the arrow). The inset shows the proposed band diagram of the device. Dipole barriers at ITO/m-MTDATA and Alq₃/Mg are taken to be -0.5 eV and 0.8 eV, respectively. All the HOMO and LUMO levels are drawn with respect to vacuum level. The exciton binding energy is taken to be ~0.9 eV for all organic materials. Exciplex emissions at m-MTDATA/ Alq₃ interface were also indicated for 2 and 5 nm NPB.....94

Figure 5.1

(a) Current density versus voltage characteristics and (b) EL spectra for devices with various thicknesses of BCP (II) layer. The insets in (a) shows the proposed band diagram for the improved device. Dipole barriers at ITO/m-MTDATA and Alq₃/Mg are taken to be -0.5 eV and 0.8 eV, respectively. All the HOMO and LUMO levels are drawn with respect to vacuum level. The exciton binding energy is taken to be ~0.9 eV for all organic materials. Inset in (b) shows the EQE or devices with various BCP (II) thicknesses.....101

Figure 5.2

Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of BCP (I) layer. The insets in (a) and (b) show the EQE versus current density and EL spectra curves, respectively...102

Figure 5.3

Normalized EL spectra for various applied voltage of the optimized device.
Inset shows the variation of the CIE coordinate for various applied voltage.104

Figure 5.4

Spectral of m-MTDATA (PL), BCP (PL), and m-MTDATA/BCP (EL). Inset shows the EQE versus current density for device with structure of m-MTDATA/BCP.....105

Figure 6.1

(a) and (b) are the band diagrams for devices A and B, respectively.....110

Figure 6.2

Current density (a) and luminance (b) as functions of voltage for device A with various thicknesses of Alq₃(I) layer.111

Figure 6.3

(a) Emission spectra and (b) CIE color coordinates of device A with various Alq₃ (I) thicknesses biased with various voltages. Pure Alq₃ emission spectrum is also drawn in (a). The CIE coordinates of equal-energy white, Alq₃ emission and Alq₃-exciplex are also indicated in (b). The insets in (a) and (b) show the EQE and emission spectra at various applied voltage for device A with X = 10 nm, respectively.....114

Figure 6.4

Emission spectra for devices with a structure of ITO/ NPB (30-Y nm)/ DCM/ NPB (Y nm)/ Alq₃/ Mg:Ag for various Y's. Insets (a) and (b) show the CIE color coordinate and EQE for the devices with various Y's, respectively....115

Figure 6.5

Current density (a) and luminance (b) as functions of voltage for device B with $Y = 5$ nm and various thicknesses of $\text{Alq}_3(\text{I})$ layer.....117

Figure 6.6

(a) Emission spectra and (b) CIE color coordinates for device B with $Y = 5$ nm but various $\text{Alq}_3(\text{I})$ thicknesses biased with various voltages. The equal-energy white is also indicated in (b). The insets in (a) and (b) show the EQE and emission spectra at various applied voltage for the device with $X = 10$ nm, respectively..... 118

Figure 7.1

Phosphorescence OLED fabricated with sequential doping with N cells (a) and random doping (b).....122

Figure 7.2

(a) Normalized emission spectrum for device with various $\text{Ir}(\text{ppy})_3$ thicknesses. Also included, spectrum from device fabricated using random doping, (b) EQE for devices with various thickness of CBP with six cells as emission layer. Inset in (a) shows EQE versus current density for devices in (a); Inset in (b) shows the normalized emission spectrum for devices in (b).....126

Figure 7.3

The proposed simplified Jablonski diagram of photophysical processes in the presence of other $\text{Ir}(\text{ppy})_3$ molecules nearby.....130

Figure 7.4

(a) EQE for devices with various thickness of CBP with same total thickness of emission layers, (b) Normalized emission spectrum for devices in (a). Inset in (a) shows EQE versus CBP thickness at current density of $50 \mu\text{A}/\text{cm}^2$ (squares) and the fitting curve (solid line) utilizing the Förster-type quenching rate, with a Förster radius of around 4 nm.....132

Figure 7.5

(a) Current density (J) and Luminance (L) versus voltage for devices with different number of cells. (b) Normalized emission spectrum for devices in (a). Inset in (b) shows EQE versus current density for devices in (a).....134

Figure 8.1

Schematic diagram of fluorescent OLED fabricated with sequential doping with N cells (a) and co-evaporation method (b).139

Figure 8.2

(a) J-V and L-V curves for devices with various DCM thicknesses (six cells). (b) Normalized emission spectra for devices in (a). Inset in (b) shows EQE versus current density for devices in (a).141

Figure 8.3

(a) J-V and L-V curves for devices with various Alq₃ thicknesses (six cells). (b) Normalized emission spectra for devices with various thicknesses of Alq₃ (six cells). Inset shows the corresponding EQE.....143

Figure 8.4

(a) The proposed simplified Jablonski diagram of photophysical processes in the presence of other DCM molecules nearby. (b) shows EQE versus Alq₃

thickness at current density of $50 \mu\text{A}/\text{cm}^2$ (squares) and the fitting curve (solid line) utilizing the Förster-type quenching rate, with $R_{\text{Fr2D}} = 6.5 \text{ nm}$149

Figure 8.5

(a) J-V curves for devices with different numbers of cells. (b) Normalized emission spectra for devices in (a). Inset in (b) shows EQE versus current density for devices in (a).....152

Figure 8.6

(a) Current density and Luminance versus voltage for devices with various CBP thicknesses. (b) Normalized emission spectrum for device in (a). Inset in (a) shows the architecture of the blue OLED fabricated by sequential doping method. Inset in (b) shows EQE versus current density for devices in (a)....156

Figure 8.7

(a) Current density and Luminance versus voltage for devices with various BCzVBi thicknesses. (b) Normalized emission spectrum for device in (a)...160

Figure 8.8

EQE for devices with various thickness of BCzVBi with six cells as emission layer. Inset shows the logarithmic plot of emission peak and fraction of aggregation (f) versus BCzVBi thickness.....161

Introduction

1.1. Introduction

Organic light-emitting diode (OLED) has been regarded as the next generation flexible flat panel display technology and a new platform for low-cost illumination source. The main advantage of these organic semiconductors is their capability to be deposited onto a variety of low cost substrate such as thin film plastic, glass, metal foil, which require no lattice matching as that commonly applied in inorganic semiconductor. Combined further with the relatively ease processing and synthesis of these organic semiconductors, which is still researched by many chemists, it is understandable why the field attracts so much interest in the scientific community.

1.2. What is organic light-emitting diode?

OLED is a device that converts electrical power into light by utilizing various organic semiconductor materials. A simple OLED structure is illustrated in Figure 1.1. It begins with a simple glass coated with an indium tin oxide (ITO). The ITO is the most widely used transparent conductor, it is optically transparent and electrically conductive. With a high work function, it is used to inject holes into OLEDs. Adjacent to the ITO anode is usually deposited with a hole transporting or injecting layer to facilitates the hole transportation or injection. On the side near the cathode,

likewise, an electron transporting or injecting layer was deposited. As a cathode to inject electron, low work function metal such as Mg, Ca, or Al can be applied with some mixture of Ag for preventing oxidation of Mg. In between ETL and HTL is the emission layer.

The current state of the art structure of OLED, however, utilizes various different layers to optimize every process involved in light generation including carrier injection, excitons confinement, excitons harvesting, light out-coupling, etc.

Figure 1.1 Three dimensional illustration of OLED structure. Emission of light is shown by arrows.

1.3. Brief history of organic light-emitting diode

This section gives a short review of the progress and development of OLED which has recently seen its applications commercialized. Since it was first developed, OLED has attracted great interest because of its potential application in display technology.^{1,2} This brief review of the history of OLED is not intended to be comprehensive, but just to give an overview about the vast and very exciting development of OLED. For more comprehensive reviews on OLED developments and future trends, readers can refer to Refs [1, 2].

The work on OLED was initiated in 1987 when Tang and VanSlyke accidentally discovered that their thin film organic photovoltaic developed at Kodak Laboratory emitted a greenish color.³ Further investigation has led them to the first ever battery-powered light-emitting device based on organic material.⁴ Although organic semiconductor is known to have very low carrier mobility ($<10 \text{ cm}^2/\text{Vs}$), the usage of thin nanometer-thick and smooth film enables the device to operate at low voltage. The device was developed using thermal evaporation in high vacuum ($\sim 10^{-5}$ Torr) where high quality thin film may be produced. The most important technological breakthrough by Tang *et al.* is the usage of double organic layers, one for hole and another for electrons transport (Figure 1.1). Previously, single layer OLED resulted in a very poor external quantum efficiency (EQE) [$\sim 0.05\%$ photon/electrons], which is mainly because of the poor balance of the electrons and holes and that the emission layer occurred near the cathode where plasmon quenching induces further loss. In the double-layer device, these two issues are solved, carrier injection is more balanced and emission layer is located far from the metal electrodes, enabling an EQE as high as 1%. To have high electrons injection, low work function metal magnesium (Mg)

was used as cathode. The Mg was mixed with silver (Ag) to improve its adhesion with the organic and preventing Mg being oxidized. Transparent indium-tin-oxide (ITO) was used for hole injection. This device emitted a green color light from the Alq₃ layer (Figure 1.2).

To further increase the device efficiency, in 1989, VanSlyke, Tang and Chen doped a small amount of highly efficient fluorescent-dye into Alq₃ layer. Alq₃, which has poorer efficiency acts as the host and transfers the energy to the dye which emits light more efficiently. EQE of 2% was achieved with optimum dopant concentration.⁵ The amount of dye doped was so small (0.25-1%mol) so that the current was not affected much.

Figure 1.2 The first OLED structure employed by Tang *et al.*⁴ (a) and subsequently improved device through doping (b).⁵

The OLED developed by Tang *et al.* was based on small-molecules organic material. Burroughes *et al.* discovered the first polymer (large-molecules) organic light emitting devices in 1990 at the University of Cambridge.⁶ Burroughes used poly(p-phenylene vinylene) [PPV] stacked between two electrodes, ITO and aluminum, as hole and electron injecting metal, respectively. The initial device has very poor efficiency which primarily because of the usage of single layer and high work function aluminum metal which injects electrons poorly.

To improve the performances of polymer-based OLED, an electron transporting layer (ETL) was spin-coated between PPV and cathode.⁷ Ten-fold increase in efficiency was achieved. The ETL has dual functions of increasing the electron injection and providing a charge confinement at the PPV-ETL interface.

Although OLED is distinctive by their process simplicity and material properties, the working lifetime and stability of the device were very poor. Device lifetime was reported from only a few hours to several hundred hours in the early years. In 1996 VanSlyke, Chen and Tang modified the small-molecule OLED structure by introducing a new improved holes transport material (a benzidine with naphthyl substituents), which has higher glass transition temperature and further included a thin buffer layer (copper-phthalocyanine) between the ITO and hole transport layer (HTL).⁸ Both modifications were able to improve the device lifetime to 4000 hours operating at a luminescence of 510 cd/m². Although significant improvement in efficiency and lifetime was obtain by a thin buffer layer, the mechanism involved is still in question. A similar technique has also been applied for polymer OLED where a conducting polymer (polyethylene dioxythiophene) was used as a buffer between ITO and electroluminescence polymers.⁹

Besides modifying the anode side, Hung, Tang and Mason in 1996 modified the cathode side of the OLED.¹⁰ They introduced a very thin (mono) insulating layer of lithium-fluoride (LiF) between ETL and aluminum cathode which was able to improve the device efficiency and also reduce the operating voltage. Many mechanisms have been suggested to explain the improvement of electron injection, such as band bending, insulator-assisted tunneling, LiF disassociation during deposition, and lowering metal work function by chemical reaction.

In OLED, most of the voltage drops in the transporting layers which do not contribute directly to the light emission process. To reduce the voltage, p and n-type doping were introduced at the transporting layers.^{11,12} The p-i-n structure significantly decreases the voltage and increases the power efficiency of the device.

All the OLEDs that we have described above exploit fluorescence to obtain light, in 1998 a team led by Stephen R. Forrest of Princeton University and Mark E. Thompson of the University of Southern California engineered a device that harvests light from phosphorescent or forbidden transition-state.¹³ In OLED, when hole and electron recombine, they form an excited bound state termed exciton. The exciton has four-fold spin multiplicity, in which only one is able to produce light via fluorescence, while the other three are forbidden to produce light, due to the spin conservation rule. To enable this forbidden state to emit light, a principle known as spin-orbit coupling was applied. A new type of organic dopant which has a heavy metal in the center of the molecule was introduced to harvest these forbidden excitons (Figure 1.3). The internal efficiency as high as 100% has been reported from this phosphorescence-OLED.¹⁴

Figure 1.3 Electrophosphorescence¹³ (top) and combined fluo-phosphorescence¹⁵ (bottom) structures reported by Baldo *et al.*

Electrophosphorescence enables improvement of the OLED efficiency by four times. With further improvements in carrier balance and exciton confinement, both green¹⁶ and yellow¹⁴ emitting devices have reached the efficiency close to their maximum theoretical limit. Blue OLED, however, still suffers from many problems such as low quantum efficiency and relatively shorter lifetime. Although the developments of better materials for blue OLED have been extensive in recent years¹⁷⁻²³, those that emit in deep blue are still rare.^{19,20} Device that emits deep blue emission that matches the requirement of the National Television Standards Committee is important to allow full true-color coverage for display application.¹⁹

Other challenges faced in blue OLED include exciton confinement, suitable wide band gap host material, carrier injection to the host material, and carrier confinement. To solve the issue of host material, Holmes *et al.* used direct charge trapping in the guest molecules.²⁴ Most of the excitons are usually formed in the host molecules, which then transfer the energy to the guest molecule where the final emission takes place. By allowing a direct exciton formation within the guest molecule, the host molecules no longer function as the exciton formation region. This therefore eliminates the various requirements for the host.²⁴ The other challenges still remain to be solved.

Another important development takes place recently is the white OLED (WOLED). WOLED has a large potential for solid-state lighting and flat-panel display backlights due to its high efficiency and surface emitting nature. The application of electrophosphorescent in WOLED has produced device with efficiency exceeding that of incandescent bulbs.²⁵

Various different architectures have been applied to achieve efficient color-balanced WOLED. The first method is by solution-processed WOLED. The simplest solution-processed WOLED incorporates polymers with several emissive chromophores, which is a blend²⁶⁻²⁸ of polymers and small molecules coated onto the ITO by spin coating²⁹ or inject printing.³⁰ This architecture, however, suffers from a very poor carrier injection and balance. In some cases an additional vacuum-deposited electron-transporting layers may be incorporated to improve the carrier injection and balance.³¹ However this further complicates the processing processes due to the extra vacuum deposition steps. Due to various problems in carrier injection and balance and material impurity, the polymer-based WOLED only capable to reach relatively low power efficiency.

The second method reported in literature is device architecture for small molecules utilizing multiple emissive layers.³²⁻³⁴ To obtain a balanced white light, device with two or more emission layers are employed. By controlling the carrier recombination, carrier trapping, and exciton diffusion, the emission of the red, green, and blue can be tuned appropriately to obtain desired color purity. This technique however suffers from a color-shift with increase in current.³⁵

To eliminate color-shift, devices with a single emission layer doped with two or three dopants have been reported.^{25,36-38} To balance the red, green and blue emission, the concentration of each dopant is carefully controlled. The architecture has been used to produce a WOLED with high power conversion of 42 lm/W.²⁵

As mentioned above, phosphorescence enables the emission from the triplet exciton. However due to the long lifetime of triplet exciton, unlike the fluorescent WOLED, phosphorescent WOLED suffers from a large current-dependent loss. The

details of various current-dependent losses are discussed in section 2.7. The efficiency of a typical phosphorescent device drops significantly with an increase in current injection. To reduce the efficiency roll-off, Sun *et al.* combine the usage of both singlet and triplet excitons.³⁹ Based on the fact that the triplet exciton has much longer diffusion length than that of singlet exciton,⁴⁰ the emission region is designed to enable extraction of singlet and triplet into two independent channels. This device has been shown to perform well at high current injection with relatively high power conversion efficiency (see Figure 1.4).

To further improve device efficiency, tandem structure may be utilized.^{41,42} By stacking two or more, similar WOLEDs⁴¹ or independent red, green and blue OLEDs,⁴³ the current conversion of the WOLED can be greatly enhanced.

Kodak produced the first commercial OLED display for its camera in 2002.³ Recently Sony announced that it will launch the first commercial television using OLED in December 2007.

OLED has developed from a laboratory device into a commercialized product in twenty years' time. Since it was discovered, major improvements have been obtained, such as device efficiency (from 1% to ~100% photon/electron), low operating voltage (<10V), long lifetime (~10000 hours), multicolor emission, etc. The distinct profiles certainly make OLED a strong candidate for many futuristic photoemission devices.

Figure 1.4 The singlet and triplet excitons are harvested in two different channels (top). Electroluminescence spectrum at various different current densities shows an insignificant spectrum shift (below) as reported by Sun *et al.*³⁹

1.4. Thesis outline

As the main function of OLED is to produce light, it is important to understand all the processes involved. In this thesis, our main objective is to optimize every processes contribute to the emission of light in the device. To start this thesis, in chapter two, we briefly discuss the physics of organic light-emitting diode, and then continued with chapter three which describes the various types of materials, fabrication and characterization of OLED. These two chapters provide the basic understanding of OLED device which will serve as a perfect prelude for the rest of the thesis.

The rest of the chapters discuss various optimization techniques applied to improve the performance of the OLED using multilayer structure. In brief, we shall first describe the processes involve in light production. Prior the light emission, quasi-particle, excitons, were formed by recombination of electrons and holes injected from the respective electrodes. In the process of carrier recombination, not all electrons or holes contribute to the excitons formation responsible to efficiency losses. This is due to the imbalance of carrier injections and transportations in the device. In chapter four we introduce three techniques to tune the balance of the carrier injection in typical OLED structure.

The recombination of carriers (excitons formation) normally occurs at one organic layer. However if both types of carriers are present at two different organic layers, the excitons can be formed at both layers.¹¹ Those excitons recombine at higher band-gap layer then transfer its energy to the lower band-gap layer whereby final radiative emission occurred. The energy transfer process may reduce the device efficiency. In

chapter five, we improve the performances of a typical blue OLED by introducing a structure that confines the excitons within the emission layer.

In chapter six, we introduce two multilayer structures that capable to produce white emission. The structure utilized two exciton sources to achieve different color. Furthermore the structure requires no doping technique and capable achieving reasonable efficiency.

Preceding the exciton formations, only one quarter (singlet) of those excitons can recombine radiatively, while the rest (triplet) decay through non-radiative channels due to the spin disparity. To harvest the triplet excitons, phosphorescent dopant (host-guest system) was introduced.¹³ Phosphorescent molecule mixes the singlet and triplet excitons by spin-orbit coupling utilizing a heavy metal ligand. Strangely, for every host-guest system, there is an optimum doping concentration correspond to maximum performances. In chapter seven we investigate the quenching mechanism in the host-guest system. Chapter eight discusses a new technique termed sequential doping to achieve the host and guest system.

This thesis is ended with conclusions and recommendation for future works.

Physics of organic semiconductor

2.1. Organic semiconductor

Organic is a type of chemical compound which consists of carbon atoms. Carbon belongs to group IV in the periodic table which is capable of forming four covalent bonds with other atoms. The tetrafold bonding capability combined with the ability of forming stable single, double and triple bonds with other atoms allow carbon to form thousands to millions different types of materials from the simple hydrocarbon like methane (CH_4) to the ever complex human deoxyribonucleic acid (DNA) molecule. This infinite possibility is one of the major advantages of organic materials.

Organic semiconductor is a class of organic material which has an alternating single and double carbon-carbon covalent bonds, or simply called conjugated bonds. Conjugated bonds require the electrons in the carbon atoms to form sp_2 hybrid orbital (σ -bond) which lets an electron to form a loose p_z -orbital which is perpendicular to the plane containing all the carbon atoms. The overlapping between the neighboring p_z electron of the carbon atoms forms the so called π -bond which is illustrated in Figure 2.1.⁴⁴ The delocalized π -electrons are free to move within the molecule and enable charge transport in organic materials. In analogy to the inorganic semiconductor, organic semiconductor also possesses a valence band-like orbital which is called the highest occupied molecular orbital (HOMO) and a conduction

band-like orbital which is called the lowest unoccupied molecular orbital (LUMO). Interactions between the π electrons and the σ electrons within the molecule result in the opening of the HOMO and LUMO levels. In Figure 2.2 we illustrate the opening of the HOMO and LUMO for the case of two-electron interactions. The overlaps between the π electrons open the $\pi - \pi^*$ levels, while the σ electrons open the $\sigma - \sigma^*$ levels. When a large number of electrons are involved, the energy levels may form a discontinued band, similar with the conduction and valence bands in inorganic semiconductor. Most of the time the HOMO and LUMO levels are formed by the π -bonds, hence their optical transition corresponds to the transition of the π -electrons, represented by the notation $\pi - \pi^*$.

Figure 2.1 Illustration of the π electrons in anthracene molecule. Adapted from Ref. [44].

Figure 2.2 Splitting of the π and σ electrons energy levels due to wavefunctions overlap. The HOMO and LUMO are formed by the $\pi - \pi^*$ levels, respectively.

Figure 2.3 Bandgap for various molecules as a function of number of rings. Adapted from Ref. [44].

The band gap according to the perimeter free electron theory is inversely proportional to the molecule size, i.e. larger molecule has a smaller band gap. This is an analogy with the 1D quantum box. As the size of the box reduces, the electron becomes more localized and its energy increases. Despite of the simple assumptions of the perimeter free electron theory, it gives some accurate prediction of the band gap of some classes of organic semiconductor, such as the polyacenes. This is illustrated in Figure 2.3 for polyacenes molecules, where a linear relationship between the number of rings and band gap is clearly shown.

The vibrational component also plays an important role in the spectral properties of the organic semiconductor. In fact, almost all the absorption and emission processes in organic molecules involve the higher mode of vibrational state.⁴⁵ The electronically excited molecule has a relatively short lifetime in the upper electronic levels; returning eventually to the ground state. The energy released by the excited state can appear as fluorescence, phosphorescence, heat, or combination of all.

The configurational coordinate diagram of the ground and excited state of a molecule is shown in Figure 2.4, denoting in one dimension the potential surfaces associated with the electronic and vibrational states. In general the ground and excited states acquire two different stable configurational coordinates which are displaced by ΔQ as shown in the Figure 2.4. As required by quantum mechanics, for an electronic transition to occur, the wavefunction of the excited state must overlap well with the ground state, i.e. possesses a large Frank-Condon overlap factor.⁴⁶ Therefore, the absorption is dominated by transition from the zero order vibrational mode of the ground state to the higher order vibrational mode of the excited state (S^{v0}_0 - S^{vn}_1). The excited electrons then experience a fast vibrational relaxation by releasing heat to the

zero order modes ($S^{v_n}_1 - S^{v_0}_1$). Light emission occurs from transition of the zero order vibrational mode of the excited state to various higher order vibrational mode of the ground state ($S^{v_0}_1 - S^{v_n}_0$). This causes the emission peak to be red-shifted compared to the absorption peak. The energy difference between the peaks is called the Stoke's shift.

Figure 2.4 Illustration of the Frank-Condon principle (Stoke's shift) in molecular structure. The emission spectrum (red arrow) is red shifted compared with the absorption spectrum (blue arrow)

2.2. The excitons

2.2.1 Formation of excitons

Before emitting a photon, recombination between electron and hole is preceded by formation of a coulomb-interactive unstable pair called exciton. There are two types of excitons, classified by their binding energy: the loosely-bounded Wannier and the tightly-bounded Frenkel excitons.⁴⁴ In organic semiconductor, the exciton binding energy is large $\sim 0.25\text{-}0.9$ eV, hence it is classified as Frenkel excitons.⁴⁷

2.2.2. Multiplicity of excitons (Singlet and Triplet)

Since each charge has two possible spin states, their pair, the exciton, has fourfold states. Based on Pauli's principle, the total wave function of a two-electron system must be anti-symmetrical with the interchange of the particles.⁴⁶ Hence, if the coordinate function is symmetrical, the spin function must be anti-symmetrical, and vice versa. Considering a configuration where one electron is in an orbital φ_A and the second electron is in a different orbital φ_B , from the product of the two orbitals, we can construct two different orbital functions that are symmetric or anti-symmetric with respect to permutations:

$$\varphi_s(1,2) = \frac{1}{\sqrt{2}}(\varphi_A(1)\varphi_B(2) + \varphi_A(2)\varphi_B(1)) \quad (2.1)$$

$$\varphi_a(1,2) = \frac{1}{\sqrt{2}}(\varphi_A(1)\varphi_B(2) - \varphi_A(2)\varphi_B(1)) \quad (2.2)$$

Similarly to the orbital functions, the spin function (χ) may also be expressed in the same way. For the symmetrical spin function:

$$\chi_s = \chi_1(\uparrow)\chi_2(\uparrow) \quad (2.3)$$

$$\chi_s = \chi_1(\downarrow)\chi_2(\downarrow) \quad (2.4)$$

$$\chi_s = \chi_1(\uparrow)\chi_2(\downarrow) + \chi_1(\downarrow)\chi_2(\uparrow) \quad (2.5)$$

where $\uparrow$ and $\downarrow$ represent the possible spin states of each electron. And the anti-symmetrical spin function can be written as:

$$\chi_a = \chi_1(\uparrow)\chi_2(\downarrow) - \chi_1(\downarrow)\chi_2(\uparrow) \quad Spin=0 \quad (2.6)$$

The total wave function is the product of orbital and the spin function:

$$\psi_{sl} = \phi_s \chi_a \quad \text{This is called singlet wave function} \quad (2.7)$$

$$\psi_{tl} = \phi_a \chi_s \quad \text{This is called triplet wave function} \quad (2.8)$$

Because of the difference in spatial symmetry, the singlet state has a higher energy compared to the triplet state. The electron-electron repulsion is smaller in the triplet exciton, hence resulting in less potential energy.

2.3. The dimers

When two similar molecules are positioned close one another such that their electronic wavefunctions start to overlap, a new state is formed with different spectral properties compared to molecular spectra. This new state is called the dimer.⁴⁴ The dimer has additional intermolecular interaction energy (V_{12}) comparing that of isolated molecule. The Hamiltonian operator of a dimer therefore can be written as:

$$H = H_1 + H_2 + V_{12} \quad (2.9)$$

where H_1 and H_2 represent the energy operators of the isolated molecules.

The ground state of the dimer can be approximated as:

$$\psi_G = \psi_1 \psi_2 \quad (2.10)$$

where ψ_1 and ψ_2 are the ground state wavefunctions of the isolated molecules.

Therefore the ground state energy can be approximated as:

$$E_G = E_1 + E_2 + \langle \psi_1 \psi_2 | V_{12} | \psi_1 \psi_2 \rangle, \quad (2.11)$$

where E_1 and E_2 are the energy of the state ψ_1 and ψ_2 , respectively.

The excited state wavefunction can be written as linear combination of the unperturbed excited state wavefunction of:

$$\psi_E = c_1 \psi_1^* \psi_2 + c_2 \psi_1 \psi_2^* \quad (2.12)$$

where ψ_1^* and ψ_2^* are the excited state wavefunctions of the isolated molecules.

Using both Eq. (2.9) and (2.12), the dimer excited state energies can be calculated by:

$$E = \min \langle \psi_E | H | \psi_E \rangle \quad (2.13)$$

To solve (2.13), set the derivative of E with respect to c_1 and c_2 to be zero.

$$\left. \frac{dE}{dc} \right|_{c_1, c_2} = 0 \quad (2.14)$$

Further by assuming that $E_1 = E_2$, we arrive with:

$$c_1 / c_2 = \pm 1 \quad (2.15)$$

and

$$E(\pm) = E_1^* + E_2 + W \pm \beta \quad (2.16a)$$

or

$$E(\pm) = E_1 + E_2^* + W \pm \beta \quad (2.16b)$$

where β is the resonance interaction energy

$$\beta = \langle \psi_1^* \psi_2 | V_{12} | \psi_1 \psi_2^* \rangle \quad (2.17)$$

and W is the columbic interaction energy arising from the overlap between the excited wavefunction of one molecule with the ground state of the other molecule:

$$W = \langle \psi_1^* \psi_2 | V_{12} | \psi_1^* \psi_2 \rangle \quad (2.18)$$

The corresponding stationary states are:

$$\psi_E(\pm) = \frac{1}{\sqrt{2}} (\psi_1^* \psi_2 \pm \psi_1 \psi_2^*) \quad (2.19)$$

Depending on the alignment of the molecules, the dimer emission can be blue or red-shifted from their monomer. The geometry dependence of dimer emission is illustrated in Figure 2.5.

Figure 2.5 Different orientation of molecule alignment determines whether dimer state has larger or lower (or both) bandgap than the monomer. Adapted from Ref. 44.

2.4. The excimers

Another type of excited quasi-particle that produces a red-shifted in the emission spectrum is called the excimer. The difference between dimer and excimer is that the latter does not have a stable ground state. Excimers are molecular associates that exist only in excited electronic states ($A+A^*$).⁴⁸ The absorption spectrum of excimer is the same as that of the monomer, unlike the dimer. Figure 2.6 illustrates the potential energy diagram of excimer and monomer.

2.5. The exciplexes

Exciplexes are a class of excited quasi-particle similar to those excimers but involve two different molecules ($A+B^*$ or A^*+B).⁴⁹ The emission spectrum does not resemble any of the constituent molecules and is normally much red-shifted.

Figure 2.6 Potential diagrams of excimer and monomer. The monomer possesses a stable excited and ground state while excimer only has a stable excited state. Emission is indicated by the dash-arrows. Adapted from Ref. 48.

2.6. Photophysical processes in organic

2.6.1. Jablonski diagram

A complete Jablonski energy diagram representing various photophysical processes in a typical molecule is shown in Figure 2.7.⁵⁰ The diagram schematically displays the singlet ground state, excited singlet (S) and triplet (T) states. For polyatomic molecules, the spacing between the vibrational levels decreases rapidly with increasing energy,⁵¹ and the density of states increases rapidly as the vibrational energy increases.

Emission or luminescence is represented by the straight arrows referred as fluorescence (F) and phosphorescence (P), depending on the spin multiplicity. Radiationless transitions between states of the same and different multiplicity are called internal conversion (IC) and intersystem crossing (ISC), respectively.

Figure 2.7 Jablonski diagram of a single molecule. A and VR mean absorption and vibrational relaxation, respectively. S_0 , S_1 and T_1 are the singlet ground state, singlet excited state, and triplet excited state, respectively. Adapted from Ref. 50.

2.6.2. Phosphorescence and fluorescence

According to perturbation theory, the transition rate from one state to another depends on the electronic dipole moment between the initial and final electronic states. However, based on symmetry consideration, only states that obey a certain rule are allowed to emit light. The dipole moment operator for a two-electron system is $-\vec{e}r_1 - \vec{e}r_2$, which is symmetrical with the interchange of the two electrons. The transition rate between the initial ψ_i and final states ψ_f can be written as:⁴⁶

$$T_{i-f}^2 \propto \left| -e \langle \psi_f(r_1, r_2) | r_1 + r_2 | \psi_i(r_1, r_2) \rangle \right|^2 \quad (2.20)$$

From this equation, for non-vanishing value of transition rate, the sign of T_{i-f} must hold under particle exchange. Therefore, only those particles with the same initial and final orbital symmetry are allowed to make transitions. Notice here that the operation only applies spatially, therefore only the symmetry properties of the orbital should be considered.

In most stable molecules, the HOMO is completely filled in the ground state. Consequently, the ground state wave functions of these molecules are spatially symmetric under electron exchange. Since we already know that singlet exciton has a symmetry orbital wave function, while a triplet has anti-symmetry, thus only singlet is allowed to make radiative decay while triplet transition is forbidden. The decay of a singlet is very rapid with the rate of about 10^9 s^{-1} , which is also known as fluorescence. On the other hand, the triplet decay is very slow (few seconds), also known as phosphorescence.

The triplet state that has very slow rate of radiative transition tends to decay non-radiatively via phonon emission. This therefore limits the efficiency of the device to

25% with only singlet excitons emitting photons. However, from the first principle of time-dependent perturbation theory, we can obtain a non-zero transition rate for triplet state by using the principle called spin-orbit coupling. Spin-orbit interaction mixed the singlet and triplet state resulting in non zero transition rate. The Hamiltonian of the spin-orbit interaction of an atom is expressed as:⁵²

$$H_{so} = -\frac{e}{2m_e^2 c^2 r} \frac{d\phi}{dr} L \cdot S \quad (2.21)$$

where e is the electron charge, m_e is the electron mass, c is the speed of light in vacuum, ϕ is the electric potential, L is the angular momentum and S is the spin operator. For an atom with Ze charges, the potential ϕ is simply $Ze / 4\pi\epsilon r$, where ϵ is the vacuum permittivity, hence the Hamiltonian becomes:

$$H_{so} = -\frac{Ze}{8\pi\epsilon m_e^2 c^2 r^3} L \cdot S \quad (2.22)$$

The expectation value of r^{-3} for hydrogenic orbitals is proportional to Z^3 . Thus the overall interaction is proportional to Z^4 and spin-orbit coupling is much stronger in heavy atoms than in light ones. The stronger the interaction, the larger the transition rate of the triplet state to the ground singlet state.

2.6.3. Internal conversion

Internal conversion (IC) is a transition between two isoenergetic vibrational levels of different electronic states (S^{v0}_1 - S^{vn}_0) or (T^{v0}_1 - T^{vn}_0).⁵³ This process is responsible for the quantum loss in fluorescence as the final state decays thermally (vibrational relaxation) to the lowest vibrational mode.

In molecules, the radiationless VR transition of $S^{v_n}_1-S^{v_0}_1$ and $T^{v_n}_1-T^{v_0}_1$ happen much faster than the lifetime of the excited electronic state, therefore most of the time luminescence is observed exclusively from the lowest vibrational mode of the excited state. This phenomenon is also called the *Kasha's rule*.⁵⁰

Generally, the radiationless $S^{v_0}_1-S^{v_0}_0$ and $T^{v_0}_1-T^{v_0}_0$ transitions which are intermediated by the $(S^{v_0}_1-S^{v_n}_0)$ and $(T^{v_0}_1-T^{v_n}_0)$ transitions occur much slower than the vibrational relaxation. More interestingly, experimental results show that the rate of this radiationless transition inversely proportional to the exponential of the energy gap (ΔE), is also called the *energy-gap law*, which states:⁵⁴

$$k_{IC} = Ce^{-\alpha\Delta E} \quad (2.23)$$

where C and α are constants. This means molecules with larger bandgap have higher quantum yield.

2.6.4. Intersystem crossing

Spin-orbit coupling interaction causes the intersystem crossing (ISC), whereby the singlet excitons convert to triplet excitons or, vice versa within the same molecule.⁵³ Molecule with heavy atom tends to have higher ISC rate due to influence of spin orbit-coupling. ISC also causes loss in phosphorescence when ISC transfer rate from the isoenergetic vibrational level of the triplet to the higher vibrational mode of the ground singlet state is high.

2.6.5. Inter-molecular energy transfer (Dexter and Förster transfer)

Intermolecular energy transfer is radiationless transition which involves more than a single molecule. There are two types of intermolecular energy transfer depending on

the range of transitions. The short range transition is called the Dexter⁵⁵ transfer, while the long range is referred as the Förster⁵⁶ transfer.

Dexter energy transfer involves electron exchange between molecules. This transfer requires the overlap between wave function of the donor and acceptor, hence applies for short-range. The total spins are conserved in this interaction; however it allows cross-spin transition, i.e. singlet-triplet transition, or vice versa. The transition rate of the Dexter transfer is expressed as:⁵⁵

$$k_{D-A} = \frac{2\pi}{\hbar} |\beta_{D-A}|^2 \int F_D(E) F_A(E) dE \quad (2.24)$$

where β_{D-A} is the exchange energy interaction between molecules, E is the energy of the acceptor, $F_D(E)$ and $F_A(E)$ are the normalized emission spectrum of the donor and absorption spectrum of the acceptor, respectively. For hydrogen-like wave function, the exchange energy interaction term β_{D-A} decays exponentially with distance:

$$\beta_{D-A} \propto \exp(-\gamma r_{D-A}) \quad (2.25)$$

where r_{D-A} is the distance between the donor-acceptor and γ is the inverse Bohr (localization) radius. Hence the transition rate can be simplified as:

$$k_{D-A} = KJ \exp(-2\gamma r_{D-A}) \quad (2.26)$$

where K is related to specific orbital interaction and J is the spectral overlap integral.

Förster transfer refers to the transfer of energy between molecules with distance larger than the Van der Waals radius. The interaction is originated by dipole-dipole interaction between the molecules. The overlap between the emission spectra of the donor and the absorption spectra of the acceptor is necessary for the transfer to occur. Transition probability for Förster transfers is written as:⁵⁶

$$k_{FD-A} = \frac{1}{\tau_d} \left(\frac{R_0}{R} \right)^6 \quad (2.27)$$

where R_0 is the Förster radius which depends on the spectral overlap and τ_d is the excited donor lifetime.

Figure 2.8 Illustration of the Förster and Dexter transfer mechanism.

2.7. Current-dependent losses

Organic semiconductor suffers various bi-excitonic quenching mechanisms which limit its performances for high current applications such as lasing. In this section, we discuss various current-dependent losses occurred in OLED.

2.7.1. The singlet-singlet annihilation

The singlet-singlet annihilation can be summarized by the following equation:⁴⁴

where $^1M^*$ is the excited singlet state, 1M_0 is the ground state and k_{sq} is the bi-excitonic rate constant. The vibrational $^1M_n^*$ state then relaxes internally (thermally) to the lowest vibrational mode of the excited state [$^1M^*$]. This means that for every two excitons, only one produces a photon.

In the presence of singlet-singlet annihilation, the singlet dynamics in OLED follows:

$$\frac{d[^1M^*]}{dt} = -\frac{[^1M^*]}{\tau} - \frac{k_{sq}}{2}[^1M^*]^2 + \frac{J}{4qd} \quad (2.29)$$

where J is the current density, τ is the singlet lifetime, q is the electric charge, and d is the total length of the carrier recombination site. The steady state solution is

$$\frac{[M^*]}{[M^*]_0} = \frac{J_0}{J} \left\{ \sqrt{1 + \frac{8J}{J_0}} - 1 \right\} \quad (2.30)$$

where $[M^*]_0 = \frac{J\tau}{4qd}$ is the steady state solution in the absence of singlet-singlet

annihilation and $J_0 = \frac{16qd}{k_{sq}\tau^2}$ is the half-value singlet current.

2.7.2. The singlet-triplet annihilation

The singlet-triplet annihilation process is shown as:⁴⁴

where $^3M^*$ is the excited triplet state, $^3M_n^*$ is the n-order vibrational mode of the excited triplet and k_{st} is the bi-excitonic singlet-triplet quenching rate constant. Assuming that triplet formation is proportional to the singlet formation, the singlet-triplet annihilation produces similar quenching profile to that of the singlet-singlet annihilation. In photoluminescence systems, however, singlet-triplet annihilation is less significant due to lack of triplet excitons formation.

2.7.3. The singlet-polaron annihilation

Another important mechanism that limits the performances of OLED at high current operation is the singlet-polaron annihilation, where the exciton is quenched by the charge carrier (polaron). A single exciton can be quenched readily by a charge carrier by transferring its energy to the carrier via the long range Förster dipole-dipole interaction. In the presence of polaron, the excitons dynamics become:⁴⁴

$$\frac{d[^1M^*]}{dt} = -\frac{[^1M^*]}{\tau} - k_{sp}[^1M^*]n + \frac{J}{4qd} \quad (2.32)$$

where n is the polaron density. The steady state solution is:

$$\frac{[M^*]}{[M^*]_0} = \frac{1}{(1 + k_{sp}\tau \cdot n)} \quad (2.33)$$

If the polaron density $[n(V)]$ as a function of voltage (or current) is known, the singlet-polaron quenching can be found easily.

2.7.4. The singlet-heat annihilation

In a recent letter [Appl. Phys. Lett. 86, 213506 (2005)], Nakanotani *et al.*⁵⁷ reported the observation of a new phenomenon, termed singlet-heat annihilation (SHA), in organic light-emitting devices (OLED). It was discovered that OLED performance was dependent on the substrate being used. For devices with a better heat-release substrate (sapphire), the roll-off efficiency was better than for devices with substrate with less heat-release capability (glass). The difference was related to the Joule heating of OLED, which quenched the singlet excitons. The physics behind this newly discovered heat related exciton quenching is still not completely understood yet.

In spite of this interesting observation, some doubt remains about the calculation of the SHA rate (Eq. 4 in Ref. 57). The SHA process is written as:

where $^1M^*$ is the singlet excited state, M^+ and M^- are the positively and negatively ionized molecules at the ground-state, respectively.

In addition to this process, the concentration of singlet-molecules becomes:

$$\frac{d[^1M^*]}{dt} = -\frac{[^1M^*]}{\tau} - \frac{k_{sq}}{2}[^1M^*]^2 - k_{th}JV + \frac{J}{4qd} \quad (3.35)$$

where J is the current density, V is the voltage across the OLED, τ is the singlet lifetime, k_{sq} is the rate of singlet-singlet annihilation (SSA), k_{th} is the rate of SHA, q is the electric charge, and d is the total length of the carrier recombination site. The additional SHA is represented in the equation by $k_{th}JV$.

However, from the SHA process in Eq. 3.34, it is clear that the annihilation is proportional to both the singlet concentration and the Joule-heat. So instead of $k_{th}JV$, the additional term introduced by SHA process should be written as $k_{th}[^1M^*]JV$. Replacing the SHA-term in Eq. 3.35 by $k_{th}[^1M^*]JV$, the steady-state quantum efficiency becomes:

$$\frac{\eta_{SH}}{\eta_0} = \frac{J_0}{4J} (1 + \alpha k_{th}JV) \left[\sqrt{1 + \frac{8J}{J_0(1 + \alpha k_{th}JV)^2}} - 1 \right] \quad (3.36)$$

where η_0 is the external quantum-efficiency without annihilations, and J_0 is the characteristic current-density given by $J_0 = \frac{16qd}{\tau^2 k_{sq}}$. It can be seen from Eq. (3.36)

that, a real and positive value of quantum-efficiency can be always obtained for any J , while Eq. (6) in Ref. 57 will result in imaginary value for a large J , which is physically impossible.

By choosing the correct fitting parameters, we are able to fit the experimental curve, as was obtained by Nakanotani *et al.* using $k_{th}JV$ as the SHA term. Figure 2.8 shows the normalized quantum efficiency versus current density curves based on Eq. 3.36 (square), Nakanotani's model from Ref. 57 (triangular), and SSA model without SHA (star), respectively. It can be seen that our model fits well with the fitting-curve calculated in Ref. 57. Both models show that the addition of SHA affects the efficiency roll-off at large current density, where sufficient amount of heat quenches the large singlet-concentration, resulting in significant reduction of the quantum-efficiency. It is worth mentioning that all fitting parameters used in obtaining the square curve in Figure 2.9 [Eq. (3.36)] are the same as those used in Figure 3 in Ref.

57, except for the value of m . In our model, $m = 4$, while $m = 0.7 - 1.4$ in Nakanotani's model.⁵⁷ In fact, our value of m is closer to the m parameter extracted by Nakanotani *et al.* from the J-V characteristics ($m = 5 - 6$).⁵⁷

In conclusion, we have proposed an improved mathematical model explaining the SHA based on the original one proposed by Nakanotani *et al.* We believe our model describes the SHA process more precisely.

Figure 2.9 Normalized quantum efficiency (η_{SH}) vs current density (J) characteristics of OLED, based on SSA (star) and SHA model with rate of $k_{th}JV$ (triangular) and $k_{th}[^1M^*]JV$ (square). The parameters used were $J_0 = 10.3 A/cm^2$, $\tau^2 k_{sq} k_{th} = 1 \times 10^{-10}$, $m = 0.7$ for the triangular plot, $\tau k_{th} = 2 \times 10^{-6}$ and $m = 4$ for the square plot.

2.7.5. The triplet-triplet annihilation

The triplet-triplet annihilation reaction is shown as:⁵⁸

where k_{tt} is the bi-excitonic triplet-triplet quenching rate constant. It only occurs in phosphorescent materials with strong spin-orbit coupling. In some special cases, triplet-triplet annihilation can be used to produce up-conversion fluorescence.⁵⁹ Triplet-triplet annihilation is also responsible for delayed fluorescence in organic semiconductor.⁵⁰

2.8. Energy levels and alignments at organic molecular interfaces

Molecular interfaces play significant role in carrier transport and injection in organic semiconductor. Therefore, before we proceed with discussion on carrier transport and injection in organic semiconductor, here we shall briefly discuss the energetics at the organic molecular interfaces, which are still under intensive investigations.^{60, 61} An extensive review of organic interfaces would be beyond the scope of this thesis. For more comprehensive reviews, readers can refer to Refs. [60, 61].

The organic molecular interfaces can be categorized into two types, the metal-organic⁶² and organic-organic heterojunction interfaces⁶³. The energy alignments in both interfaces are significantly different. We shall firstly discuss energy bandgaps in organic semiconductor in the following.

2.8.1. Transport versus optical bandgaps

In inorganic semiconductor, the energy levels and carrier transports are well described in term of delocalized states and the single band approximation. The transport gap, or the single particle gap, differs by only few meV to the optical gap due to the small exciton binding energy in inorganic semiconductors.

In organic semiconductor, the situation is significantly different. First of all, localization and polarization dominate the carrier transport, and secondly the exciton binding energy is large ($\sim$ eV).⁴⁴ The single molecule energy gap therefore differs significantly with the optical gap of the condensed state. The overall optical gap (E_{Opt}) of organic thin film can be written as:

$$E_{Opt} = E_{Gap} - E_P - E_{Ex} = E_{Tr} - E_{Ex} \quad (2.38)$$

where E_{Gap} represents the single molecule HOMO and LUMO gap, E_P represents the energy lowering due to polarization, E_{Ex} represents the exciton binding energy and E_{Tr} is the transport gap.

The transport gap (E_{Tr}) of an organic film differs from the optical gap by its exciton binding energy. The exciton binding energy, however, varies with organic materials ranging from a few kT to over 1 eV.⁶¹ Therefore it is complicated to determine the true transport levels in organic materials. Throughout this thesis, for simplicity, we assume that the exciton binding energy for various organic materials utilized in this thesis are fixed at $\sim$ 0.9 eV (which is taken from NPB).⁶¹

2.8.2. Metal-organic interfaces

Intermolecular interactions of organic molecules are via the weak Van der Waals forces. It is therefore natural to assume that the metal-organic interface consists of

weakly interacting bonds with no active electronic defects, i.e. without gap states. For this case, the Schottky-Mott limit in the metal-semiconductor interfaces and the Anderson rule for semiconductor heterojunctions must be applied. Recent studies, however, show the opposite, where both of these rules are violated. In most cases, there appear to be a large dipole barrier (up to 1.2 eV) at the interface between the metal and organic.⁶⁴⁻⁶⁶ The origin of these dipoles can be categorized into three classes: 1) interface charge transfer, 2) formation of covalent bond at the interface, and 3) reduction of the metal work function by pillow effect.⁶²

Interface charge transfer

For this case, the metal work function is smaller or equal to the organic electron affinity (EA), causing the electron to be transferred to the LUMO of the interface molecules. This results in formation of dipole barrier at the interface which shifts up the LUMO level of the organic molecule. The dipole barrier stops further electron transfer process to the organic molecules. The electrons that are transferred to the interface organic molecule remain localized at the interface. This results in the absence of band bending of the energy level of the organic molecules, unlike in the case of inorganic semiconductor. A detail study of this phenomena has been reported for the interface of 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI)/Ag.⁶⁷

Formation of covalent bonds

This type of interface occurs in a reactive interface where the energy alignment is determined by the chemical bonds between the reactive metal with the organic molecules. One example of such an interface is the Alq₃/Mg interface.⁶⁴ The Mg work function falls between the HOMO and LUMO levels of the Alq₃ molecule. This means electrons transfer from Mg to Alq₃ is not favorable. The experimental data

show that there is a dipole barrier of approximately 0.5-0.8 eV pointing down from Mg to Alq₃.^{61,64} Studies also show that the interface forms a new Mg:Alq₃ organometallic complex that gives rise to a density of filled states.⁶⁸ These filled states lead to Fermi level pinning at the upper part of the Alq₃ gap. The alignment of the Fermi level results in electrons transfer from the filled states of the organic molecule to the metal, which introduces interface dipole barrier pointing down from metal to organic. The interface dipole reduces the electron barrier from the metal to the organic molecules.

Pillow effect

The work function of a metal is a summation of the bulk chemical potential (μ) and the surface dipole (SD).⁶² The SD contribution is modified by the presence of adsorbates.^{69,70} In the presence of a large adsorbate such as the organic molecule, the repulsion between the electrons of the metal surface and the organic molecules suppress the electron tail of the metal surface (pillow effect) and reduces the metal work function.⁶² This causes a sudden downward shift in the vacuum level from the metal to the organic molecule, resulting in an increase in the hole barrier from metal to the organic material. The pillow effect significantly affects metals with large SD contribution to their work function, e.g. Au. For metal/semiconductor with small SD contribution such as Sm and PEDOT:PSS, only a small dipole barrier is formed at the metal-organic interface.^{62,71}

2.8.3. Organic-organic heterojunction interfaces

Extensive studies of various organic-organic heterojunctions interfaces have been reported in the literature.^{63,72-74} It is discovered that for majority of cases, the

molecular level alignment follows the vacuum alignment rule.^{63,73,74} This is due to the weak interacting nature of the molecules at the heterojunctions. However, when the materials forming the heterojunction have significantly differing ionization energy (IE) and EA, or also called donor/acceptor interface, the vacuum alignment rule is not satisfied.⁷² However, the dipole barrier induced at the organic-organic interface is much weaker than that in the metal-organic interface. Therefore it remains valid, as far as charge injection is concerned, to assume aligned vacuum levels at various organic-organic interfaces for a first order approximation.

2.9. Carrier injection and transport

Organic light-emitting diodes (OLED) have two terminals to inject electrons and holes respectively. Injection and transport of these charges determine the current profile, and hence, the performance of the device. When a device conducts electrical charges, the current profile can be either limited by the interface or bulk properties. Organic semiconductors differ from their inorganic counterparts mainly for the intermolecular (atomic) distance and the force that holds the molecules together. Inorganic semiconductor exists in a crystalline form where atomic orbital strongly overlap each other forming covalent (ionic) bonds between atoms. This strong bonding and the crystallinity of the structure are the basics for the formation of continuous-band states in the material. However, in organic semiconductor, molecules are separated by a relatively large distance, and the overlap between molecular orbitals is weak. Only a weak dipole-dipole interaction, well known as Van der Waals force, holds them together. In contrary to inorganic semiconductor, *charge injection and transport in organic are still not completely understood.*⁷⁵ The difficulty to

develop theoretical models is probably because of the absence of crystallinity and the weak intermolecular overlapping of the organic semiconductor. Another important point is the fact that the single electron approximation does not apply in organic semiconductor. In the presence of charge carrier, molecules deform and the molecular energy levels shift. Furthermore the charge carriers are localized. However, numerous studies on the current injection of the organic semiconductor show many similarities with the well studied, theoretically and experimentally, inorganic semiconductor and insulator. Here we summarized various mechanisms used to explain carrier injection and transport in organic semiconductor reported in literature.

2.9.1 Charge injection from metal to semiconductor (interface-limited)

2.9.1.1 Fowler-Nordheim tunneling

Fowler-Nordheim (FN) tunneling, also known as cold or field emission refers to a quantum mechanical process where electrons are able to surpass a relatively high energy potential barrier. The theoretical work was developed to consider the tunneling of electrons from metal to crystalline material or vacuum where electrons exist in continuous wave-state. Although in principle, the theory is applicable only to inorganic semiconductors, a study on organic semiconductor has also shown a similar characteristic.⁷⁶ The FN current has a form of:

$$J = \frac{3e^2 F^2}{8\pi h \Delta} \exp\left\{\frac{-8\pi\sqrt{2em}\Delta^3}{3hF}\right\} \quad (2.39)$$

where e is the electron charge, F is the electric field inside the material, h is the Planck constant, m is the effective mass of electron, Δ is the energy potential barrier. If carrier injection follows this expression, then the plot of $\ln(J/F^2)$ forms a straight

line with $(1/F)$. The system used in this study was ITO/ MEH-PPV/Ca, where MEH-PPV is poly(2-methoxy,5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene).⁷⁶

2.9.1.2 Richardson-Schottky thermionic emission

Richardson-Schottky (RS) emission is also known as thermionic emission because the electron is released from the metal thermally. When first developed by Richardson, the effect of electric field was neglected and the amount of current was only dependent on the temperature of the material. Later on, Schottky considered the effect of barrier-lowering at the presence of electric field. For RS emission, the typical electric field is much smaller than that in FN emission. The current profile of RS emission can be expressed as:

$$J = \frac{4\pi em}{h^3} (kT)^2 \exp\left\{\frac{-e(\Delta - \Delta')}{kT}\right\} \quad (2.40)$$

where k is the Boltzmann constant, T is the temperature of the metal and Δ' is the term added by Schottky to include the effect of barrier reduction by the electric field:

$$\Delta' = \sqrt{\frac{eF}{4\pi\epsilon}} \quad (2.41)$$

ϵ is the dielectric permittivity of the material. For this type of emission, the plot of $\ln(J/T^2)$ versus $\sqrt{F}$ is a straight line. Although the characteristic of the RS emission has been observed in organic semiconductor,⁷⁷ the exact value of the constant does not really agree with the calculated one. In fact, they differ by as much as ten-fold in magnitude. In general, however, the RS equation is usually used in semi-empirical form:

$$J = AT^2 \exp\left\{\frac{-e(\Delta - \Delta')}{kT}\right\} \quad (2.42)$$

where A is known as the modified Richardson's constant obtained experimentally. The organic system ITO/TPD/Al, where TPD is N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, was shown to follow the RS characteristic.⁷⁷

2.9.1.3 Emtage and O'Dwyer thermionic effect in insulator

RS emission describes a one-way electron emission from metal into the conduction band of a material. However, when the electron mobility in a material is very low, the electron density in the bulk becomes relatively large, causing a backflow of electrons to the metal. Emtage and O'Dwyer (EO) considered the effect of space charge and backflow by diffusion to obtain the RS effect in an insulator.⁷⁸ EO solved the drift-diffusion equation where the solutions involve an integral which can be explicitly evaluated in the limits of high and low field. The low field solution is:

$$J = N_0 e \mu F \exp\left(\frac{-e\Delta}{kT}\right) \quad (2.43)$$

where $N_0 = 2(2\pi m k T / h^2)^{3/2}$ and μ is the electron mobility. The high field solution is:

$$J = N_0 \mu \left(\frac{kT}{e}\right)^{1/2} (16\pi e F^3)^{1/4} \exp\left(\frac{-e(\Delta - \Delta')}{kT}\right) \quad (2.44)$$

2.9.1.4 Work of Scott and Malliaras

Although the significant influence of backflow into metal was highlighted by EO, its presence and term are not explicitly clear from the EO solution. The detailed-balance of electrons flow at the interface was exploited by Scott and Malliaras (SM) to determine the equilibrium current flow.⁷⁹ The net current, that was calculated by subtracting the thermal-injection with the recombination showed a result similar to that of the EO solution. In their work, the recombination or return flow that originated from the image-force attraction of the charge was clearly indicated. Recombination is assumed to be limited at a critical distance (R_c) from the metal where the image potential exceeds the thermal energy. Using a detailed-balance approach at R_c , SM were able to obtain a closed-form for the current:⁷⁹

$$J = 4N_0e\mu F(\zeta)^2 \exp\left(\frac{-e\Delta}{kT}\right) \exp(f^{1/2}) \quad (2.45)$$

where ζ is a function of the reduced electric field ($f=e^3F/4\pi\epsilon k^2T^2$):

$$\zeta = f^{1/2} + f^{-1/2} - f^{-1}(1 + 2f^{1/2})^{1/2} \quad (2.46)$$

2.9.1.5 Phonon-assisted charge hopping from metal to organic molecules

All the models described above are based on the presence of continuous electron states in vacuum or in crystalline structure. However, in organic semiconductor, electrons are highly localized on their respective molecule, and the applicability of those injection theories is questionable. In molecular materials, ballistic transport is not possible, instead, electrons move from site-to-site via thermal hopping mechanism. One model that has been used to describe the rate of transition of electron in this type of material was described by Emin⁸⁰ using the molecular crystal model

developed by Holstein.^{81,82} In this model, a one-dimensional chain of molecules is considered. Electrons from one molecule are able to transport to another molecule by a phonon-assisted process, i.e. the phonon perturbs the chain molecules to enable electrons transfer. This phonon assisted charge movement in a molecular crystal is also known as polaron hopping. The electron transfer rate from metal to organic molecules may also be governed by the same mechanism.

The hopping rate of a polaron from one energy site g to another g' with energy difference of Δ is given by:

$$R(\Delta) = \left(\frac{J_{g,g'}}{\hbar} \right)^2 \left(\frac{2\pi}{\omega_0} \right) \exp(-2S) \exp\left(-\frac{e\Delta}{2kT}\right) \times \sum_{e\Delta/\hbar\omega_0=-\infty}^{\infty} \left\{ I_{e\Delta/\hbar\omega_0} \left[(2E_b/\hbar\omega_0) A_n \operatorname{csch}\left(\frac{\hbar\omega_0}{2kT}\right) \right] - \delta_{e\Delta/\hbar\omega_0,0} \right\} \quad (2.47)$$

where $S = (E_b/\hbar\omega_0) \coth(\hbar\omega_0/2kT)$, $I_{e\Delta/\hbar\omega_0}$ is a modified Bessel function of order $e\Delta/\hbar\omega_0$; $J_{g,g'}$ is the electronic transfer integral, which is a measure of the molecular overlap between site g and g' ; ω_0 is the optical phonon frequency for zero wave vector; and E_b is the polaron binding energy in the limit of $J_{g,g'} = 0$ (i.e. no electronic overlap between adjacent molecules). The phonon bandwidth determines the relaxation amplitude coefficients A_n . We will examine this equation in the limits of high and low temperatures. First, the low temperature region refers to $\hbar\omega_0/2kT \rightarrow \infty$, accordingly $\operatorname{csch}(\hbar\omega_0/2kT) \cong 2\exp(-\hbar\omega_0/2kT)$ approaches zero. Thus, the argument of the Bessel function is sufficiently small so that,

$$I_{e\Delta/\hbar\omega_0}(x) \approx x^{\left| \frac{e\Delta}{\hbar\omega_0} \right|} / \Gamma\left(\left| \frac{e\Delta}{\hbar\omega_0} \right| + 1\right) \quad (2.48)$$

and $S \approx (E_b / \hbar \omega_0)$. Here Γ is the gamma function. In this low temperature limit, the transition rate becomes:

$$R(\Delta) = \left(\frac{J_{g,g'}}{\hbar} \right)^2 \left(\frac{2\pi}{\omega_0} \right) \exp\left(-\frac{2E_b}{\hbar \omega_0} \right) \exp\left(-\frac{e(\Delta + |\Delta|)}{2kT} \right) \\ \times \frac{[2E_b / \hbar \omega_0]^{\left| \frac{e\Delta}{\hbar \omega_0} \right|}}{\Gamma\left(\left| \frac{e\Delta}{\hbar \omega_0} \right| + 1 \right)} \sum_{e\Delta / \hbar \omega_0 = -\infty}^{\infty} A_n \quad (2.49)$$

This expression is similar to that describing the transition rate developed by Miller and Abraham for conduction by impurities in a semiconductor.⁸³ The rate is an asymmetrical function of energy, where transition to a site with higher energy results in an exponentially decreasing rate, while transition to a lower energy site occurs at a constant rate. As in the work of Miller and Abraham, the relation between the transition rate and the inter-site distance is indicated by the term $J_{g,g'}$. It can be proven that for hydrogen-like wave function, the overlap integral $J_{g,g'}$ exponentially decays with distance:

$$J_{g,g'} \propto \exp(-\gamma r_{g,g'}) \quad (2.50)$$

where $r_{g,g'}$ is the distance between the site and γ is the inverse bohr (localization) radius. For comparison, the complete form of Miller and Abraham transition rate is:

$$R = \nu_0 \exp(-2\gamma r_{g,g'}) \exp\left(-\frac{e(\Delta + |\Delta|)}{2kT} \right) \quad (2.51)$$

where ν_0 is called the attempt-to-jump frequency.

Secondly, for high temperature limit ($kT \gg \hbar\omega_0/3$), the transition rate is rather complicated. However, it has been shown by Emin that in this region the transition rate becomes:

$$R(\Delta) = \frac{(J_{g,g'})^2}{\hbar} \left(\frac{\pi}{2E_b kT} \right)^{1/2} \exp \left(-\frac{E_b}{2kT} \left(1 + \frac{\Delta}{2E_b} \right)^2 \right) \quad (2.52)$$

which has the same form as the expression derived by Marcus for electron transfer with molecular reorganization energy equal to $2E_b$.⁸⁴ The phonon-assisted polaron transition derived by Emin can be considered as a generalized expression for electron transfer in a molecular-crystal material.

2.9.1.6 Gaussian disorder hopping model from metal to organic molecules

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the two states responsible for the hole and electron transport in organic material, respectively. They are analogous to valence and conduction band in inorganic semiconductor. However, because of the weak intermolecular overlap, HOMO and LUMO states do not form bands. Small energy broadening is expected because of the dipole-dipole interaction between molecules. This broadening has been considered theoretically by Young, who found that the dipole-dipole interaction results in a Gaussian shaped density of state with width of σ .⁸⁵

$$\sigma^2 = \sigma_0^2 + x \left(7.04 \frac{P}{a^2 \epsilon_r} \right)^2 \quad (2.53)$$

where σ_0 is the width of the density of state without the presence of dipolar molecules, a is the intermolecular distance, ϵ_r is the dielectric constant, P is the dipole moment of the dipolar molecule, and x is the fraction dipolar molecules. Carrier hopping occurs from the metal Fermi level to the molecule Gaussian-broadened state with a rate that is determined by Eq (2.51).^{86,87} This model fits well with the experimental result of the Al/Alq₃/Mg system at various temperatures, where Alq₃ is tris(8-hydroxy-quinolino) aluminium.⁸⁸

Figure 2.10 Illustration of carrier injection from the metal to the Gaussian state of the organic molecule from Ref. 87.

2.9.1.7 Interface-limited injection from broaden interface state to bulk state

Interfaces of organic semiconductors play an important role in determining current injection. Therefore, surface science investigations of metal and organic materials are crucial to understand carrier injection. Unfortunately, the energy alignment at this interface is not well understood yet. Several studies have shown that

the Schottky-Mott rule of vacuum level alignment in metal-organic interface is not valid.^{72,89,90} The violation of the Schottky-Mott rule further complicates the determination of the energy barrier experienced by the carrier, where for the former the barrier is easily obtained by comparing the bulk properties (ionization potential (IP) or electrons affinity (EA)) of each material. It has been shown that at metal-organic interface, there exists a dipole barrier that shifts the vacuum level of the material.⁷² The origin of this dipole barrier has been discussed by charge transfer, formation of covalent bond and molecules adsorbates (see section 2.7).⁶²

The effect of the dipole barrier to the injection of the carrier was considered by Baldo and Forrest.⁹¹ The dipole barrier, which is formed by aligned molecules that have intrinsic dipole moments, causes an increase in the width of the Gaussian state at the interface. By calculating the effect of molecule alignment at the interface, Baldo and Forrest have shown that the increment is four times of the bulk of the material. The carrier injection to the bulk is limited by this broaden interface state. This mechanism of carrier injection has been shown to produce power-law current profiles.

Figure 2.11 Illustration of carrier injection from the interface state (metal-organic) to the bulk state from Ref. 91.

2.9.2 Bulk-limited transport

When the energy barrier between electrode and semiconductor (insulator) is small enough, the current profile is not limited by their interface, but by bulk properties. Here we consider only two types of bulk-limited conduction that have been widely applied in OLED.

2.9.2.1 Space charge limited

In the limit when charge concentration in the material becomes so large that the field is altered, the carrier transport is limited by the space-charge effect. It can be shown that for this type of transport, the current follows:

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3} \quad (2.54)$$

where d is the thickness of the layer, μ is the carrier mobility and V is the applied voltage. For space-charge limited current, the thickness and the field do not relate linearly. This means that, for a fixed current, the value of the applied voltage does not increase linearly with the device thickness. The presence of this type of transport has been observed in OLED.⁹²

The mobility of carriers in organic material is electric field (E) dependent, following the Poole-Frenkel behavior:^{93,94}

$$\mu = \mu_0 \exp\left(-\frac{\Theta}{kT}\right) \exp(\gamma \sqrt{E}), \quad (2.55)$$

where μ_0 is a temperature-independent prefactor, Θ is the activation energy, T is the temperature, and γ is the Poole-Frenkel factor, which is written as $\gamma = \beta \left(\frac{1}{kT} - \frac{1}{kT_0} \right)$, where β is a constant.

2.9.2.2 Trap-filled limited

In the presence of a lot of neutral carrier traps, the electrons are more likely to fill the traps than to contribute to transport. Those trapped electrons deter the electric field inside the material. If the trap density is large, the effect can be significant. For exponentially distributed trap density, the current follows:

$$J = a \frac{V^{m+1}}{d^{2m+1}} \quad (2.56)$$

where a is a constant that depends on the material properties, and $m=T_l/T$, where T_l is the trap characteristic temperature and T is the temperature of the material. The relation between the voltage and device thickness is non-linear. This mechanism has been attributed to carrier conduction in OLED.^{95,96}

Materials and characterization of organic light-emitting diode

3.1. Organic materials for OLED

Based on functionality, the organic materials utilized for OLED can be categorized into various classes: hole transporting or injecting, hole blocking, electron transporting, host, and guest or dopant materials.

Hole transporting or injecting materials

Hole transporting or injecting materials are organic material which has a preference to transport hole than electron carrier. Generally these materials have a shallow HOMO level and possesses a high hole mobility to facilitates both hole injection and transportation. Some examples of organic semiconductors that belong to this class are NPB, m-MTDATA, and CuPc. Their molecular structure and properties are shown in Table 3.1.

Hole blocking materials

As the name implies, these materials block hole transport. The ideal hole blocking materials are certainly those that have deep HOMO level to block injection of hole. In term of mobility, this type of material ideally should have low hole mobility. In this thesis we use BCP as the hole blocking material.

Electron transporting materials

To inject and transport electron, this type of organic semiconductor should possess a relatively deep LUMO level. Deep LUMO level will ease the electron injection to the materials. Certainly the electron mobility must be relatively high. In this thesis we utilize Alq₃ as the electron transporting material.

Host materials

Host material provides a venue for electron and hole recombination. So it is ideal for this material to be ambipolar in carrier transport. The band gap should also be large (emit in UV) to facilitate sensitization by guest emitting in the visible range.

Guest or dopant materials

Guest or dopant materials are usually incorporated in the host material in a small amount. It has a function as light emitter. Ideally, it should have very high quantum yield. Carrier mobility is not so important for this material. As the emission process usually involves Förster transfer from the host to the guest materials. It is important that the emission spectrum of the host material overlaps with the absorption spectrum of the guest material.

Table 3.1 Various types of organic materials used for OLED.

TYPE	NAME	CHEMICAL STRUCTURE	$\lambda_{\text{ABS}}, \lambda_{\text{PL}}$ (nm)	HOMO (eV)	LUMO (eV)* [HOMO + E_{Opt} + E_{Ex} (~0.9 eV)]
Hole Transporting or Injecting Materials (HTL/HIL)	N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine [NPB]		339, 420	-5.2 ⁹⁷	-1.2
	4,4',4''-Tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine [m-MTDATA]		341, 425	-5.1 ⁹⁸	-1.0
	Copper-phthalocyanines (CuPc)		-, -	-5.2 ⁶¹	-2.7

Hole Blocking Material (HBL)	2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline [BCP]		277, 387	-6.4 ⁶¹	-2.0
Electron Transporting Material (ETL)	Tris(8-hydroxy-quinolato)aluminium [Alq ₃]		259, 532	-5.8 ⁶¹	-2.2
Host Material	4,4'-Bis(carbazol-9-yl)biphenyl [CBP]		292, 369	-6.3 ⁶¹	-2.3

Fluorescent dopants	4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran [DCM]		468, 620		
	4,4'-Bis(9-ethyl-3-carbazovinylenes)-1,1'-biphenyl [BCzVBi]		384, 438		
	4-(Dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran [DCJTb]		501, 602		

Phosphorescent dopants	Tris(2-phenylpyridine) iridium(III) [Ir(ppy) ₃]		282, 513		
	Tris(1-phenylisoquinoline) iridium(III) [Ir(piq) ₃]		324, 615		

* LUMO level is estimated using Eq. 2.38 assuming exciton binding energy of 0.9 eV

3.2. Fabrication of OLED

The fabrication of OLED starts with cleaning of the ITO-glass substrate. The cleaning sequence is as follows. The ITO-glass was firstly cleaned with a special chemical of decon 90 diluted with water, then loaded into an acetone basket for ultrasonication treatment for about 30 minutes, subsequently, the ITO-glass was loaded into an alcohol basket to dissolve the residue acetone left for 30 minutes by ultrasonication treatment. The ITO-glass was then washed with de-ionized water to dissolve the alcohol. It was finally dried inside a 110 C oven for a couple of hours.

Figure 3.1 shows the schematic diagram of the fabrication facilities. The fabrication chamber consists of three sections which are separated by vacuum valves. The first section is dedicated for plasma treatment. The cleaned ITO-glass is loaded into this chamber for oxygen plasma treatment. To ignite the plasma, a 15 Pa oxygen pressure was used with a 1.5 kV DC discharge voltage. The samples were treated with plasma for approximately 2-3 minutes. Oxygen plasma treatment has been shown to improve smoothness and increase the work function of the ITO to improve the capability of hole injection.⁹⁹ The plasma chamber is equipped with a two-stage pumping system which can pump the vacuum to 2×10^{-4} Pa.

The next section adjacent to the plasma chamber is the main deposition chamber. The samples treated with oxygen plasma are transferred into the main chamber without breaking the vacuum. The main chamber is equipped with ten sources, each of which is heated by a tantalum heater. The opening and closing of shutters control the deposition sequences. The deposition rate and thickness is measured by a crystal sensor, quartz oscillator combined with a frequency meter. In order to obtain large-area uniformity and abrupt interfaces, the chamber is equipped with three sets of

shutters, besides the shutters for each crucible, there is also a big shutter between the crucibles and substrates, and a small shutter under each substrate. The thickness/rate crystal sensor is installed in the center of the substrate holders, which is designed in planetary rotation, and the rotation rate can be adjusted. Four samples with the same/different structure can be fabricated during a single run.

The final section of the chamber is dedicated for device encapsulation with glove box. The OLED can be transferred directly to the glove-box in nitrogen environment. The glove box is also equipped with UV lamp for curing purpose.

Figure 3.1 A schematic diagram of the clustered fabrication facilities.

3.3. Characterization of OLED

Organic light-emitting diode is a device that converts electrical energy into light, or photons. The methodology on measurement of photon is called radiometry. Basic units of the radiometry such as the radiant energy, radiant power, irradiance, radiant intensity, and radiance are tabulated in Table 3.2.¹⁰⁰ Figure 3.2 shows the illustration of the explanatory notes in Table 3.2.

For display applications one needs to consider the human eye response which is only capable of detecting light in the wavelength range of 380-780 nm (visible spectrum). The matching of brightness with respect to the human eye response is the fundamental operation in photometry. Table 3.3 shows basic photometric quantities.¹⁰⁰ The sensitivity of the human eye is characterized by the luminous efficacy $[V(\lambda)]$ which can be divided into two categories, the photopic and scotopic. Figure 3.3 shows the photopic and scotopic response of the retina. Photopic (day vision) corresponds to the sensitivity of the cone receptors in the retina. Meanwhile the scotopic (night vision) refers to the sensitivity of the rods receptors in the retina.

Term	Symbol	Defining Equation	Explanatory Notes and Formulae		Units
Radiant energy					$J \text{ (joule)}$
Radiant power	P_e		$d^2 P_e = L_e \frac{dA_1 \cos \varepsilon_1 dA_2 \cos \varepsilon_2}{r^2}$		$J \cdot s^{-1} = W \text{ (watt)}$
Irradiance	E_e	$E_e = \frac{dP_e}{dA_2}$	dA_1 = surface element of source dA_2 = surface element of receiver		$W \cdot m^{-2}$
Radiant intensity	I_e	$I_e = \frac{dP_e}{d\omega_1}$	$d\omega_1$ = element of solid angle with apex (1) at surface of source $d\omega_2$ = element of solid angle with apex (2) at surface of receiver		$W \cdot sr^{-2}$
Radiance	L_e	$L_e = \frac{d^2 P_e}{dA_1 \cos \varepsilon_1 d\omega_1}$ $= \frac{d^2 E_e}{dA_2 \cos \varepsilon_2 d\omega_2}$ $= \frac{d(E_e)_n}{d\omega_2}$	ε_1 = angle between given direction (1)-(2) and the normal n_1 of dA_1 ε_2 = angle between given direction (1)-(2) and the normal n_2 of dA_2	$dA_1 \cos \varepsilon_1 = dA_1$ orthogonally projected on plane perpendicular to given direction (1)-(2) $dA_2 \cos \varepsilon_2 = dA_2$ orthogonally projected on plane perpendicular to given direction (1)-(2)	$W \cdot m^{-2} \cdot sr^{-2}$

Table 3.2 Basic radiometry units. Adapted from Ref. 100.

Term	Symbol	Defining Equation	Explanatory Notes and Formulae	Units
Luminous flux (or power)	F_v (or P_v)	$F_v = K P_e$ $F_v = K_m \int_{\lambda} P_{e\lambda} V(\lambda) d\lambda$	P_e : Radiant flux (W) K : Luminous efficacy ($lm \cdot W^{-1}$) K_m : Max. luminous efficacy ($683 lm \cdot W^{-1}$)	lm
Luminous intensity	I_v	$I_v = \frac{dF_v}{d\omega_1}$	$d(E_v)_n$: Illuminance on dA_2 normal to the direction (1)-(2)	cd $(lm \cdot sr^{-1})$
Luminance	L_v	$L_v = \frac{d^2 F_v}{dA_1 \cos \varepsilon_1 d\omega_1}$ $= \frac{dI_v}{dA_1 \cos \varepsilon_2}$ $= \frac{d^2 E_v}{dA_2 \cos \varepsilon_2 d\omega_2}$ $= \frac{d(E_v)_n}{d\omega_2}$		$cd \cdot m^{-2}$ $(lm \cdot m^{-2} \cdot sr^{-1})$
Illuminance	E_v	$E = \frac{dF_v}{dA_2}$	$V(\lambda)$: Relative photopic luminous efficiency function	$(lm \cdot m^{-2})$
Luminous efficacy function	$K(\lambda)$	$K(\lambda) = K_m V(\lambda)$		

Table 3.3 Basic photometry units. Adapted from Ref. 100.

Figure 3.2 Illustration of explanatory notes in Table 3.2 and 3.3. Adapted from Ref. 100.

Figure 3.3 Photopic and scotopic human eye response

Colorimetry is a branch of color science concerns with specifying numerically the color of a physically defined visual stimulus. Colors can be constructed based on linear mixture of three monochromatic beams of R, G and B whose radiant powers have been suitably adjusted. The Commission Internationale de l'Eclairage (CIE) color-matching functions $\bar{x}, \bar{y}, \bar{z}$ are shown in Figure 3.4. correspond to the three monochromatic colors. Quantitatively chromaticity of a given color can be assigned with a color coordinate (x , y , and z), which is determined by integral summation of the spectral $S(\lambda)$ with the color-matching function for an equal power:

$$x = \frac{\int S(\lambda) \bar{x}(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (3.1)$$

$$y = \frac{\int S(\lambda) \bar{y}(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (3.2)$$

$$z = \frac{\int S(\lambda) \bar{z}(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (3.3)$$

By convention, chromaticity is stated in term of x and y only, since $x+y+z=1$. An example of CIE coordinate diagram is shown in Figure 3.5.

For white color, there are two more important parameters that can be used to define the whiteness numerically, they are the color rendering index (CRI) and correlated color temperature (CCT). CRI measures similarity of the color perceived after reflection from an object in comparison with reflection from standard white source from the blackbody radiation. The index of CRI has been scaled to 100 for a perfect matching. CCT measures the correlated temperature if the color is produced by blackbody radiation.

Figure 3.4 Color matching function of CIE

Figure 3.5 CIE Coordinate

External Quantum Efficiency (EQE)

The figure of merit of organic light-emitting diode is measured by their capability to emit photon per injected carrier, which is called the quantum efficiency. As part of the light created is trapped in substrate and quenched by surface plasmon, a more relevant figure of merit used is the external quantum efficiency. It is the measure of the effective photon radiated to the free space per injected carrier. The overall external quantum efficiency can be written as:

$$\eta_{ext} = \eta_{int} \gamma_{e-h} \chi_{s/t} \phi_{opt} \quad (3.4)$$

where η_{int} is the internal quantum efficiency, γ_{e-h} is the current balance factor, $\chi_{s/t}$ is the singlet and triplet ratio (for fluorescence), and ϕ_{opt} is the factor of optical output coupling.

Current efficiency is a measure of luminance per injected 1 A current viewed perpendicularly (cd/A). Power efficiency is a measure of luminous flux per watt of electrical power (lm/W). EQE can be measured indirectly by assuming a Lambertian emission pattern and calculating from the current efficiency and emission spectral of the device.

Balancing the electron-hole current

4.1. Introduction

As discussed in chapter three, the balance of current injection and transport is an important factor that determines the performance of the device. In a typical OLED, the hole experiences a smaller barrier compared to electron,⁹⁷ moreover hole mobility is an order of magnitude higher than that of electron.¹⁰¹ For example, in a typical ITO/NPB/Alq₃/Mg:Ag structure, where NPB has a hole mobility of 10^{-5} cm²/Vs, and Alq₃ has an electron mobility of 10^{-6} cm²/Vs, the hole experiences an overall energy barrier of around 1.0-1.7 eV (depends on the ITO work function) from ITO to Alq₃, while electron needs to overcome a larger barrier of 2 eV from Mg to NPB.⁹⁷ Numerous strategies have been reported in order to improve the balance of carriers, such as anode^{8,102} or cathode¹⁰ modification, hole blocking,¹⁰³ doping,¹¹ and annealing¹⁰⁴.

Cathode modification and doping, for example, have been shown to increase electron injection, so as to improve the electron-hole balance. As a result, the total current and efficiency can be improved simultaneously. On the other hand, modification of the anode, for example, has been shown to improve the current injection but sacrifices the efficiency, or vice versa. Insertion of a HBL between HTL and ETL has also been shown to improve the efficiency but not the current.¹⁰³

In this chapter, we shall discuss three different approaches used to increase the device efficiency. The first is the usage of CuPc as a buffer layer on the ITO layer for improved performance. The effect of oxygen plasma treatment is also investigated. The second approach is by insertion of a thin HBL to impede the hole current to balance the carrier flux in the device. In the last part an extension of the second approach where instead of using the hole-blocking layer, we utilized an electron transporting layer to block the hole.

4.2. Role of CuPc and oxygen treatment in balancing current injection

4.2.1. Introduction

The role of CuPc in Alq₃-based OLED inserted between ITO and HTL has been subjected to controversies.¹⁰⁵⁻¹¹¹ Many reported the role of CuPc as a hole-injection layer, which improves the current injection,¹⁰⁵⁻¹⁰⁷ while other reports showed that insertion of CuPc layer impeded hole injection from ITO anode, resulting in reduced total current.¹⁰⁸⁻¹¹⁰ Applying CuPc as a HBL has been able to improve device stability and lifetime.¹⁰⁸⁻¹¹⁰ The decrease in hole-current results in more balanced electron-hole injection, cationic Alq₃ is prevented, thus the lifetime is increased.¹¹⁰ Some reports have tried to explain the discrepancies on the role of CuPc interlayer in OLED.^{105,106,111} Previously a systematic study on CuPc has been presented, in which, devices with different CuPc thicknesses were investigated.¹⁰⁷ However, their studies also suggest that CuPc acts as a hole-injection layer.

In this section, we shall present the detail analysis on the role of CuPc in OLED by a comparative study, in which we fabricated four identical OLEDs, except for CuPc thickness, in the same run to guarantee a meaningful comparison.

4.2.2. Theory of carrier injection and transport

In order to understand the effect of CuPc interlayer on the current profiles, we need to distinguish the transport and injection mechanism between devices with CuPc and without CuPc interlayer, particularly for the holes. For devices without CuPc interlayer, basically, four layers (anode, HTL, ETL and cathode) determine the carrier transport and injection. Holes, in particular, are injected from anode side (ITO) into the HTL (NPB). The injection process at this interface has been studied by analytic and numerical-simulation techniques^{105,106,86,87}. Inside the NPB layer, the hole is then transported via inter-molecular hopping or known as Miller-Abraham hopping (Eq. 2.50). Upon reaching the ETL (Alq₃), holes need to overcome the energy barrier at the NPB/Alq₃ interface to further form excitons with the electrons so as to enable fluorescence. The injection mechanism at NPB/Alq₃, or in general, at the organic-organic interface (OOI) has been studied previously by Arkhivop *et al.*¹¹²

For devices with CuPc interlayer, the hole-injection is a bit modified by the presence of one additional organic layer. Holes are injected from the ITO side into the CuPc layer to further hop into the CuPc/NPB interface. At the ITO/CuPc interface, the value of the energy barrier is lower than that at ITO/NPB.^{106,111} Furthermore the hole's hopping-frequency inside CuPc layer is about an order higher than that in NPB,¹⁰⁵ therefore, higher hole-injection is expected. However, with CuPc interlayer, hole experiences an additional OOI with an energy barrier equals to the difference

between that at ITO/CuPc and ITO/NPB interfaces. Examination of the injection mechanism at the CuPc/NPB interface, an additional OOI compared to the standard device without CuPc, is crucial to understand the current-profile. To do this, we adopt the approach taken by Arkhivop *et al.*¹¹²

Carrier injection at OOI can be modeled with a two-steps process: carrier injection from CuPc into NPB layer continued by carrier transport in the bulk NPB layer. Hole injection from CuPc to NPB is determined by the energy barrier at the interface and the width of the density of states (DOS) of the organic layer. For the transport in the bulk-side, the return-flow of carrier must be considered. The total current is calculated by integrating the transition rate from the CuPc to the NPB layer with inclusion of the return-current. Considering the two-step process, the current density can be written as:¹¹²

$$j = ev_0 \int_a^\infty \exp(-2\gamma x) \left\{ \int_{-\infty}^\infty \int_{-\infty}^\infty \Theta(\Delta + E - E' - eFx) \right. \\ \left. \times h_{CuPc}(E') \times g_{NPB}(E) \times [1 - \Gamma(x, E)] dE' dE \right\} dx, \quad (4.1)$$

where v_0 is the inter-molecular hopping frequency, e is the electron charge, a is the average intermolecular distance, Δ is the interface barrier height, γ is the inverse localization radius, F is the electric field at the NPB layer, $\Theta(E)$ describes the first-jump probability from CuPc to NPB:

$$\Theta(E) = \begin{cases} 1, & E < 0 \\ \exp\left(-\frac{E}{kT}\right), & E > 0, \end{cases} \quad (4.2)$$

$h_{CuPc}(E)$ represents the hole-occupancy at the CuPc layer:

$$h_{CuPc}(E) = \frac{N_t}{\sqrt{2\pi}\sigma_{CuPc}} \exp\left(-\left(E - \frac{\sigma_{CuPc}^2}{k_B T}\right)^2 \frac{1}{2\sigma_{CuPc}^2}\right), \quad (4.3)$$

where N_t is the hole density at CuPc layer and σ_{CuPc} is the DOS width of CuPc,

$g_{NPB}(E)$ is the normalized Gaussian DOS of the NPB layer:

$$g_{NPB}(E) = \frac{1}{\sqrt{2\pi}\sigma_{NPB}} \exp\left(-\frac{E^2}{2\sigma_{NPB}^2}\right), \quad (4.4)$$

with σ_{NPB} is the DOS width of NPB, and $\Gamma(x, E)$ is the probability of the carrier to jump-back to the initial organic layer (CuPc):¹¹²

$$\ln(\Gamma(x, E)) = -2\pi N_t \int_0^x r^2 dr \int_0^1 dz \int_{-\infty}^{E+2kT(x-r)+eFrz} g_{NPB}(E'') dE'', \quad (4.5)$$

where $z = \cos \theta$ with θ being the angle between the field and the jump direction,

Figure 4.1(a) shows the injection current, assuming zero DOS-width of CuPc, as a function of electric field with return-current included (solid line) and excluded (dashed line). We assume the energy barrier to be ~ 0.5 eV.¹¹¹ The current curve with the return-current included (solid line) has a steeper profile compared with the curve without return-current (dashed line). The ratio of return-current and injected current is also plotted in Figure 4.1(a). It is clear that at low-field region, the return-current is comparable with the injected-current. The return-current become less significant at high-field region. For the device with CuPc, the return-current occurs at two interfaces: the ITO/CuPc and CuPc/NPB. Since this return-current is field dependent, its existence may result in a steeper current profile.

In the above analysis, the width of the DOS of CuPc layer is assumed to be zero. Here we discuss the consequence of a non-zero DOS width of CuPc. The DOS

broadening inside of amorphous material is induced by the randomly oriented dipole moment (Eq. 2.52).⁹¹ This broadening affects the carrier occupancy inside the material. Eq. 4.3 clearly shows that, with DOS-width of σ_{CuPc} , holes are more likely to occupy state $\sigma_{CuPc}^2 / k_B T$ above the transport level, hence, the effective hole-barrier becomes $(\Delta + \sigma_{CuPc}^2 / k_B T)$. Figure 4.1(b) shows the carrier-injection at CuPc/NPB interface as a function of electric field for CuPc DOS width of 0.04, 0.06, 0.08 eV, respectively. NPB DOS width is fixed for all cases. It can be observed that the current reduces with the increment of DOS width. As the DOS is broaden, the carrier experiences higher barrier at the CuPc/NPB, therefore results in less current.

4.2.3. Experimental

The device has a multilayer structure of ITO/ CuPc (varying thickness)/ NPB (100 nm)/ Alq₃ (100 nm)/ Mg:Ag (300 nm), where NPB is the HTL, and Alq₃ is the emissive as well as ETL. It is worth mentioning that, except for the thickness of CuPc layer, all other parameters of the four devices fabricated during each run are identical (the same evaporation process). This avoids the uncertainties in comparing devices fabricated with different evaporation processes. To study the hole injection as a function of oxygen content at the CuPc and NPB interface, two oxygen plasma treatments of ITO substrates were used: (1) 2.5 mins plasma treatment under an oxygen pressure of 11 Pa, (2) 3.5 mins plasma treatment under an oxygen pressure of 15 Pa.

Figure 4.1(a) Calculated current density versus electric field when return-flow is included (solid line) and when return-flow is excluded (dash line). The ratio of the return-flow current with the initial current (excluding the return-flow) is also shown. Parameters for calculation are $a=0.6 \text{ nm}$, $\Delta=0.5 \text{ eV}$, $\sigma_{\text{NPB}} = 0.08 \text{ eV}$, $\sigma_{\text{CuPc}} = 0 \text{ eV}$, $\gamma=5 \text{ nm}^{-1}$, $T=300 \text{ K}$, $v_0=10^{12} \text{ s}^{-1}$ and $N_I=10^{21} \text{ cm}^{-3}$; (b) Calculated current injection for non-zero CuPc DOS width as a function of electric field. Current injection for CuPc DOS width of 0.04 eV , 0.06 eV and 0.08 eV are shown in solid line, dash line and dot-dash line, respectively.

4.2.4. Results and discussion

Effect of CuPc thicknesses

Figure 4.2(a) shows current density versus voltage (J-V) characteristics for four samples with varied CuPc thickness of 0, 10, 20, 30 nm, respectively. The ITO substrates were treated by oxygen plasma for 2.5 mins with a pressure of 11 Pa. Steeper profiles are observed for all devices with CuPc interlayer between ITO and NPB layers. It can be seen that, at low electric field region, current seems to be impeded more than at high electric field region. As discussed in theory section, the addition of CuPc layer is expected to give a steeper current profile because of the field-dependent return-current occurred at the CuPc/NPB interface. This return-current is significant at low field but minute at high field.

From Figure 4.2 (a) it can be seen that the current density increases with CuPc thickness. Assuming electric field in the CuPc layer is uniform, thicker CuPc layer should lead to a larger operating voltage for a fixed current injection, in contrary with the observation. Previous study has shown that the hole energy barrier at the ITO/CuPc interface is independent of the CuPc thickness.¹¹¹ Therefore, the variation in the current profile can only arises from a change in current injection at the CuPc/NPB interface.

We have shown that the width of the DOS of the CuPc at the CuPc/NPB interface plays a significant role in current injection. A broader CuPc DOS shows poorer injection due to an increase in the effective hole barrier at the CuPc/NPB interface (Eq.[4.3]). Therefore there is a correlation between the widths of the DOS of the CuPc at the CuPc/NPB interface with the ITO, where when positioned close to ITO, the CuPc DOS is broaden.

DOS broadening can be caused by various doping effects in CuPc. All elements in ITO are known to easily diffuse into the organic materials.¹¹³ The properties of the CuPc on the other hand are affected significantly by oxygen molecules. Exposure of oxygen into CuPc layer results in a significant improvement in electrical conductivity of the CuPc.^{114,115} This is caused by the doping effect by oxygen that increases the hole density in the CuPc by many orders.¹¹⁵ Therefore oxygen from the ITO play a major role in the current injection at the CuPc/NPB.

A direct test to show presence of oxygen diffusion in CuPc is clearly not an easy task. However, by increasing the oxygen content of the ITO, more oxygen will be present at the CuPc/NPB interface. Inside the CuPc, oxygen acts as a dopant, which causes broadening of DOS due to columbic trapping¹¹⁶ and dipole effect^{117, 118}. The width of DOS is related to the dipole moment by:

$$\sigma^2 = \sigma_0^2 + x \left(7.04 \frac{P}{a^2 \epsilon} \right) \quad (4.6)$$

where P is the dipole moment of the $\text{CuPc}^+:\text{O}_2^-$ complex, x is the fraction of oxygen inside the CuPc, a is the intermolecular distance, ϵ is the dielectric constant, and σ_0 is the DOS width without any doping. For thin CuPc layer, large amount of oxygen diffuses from ITO to CuPc/NPB interface, producing a large CuPc DOS-width, therefore, increasing the energy barrier and shifting the J-V curve downward. For a sufficiently thick CuPc layer, oxygen diffusion to the CuPc/NPB interface is less severe, therefore, less DOS broadening and current reduction are expected.

Figure 4.2(a) Current density versus applied voltage for the devices with various CuPc thicknesses of 0, 10, 20, 30 nm, respectively. The ITO was treated with O_2 plasma treatment at $P=11$ Pa for 2.5 minutes; (b) Current efficiency as a function of current density for devices in (a).

Figure 4.2(b) shows the corresponding current efficiencies of the four samples in Figure 4.2(a). The current efficiency decreases with the presence of CuPc interlayer, which indicates an increase in the hole current that introduces a further hole-electron imbalance.

Effect of oxygen plasma treatment

The significance of oxygen diffusion on the DOS and the current profiles is confirmed with another set of experiments, in which a longer plasma treatment (3.5 mins) and higher pressure O₂ plasma were used. Figure 4.3(a) and (b) show the J-V and current efficiency curves for four devices with CuPc thickness of 0, 5, 15, 20 nm, respectively. The current for the device without CuPc is better compared with the device in Figure 4.2. The improvement may well be contributed by the increase of the ITO work function.¹¹⁹ However for devices with CuPc interlayer, the currents are reduced significantly. This contradicts with the results obtained from Figure 4.2(a). Thus, CuPc here impedes the hole injection rather than enhance hole injection. However, similar with Figure 4.2, the current also improves with CuPc thickness. Comparing the efficiency of the devices, we can see that, devices with CuPc show higher efficiency, indicating reduction in the hole current. The oxygen diffusion argument agrees well with the observed results. Due to a larger oxygen diffusion, for a thin CuPc layer, significant increase in material disorder occurred at the CuPc/NPB interface resulting in current reduction. On the other hand, as the CuPc thickness increases, the amount of oxygen at the interface is reduced and less current reduction is obtained [Figure 4.3(a)].

Figure 4.3(a) Current density versus applied voltage for the devices with various CuPc thicknesses of 0, 5, 15, 20 nm, respectively. For all devices the ITO is treated with O₂ plasma treatment at P=15 Pa for 3.5 minutes; (b) Current efficiency as a function of current density for devices in (a).

Aside of the CuPc thickness variation, the discrepancies on the role of CuPc in literatures are probably originated from the different O₂ plasma treatment of the ITO anode. Longer O₂ plasma treatment will result in larger oxygen diffusion to the CuPc/NPB interface, therefore, resulting in impediment of hole injection as Aziz *et al.* reported. Less O₂ content of ITO will result in less oxygen doping at the CuPc/NPB interface, hence, additional of CuPc layer will improve the hole-injection by reduction of hole-barrier at ITO/NPB interface as reported by Hill *et al.*

4.3. Balancing the electron-hole current with a BCP inserted between the hole-injection layer and hole-transporting layer

4.3.1. Introduction

High performance OLEDs should have a low operating voltage, high efficiency and relatively good stability. As discussed earlier, a typical OLED suffers hole leakage to the cathode, which decreases the efficiency, while electrons are more and less consumed before reaching the HTL. One way to decrease hole leakage is by inserting a HBL between the emission layer and ETL. However, because the electron mobility in HBL is much lower than that in ETL, the addition of this layer in the ETL side has been shown to increase the operating voltage significantly.¹²⁰

To increase device efficiency without increasing the voltage significantly, we blocked the holes at the HTL side. The inset in Figure 4.4 (a) shows the energy diagram of our improved design. The accumulation of holes at the interface of HBL and HIL increases the electric field in HTL. To minimize the increase of the total voltage, a thin HTL was used. The thin HTL should not affect the efficiency, as luminescence occurs at the ETL side. This design improves hole-electron balance at

the HTL-ETL interface, without significant voltage shift. Tuning of current efficiency is achieved by varying the thickness of HBL, which controls the hole injection, while voltage tuning can be realized by varying of the thickness of HTL, where drops the largest electric field. To obtain the same optical coupling, the total thickness of the organic layers was more or less kept constant in our experiment.

4.3.2. Experimental

In this experiment, we used m-MTDATA as the HIL with the HOMO level of 5.1 eV, BCP as HBL with HOMO level of 6.4 eV, NPB as HTL with the HOMO level and LUMO level of 5.2 eV and 1.2 eV, respectively, Alq₃ as ETL with the HOMO and LUMO level of 5.8 eV and 2.2 eV, respectively, and transparent ITO and Mg:Ag as anode and cathode, respectively (see Table 3.1). Four devices with a structure of ITO/m-MTDATA(80 nm)/BCP(X nm)/NPB(20 nm)/Alq₃(100 nm)/Mg:Ag(300 nm), where X was chosen as 0, 3, 5, and 10 nm, were fabricated in the same runs.

4.3.3. Results and discussion

Figure 4.4(a) and (b) show the current density-voltage (J-V) and luminescence-voltage (L-V) curves, respectively, for devices with various BCP thicknesses and fixed thickness of other layers. Both the current density and luminescence shift toward higher voltage as the BCP thickness increases. This is understood because the BCP layer blocks the hole and increases the voltage-drop across the BCP-NPB layers. The inset in Figure 4.4(b) shows the corresponding current efficiency curves for devices in Figure 4.4(b). The efficiency is maximized with a 3 nm-thick BCP layer. This clearly shows that BCP controls the hole injection to the NBP/Alq₃ interface, and

for a 3 nm-thick BCP, holes should be in perfect balance with electrons. With 3 nm-thick BCP layer, the current efficiency is around 3.25 cd/A, corresponding to a 30% increase compared to the standard device without BCP (2.5 cd/A). The current efficiency drops with further increase of BCP layer thickness to 5 and 10 nm. For these thicknesses, most of the holes are blocked by BCP at the m-MTDATA and BCP interface, resulting in lesser holes at the NPB/Alq₃ interface.

Figure 4.5 shows the operating-voltage as a function of BCP thickness at a fixed current density of 100 mA/cm². The inset in Figure 4.5 shows the corresponding electroluminescence spectrum. The voltage monotonously increases with the BCP thickness. The nonlinear voltage-thickness relation indicates that the hole experiences a trapezoid barrier in BCP as shown in the inset in Figure 4.4(a). For this type of barrier, the current injection is not only dependent on the electric field, but also the thickness of the BCP layer.¹²¹ It was reported previously that incorporation of BCP in the HTL enabled the control of hole current so that the emitting region could be shifted throughout the organic layers.³⁵ However, for all devices with less than 10 nm BCP in our experiment, the emission always originated from the Alq₃ layer (inset in Figure 4.5).

Figure 4.4 Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of BCP. The insets in (a) and (b) show the band diagram of an OLED with a HBL inserted between HIL and HTL, and the current efficiency versus current density curves, respectively. The symbols in (a) apply to (b) as well.

In addition to the variation of BCP thickness, we also varied the thickness of the NPB layer while fixing the thickness of all the other layers. The structure used was ITO/ m-MTDATA (80nm)/ BCP (3nm)/ NPB (X nm)/ Alq₃ (100nm)/ Mg:Ag (300nm), where X was chosen as 5, 10, 15 and 30 nm. Figure 4.6(a) and (b) show the J-V and L-V curves, respectively, for devices with various NPB thicknesses. It can be seen that, the current and luminescence curves shift toward lower voltage as the NPB thickness reduces. The device with a 5 nm-thick NPB even shows a better current profile compared to the standard one without BCP layer, as shown by Figure 4.6(a). However, the current efficiency is independent on the NPB thickness, as shown in the inset in Figure 4.6(b). This indicates that NPB layer does not reduce the hole current in the device. As a result, lower operating voltage can be obtained with a thinner NPB layer without affecting the current efficiency.

The inset in Figure 4.6(a) shows the operating voltage as a function of NPB thickness at a current density of 100 mA/cm². The voltage is linearly dependent on the NPB thickness, indicating holes in NPB layer experience a triangular barrier, instead of trapezoid one as in BCP. For triangular barrier, current injection depends only on the electric field.¹²¹ Based from the slope of the graph, the average electric field in the NPB layer is about 0.11 V/nm at a current density of 100 mA/cm². This value is higher than the one in m-MTDATA and Alq₃ layers of about 0.058 V/nm, which is estimated by dividing the total voltage drop with the total thickness of both layers [Electric field across m-MTDATA layer is smaller than that in Alq₃; however, as a first-order approximation, we assume the difference is insignificant]. Obviously, large band-bending indeed occurred in NPB.

Figure 4.5 The operating voltage as a function of BCP thickness at a current density of 100 mA/cm^2 for all four devices in Figure 4.4. The insert shows the electroluminescence spectrum for all devices.

It worth mentioning that further improvement can be achieved by optimizing the thickness of the m-MTDATA and Alq₃ layers. The improvement achieved by this technique is attributed to reduced surface-plasmon loss¹²² and optical interference effect,¹²³ but not the electron-hole balance. So it is expected that the optimum thickness of the BCP layer remains to be 3 nm, independent on the thickness variations of the m-MTDATA and Alq₃ layers, although such optimization is believed to further improve the performance.

Figure 4.6 Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of NPB. The device without BCP layer is also shown for comparison (represented by star). The inserts in (a) and (b) show the operating voltage as a function of NPB thickness at a current density of $100 \text{ mA}/\text{cm}^2$, and the current efficiency versus current density curves, respectively. The symbols in (a) apply to (b) as well.

4.4. Balancing the electron-hole current with an Alq₃ inserted between the hole-injection layer and hole-transporting layer

4.4.1. Introduction

Above we have achieved an improvement in device efficiency without sacrificing the operating voltage by inserting a BCP HBL between HIL and HTL. However, it is worthwhile to explore other HBLs for better performance with minimum organic materials used. Another interesting design was reported previously, whereby Alq₃ was used to modify the ITO electrode.¹²⁴ However, the large voltage increase remains a problem. Here we shall report improved device performance by inserting Alq₃ between HIL and HTL. As a traditional electron-transporting and emissive layer, Alq₃ was used to block the hole on the HTL side. To obtain the same optical coupling, the total thickness of the organic layer was more or less constant in our experiment. High current efficiency and minimum voltage shift were achieved.

4.4.2. Experimental

In this experiment, we used m-MTDATA as the HIL, Alq₃ as HBL (to differentiate this layer with the emissive layer, we denoted it as blocking-Alq₃), NPB as HTL, another layer of Alq₃ was used as ETL, and transparent ITO and Mg:Ag as anode and cathode, respectively. Devices with a structure of ITO /m-MTDATA (60 nm)/ Alq₃(X nm)/ NPB(20 nm)/ Alq₃(80 nm)/ Mg:Ag(300 nm), where X was chosen as 0, 1, 2, 4, 5, 10 and 20 nm, were fabricated.

4.4.3. Results and discussion

Figure 4.7(a) and (b) show the current density and luminance versus voltage respectively, for devices with various blocking-Alq₃ thicknesses. It can be observed that the current density monotonically shifts toward higher voltage as the blocking-Alq₃ thickness increases. The luminance, however, initially increases with 1 nm of blocking-Alq₃ layer, then drops as the thickness increases further. In term of efficiency, the device with 2 nm of blocking-Alq₃ layer shows the highest current efficiency [inset in Figure 4.7(b)]. Maximum current efficiency is improved by almost 30% from 3.1 cd/A to 4 cd/A. Table 4.1 tabulates the performances of devices with various blocking-Alq₃ thicknesses at a current density of 100 mA/cm². The observed results can be explained in term of hole blocking effect by the Alq₃ layer to balance the electron and hole current. With a 2 nm of blocking-Alq₃ layer, the balance is optimized, while further increase in thickness causes most of the holes to be blocked at the HIL/Alq₃ interface with the balance broken.

Table 4.1. Operating voltage and current efficiency for devices with various blocking-Alq₃ thicknesses at a fixed current density of 100 mA/cm².

Blocking-Alq ₃ thickness (nm)	Operating Voltage (V)	Current Efficiency (cd/A)
0	10.5	3.1
1	10.6	3.6
2	11.1	4
4	11.8	3.5
5	12.3	2.9
10	14.8	1.6
20	15.8	1.5

The current efficiency of a typical fluorescent OLED device is determined by four factors, namely (a) electron-hole balance, (b) singlet-triplet ratio, (c) fluorescent efficiency (d) and the output coupling. The ratio of electron to hole current is denoted as J_{elec}/J_{hole} .¹²⁴ Assuming 30% increase in the current efficiency corresponds to maximum current balance, this means that, in the standard device without HBL, the electron-hole balance factor (J_{elec}/J_{hole}) is around 0.77. Same value was also observed with a similar structure, but with different HIL and ETL thicknesses (see section 4.3). This indicates that the electron-hole balance factor is less dependent on the variation of HIL and ETL thicknesses. However, it is largely dependent on the interfacial energy barrier.¹²⁵ Therefore, optimization of thicknesses for HIL and HTL is not expected to improve the electron-hole balance factor, although it probably further improves the current efficiency due to enhanced optical interference effect¹²³ and reduced surface plasmon absorption.¹²²

For our optimized device, the electrons are expected to be well confined at the NPB/Alq₃ interface. Further examination of emission spectra of the devices with various blocking-Alq₃ thicknesses confirms the absence of electron in the blocking-Alq₃ layer [inset in Figure 4.7(a)]. If electrons are present in the layer of blocking-Alq₃, exciplex should be expected at the HIL/Alq₃ interface.⁹⁸ However, with a 20 nm of NPB layer, no sign of the exciplex emission was observed which indicates that electrons are well confined in the NPB/Alq₃ interface. In the following, we shall show that thin NPB resulted in electron leakage to the blocking-Alq₃ layer, introducing exciplex emission in the device.

Figure 4.7 Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of blocking-Alq₃. The insets in (a) and (b) show the electroluminescence spectra and current efficiency versus current density curves, respectively. The symbols in (a) apply to (b) as well.

In section 4.3, we showed that minimizing the NPB layer did not affect the current efficiency although reduction in voltage was observed. This enables reduction of voltage without affecting the current efficiency of the device. It is interesting to do a similar study here, since now Alq₃ HBL has an excellent electron transport property and is an efficient emitter. To do this, we varied the thickness of the NPB layer, while keeping the thickness of other layers the same. Devices with a structure of ITO/m-MTDATA(80 nm)/Alq₃(2 nm)/NPB(X nm)/Alq₃(80 nm)/Mg:Ag(300 nm), where X was chosen as 2, 5, 10 and 20 nm, were fabricated. Figure 4.8(a) and (b) show the current density and luminance versus voltage respectively, for devices with various NPB thicknesses. It is understandable that reduction of NPB thickness resulted in voltage reduction. However, different from previous observation (section 4.3), the luminance is significantly lowered as the NPB thickness reduces. From the current efficiency plot [inset in Figure 4.8(b)], it is further noted that light emission process degrades with the decrease of the NPB layer.

Figure 4.8 Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of NPB. The inset in (b) shows the current efficiency versus current density curves. The symbols in (a) apply to (b) as well.

Figure 4.9 shows the emission spectral transformation with the increase of NPB thickness. It is clearly shown that the emission spectral broadens on the longer wavelength side as the NPB thickness decreases. Furthermore, the spectral peak is slightly red-shifted. By subtracting the broadened spectrum with the original Alq₃ spectrum (peaking at 532 nm), a new spectrum was obtained with a peak wavelength of 600 nm (Figure 4.9), which corresponds to the exciplex emission for the m-MTDATA/Alq₃ system.⁹⁸ Both reduction of the current efficiency and spectral broadening can be explained in term of electron leakage into the blocking-Alq₃ layer. As the thickness of NPB is reduced, more electron leaks to the HIL/Alq₃ interface forming exciplex. The emission of exciplex from the excited Alq₃ molecules to the ground state of the HIL is known to broaden the spectral emission and reduces the efficiency.¹²⁶ The inset of Figure 4.9 shows the proposed energy band alignment in the device. The exciplex is formed when an excited singlet in blocking-Alq₃ recombines to the ground state in m-MTDATA. According to the band diagram, the peak wavelength of the exciplex emission calculated is 590 nm (there is a 2.1 eV energy difference between the lowest-unoccupied molecular orbital of Alq₃ and the highest-occupied molecular orbital of m-MTDATA), which matches well with the experimental result of 600 nm (Figure 4.9). To prevent the formation of exciplex, NPB thickness must be larger than 20 nm. This agrees with the study conducted by Zhang *et al.*, who showed NPB layer thinner than 20 nm resulted in reduction of efficiency due to electron leakage to the anode.¹²⁷

Figure 4.9 Electroluminescence spectra for devices with various NPB thicknesses. Broadened and red-shifted spectra clearly indicate exciplex formation, as the NPB thickness decreases (indicated by the arrow). The inset shows the proposed band diagram of the device. Dipole barriers at ITO/m-MTDATA and Alq₃/Mg are taken to be -0.5 eV¹¹¹ and 0.8 eV,⁶¹ respectively. All the HOMO and LUMO levels are drawn with respect to vacuum level. The exciton binding energy is taken to be ~0.9 eV for all organic materials. Exciplex emissions at m-MTDATA/Alq₃ interface were also indicated for 2 and 5 nm NPB.

The result reported here however seems to contradict with what we previously observed with BCP as a blocking layer (section 4.3), where we observed that reduction of NPB thickness only resulted in a lower voltage but not the current efficiency. In section 4.3 we have found that m-MTDATA/BCP interface is able to emit exciplex with spectrum similar to that of Alq₃ but with much reduced current efficiency. This indicates that besides blocking the holes, the BCP layer also slightly blocks electrons.¹²⁸ As the electrons are absent at the m-MTDATA/BCP interface, the formation of the inefficient exciplex was avoided.

As a final remark, the reduction in hole leakage reduces the unstable cationic Alq₃ molecules in the emissive layer.¹⁰⁸ Although HBL will be degraded due to excess of hole at this layer, it should not affect light emission as it has a role of hole-blocking and is positioned far from emission region. The increase in electric field at NPB due to addition of a thin layer of HBL was only adequate to balance the electron and hole current but not to degrade the NPB, hence in overall insertion of HBL between HIL and HTL will increase the device's lifetime.

4.5. Summary

In the first section we have observed a generalized role of CuPc in OLED. It was found that, depending on the oxygen content at the CuPc/NPB, the CuPc can have a role of hole injecting or hole blocking. For small oxygen content, CuPc acts to improve the hole injection, because of its superior transport-properties. However in the presence of large amount of oxygen, the CuPc acts to block the hole injection. As been numerically shown that as the concentration of oxygen increases, the effective barrier at CuPc/NPB increases as well. We also observed that for all devices with

CuPc the current has steeper profiles. This is contributed by the field-dependent return-current at the CuPc/NPB interface. The return-current is significant at low-field while minute at the high-field region.

In the last two sections, two different HBLs, BCP and Alq₃, were inserted between HTL and HIL to improve the electron-hole balance in OLED. The current efficiency was improved by almost 30% for devices with 3 nm of BCP or 2 nm blocking-Alq₃ layers. Variation of HTL thickness was observed to render different result for devices with BCP and blocking-Alq₃ as HBL. In devices with BCP blocking layer, the voltage reduces with reduction of NPB thickness, while the current efficiency remains unchanged. However, in devices with Alq₃ blocking layer, besides reduction in voltage, the current efficiency also decreases with reduction of HTL thickness. For devices with blocking-Alq₃ layer, as the HTL thickness reduces less than 20 nm, the electron starts to leak to the blocking-Alq₃ HBL results in the inefficient exciplex emission.

Improved blue organic light-emitting diode with an exciton confinement structure

5.1. Introduction

OLEDs offer numerous advantages such as low operating voltage, high luminance efficiency, excellent material properties (flexible), and most importantly simple fabrication on any substrates at room temperature. There are a lot of reports on green and red emitting OLEDs being optimized by various techniques, namely, the anode¹²⁹ or cathode¹³⁰ modification, organic-organic interface modification (chapter 4), doping,¹² annealing¹⁰⁴ and optical coupling.¹³¹ However, efficient saturated blue-emitting OLED, in particular, remains a challenge for many researchers. The main challenges faced in blue OLED are, (1) suitable wide band-gap materials with saturated blue color, (2) confining the high-energy exciton, (3) carrier confinement issues, (4) carrier injection in a wide band gap host materials and of course (5) the weak photopic response in blue region. Recently, there are some reports on enhanced blue-emission OLED achieved by applying new emitting-materials,¹³² wide-band-gap host for blue dopant,²³ and exciton-confining structure,¹³³ however color purity still remains a problem.

NPB is normally used as a HTL with an emission peak at 420 nm and a full-width-half-maximum of 44 nm (among the smallest of all blue materials).^{18,19} Recent

reports have shown that blue OLED utilizing NPB can be improved by adding a buffer such as the m-MTDATA.^{134,135} Furthermore, the usage of new hole-blocking materials, such as tetra (b-naphthyl)silane or boron-containing blocking material has proven to improve the efficiency up to 50%, mainly due to a reduction of exciplex emission.^{21,136} In this chapter, we shall report an exciton-confining structure for NPB-based blue OLED. Our optimized structure showed a 25% improvement in EQE.

5.2. Experimental

Electroluminescence (EL) spectra of the fabricated devices were measured with a PR650 Spectra Scan spectrometer. Luminance–current density–voltage (L-J-V) characteristics were recorded simultaneously with the measurements of the EL spectra by attaching the spectrometer to a programmable Keithley 236 source measurement unit. We assumed the emission pattern was Lambertian, and calculated the EQE from the luminance, current density and EL spectrum. All measurements were carried out at room temperature under ambient atmosphere without any encapsulation.

5.3. Results and discussion

The structure of our improved device is shown in inset Figure 5.1(a), with m-MTDATA as the HIL, BCP (I) as the HBL, NPB as the HTL and blue-emitting layer, BCP (II) as the second HBL, and Alq₃ as the ETL. Carrier and exciton confinement were achieved by sandwiching the emission layer with two wide band-gap HBLs. This structure minimizes diffusion of the high-energy exciton toward the electrodes, hence reducing the surface-plasmon absorption. Addition of a BCP (I) increases the

electric field at the HTL (see section 4.3), thereby increasing the probability of direct exciton formation at NPB layer.

To optimize the structure, two separate experiments were conducted. For the first study, the thickness of HBL near the cathode side [BCP (II)] was optimized with the HBL near the anode side [BCP (I)] absent, while varying the thickness of BCP (II). For the first set of experiment, the structure of ITO/m-MTDATA (30 nm)/ NPB (20 nm)/ BCP (II) (x)/ Alq₃ (50-x nm)/ Mg:Ag was studied. The value of x was varied from 5, 10, 20, 30 to 40 nm. In the second study, we optimized the thickness of BCP (I) by keeping the thickness of BCP (II) at 20 nm. Devices with structure of ITO/m-MTDATA (30 nm)/ BCP (I) (x)/ NPB (20 nm)/ BCP (II) (20 nm)/ Alq₃ (30 nm)/ Mg:Ag was studied, where x was varied from 0, 2, 5 to 10 nm.

For the first experiment without BCP (I), Figure 5.1(a) and (b) show the current density versus voltage and emission spectra for devices with various BCP (II) thicknesses, respectively. It can be seen that the voltage shifts monotonically toward higher value as the thickness of the BCP (II) layer increases. The increase in voltage is attributed to two factors: (a) the much lower electron mobility of the BCP (II) compared to the Alq₃, and (b) the existence of small barrier for electron at the Alq₃/BCP (II) interface.¹³⁴ From Figure 5.1(b), it can be seen that the emission mainly takes place at the NPB layer (NPB emission is peaking at 420 nm). With a thick BCP (II) layer, excitons are well confined at the NPB. When the thickness of the BCP (II) layer is reduced, Alq₃ emission starts to emerge. In the inset of Figure 5.1(b), we plotted the EQE for device with various BCP (II) thicknesses. The efficiencies are almost fixed for a BCP (II) thickness of 20 nm or above, and decreases quickly for thinner BCP (II) layer. The appearance of Alq₃ emission and reduction in EQE show

that, for thin BCP (II) layer, some excitons in the NPB layer transfer their energy to Alq₃ molecules via Förster energy transfer.¹³⁷ As Förster energy transfer is a non-radiative process, it will slow down the overall radiative-emission rate therefore introducing a loss (reducing EQE).¹³⁷ The EQE drops from 1.11% to 0.83% at current density of 10 mA/cm² for device with 20 nm and 5 nm of BCP (II) layer, respectively.

Figure 5.2(a) and (b) show the current density and luminance versus voltage [the second experiment with BCP (II) thickness fixed at 20 nm] for devices with various BCP (I) thicknesses, respectively. Introduction of BCP (I) results in increase in the operating voltage, this is understandable because holes are blocked at the m-MTDATA/BCP (I) interface, and the electric field in NPB layer is increased accordingly (see section 4.3). It can be seen from Figure 5.2(b) that, the device with 2 nm of BCP (I) shows the best performance with a maximum luminance of 1070 cd/m² at a current density of 265 mA/cm².

The inset of Figure 5.2(a) shows the EQE for devices with various BCP (I) thicknesses. It can be seen that, for the OLED with 2 nm of BCP (I) layer, there is a slight increase in the EQE from 1.11% to 1.38% at a current density of 10 mA/cm², corresponding to a 25% improvement compared to the one without BCP (I) layer. This modest increase can be attributed to two factors: better exciton confinement and increase in direct excitons formation in NPB layer. In the absence of BCP (I) layer, the high energy NPB excitons can easily diffuse to the m-MTDATA layer, and absorbed by the anode. This is because m-MTDATA has a similar band-gap with the exciton energy. By introducing a 2 nm BCP (I) layer, the diffusion is minimized and excitons are better confined in NPB layer.

FIGURE 5.1(a) Current density versus voltage characteristics and (b) EL spectra for devices with various thicknesses of BCP (II) layer. The insets in (a) shows the proposed band diagram for the improved device. Dipole barriers at ITO/m-MTDATA and Alq₃/Mg are taken to be -0.5 eV^{111} and 0.8 eV^{61} , respectively. All the HOMO and LUMO levels are drawn with respect to vacuum level. The exciton binding energy is taken to be $\sim 0.9 \text{ eV}$ for all organic materials. Inset in (b) shows the EQE for devices with various BCP (II) thicknesses. The symbols in (a) apply to (b) as well.

Figure 5.2 Current density (a) and luminance (b) versus voltage characteristics for devices with various thicknesses of BCP (I) layer. The insets in (a) and (b) show the EQE versus current density and EL spectra curves, respectively. The symbols in (a) apply to (b) as well.

For our blue OLED, there are electrons and holes piling up on both sides of NPB/BCP (II) interface. Therefore, excitons can be formed in both BCP (II) and NPB layers. The excitons formed at the BCP (II) layer can transfer its energy to the NPB layer whereby final radiative emission occurred. The energy transfer process from excited BCP (II) to NPB may reduce the device efficiency.¹³⁷ The increase in electric field in NPB due to insertion of a 2 nm BCP (I) enables more electrons to cross the NPB/BCP (II) barrier, directly facilitates excitons formation in NPB [excitons formed in BCP (II) is reduced], therefore resulting in higher EQE. As the thickness of the BCP (I) is further increased, more holes are blocked at the m-MTDATA/BCP (I) interface, increasing the electric field in NPB furthermore. For devices with BCP (I) thickness of 5 nm and 10 nm, electrons start to leak out to the m-MTDATA/BCP (I) interface.

The presence of electron at this interface is evidenced from the emission spectra, the inset Figure 5.2(b), from which we can see that as the BCP (I) thickness increases, a new peak appears at 504 nm. While the new peak resembles Alq₃ spectrum, it can not be attributed to the Alq₃ emission, as the BCP (II) layer near the cathode is very thick, which prevent any direct exciton formation or Förster energy transfer. It can be seen from Figure 5.2(a) that, EQE drops from 1.38% to 0.63% at a current density of 10 mA/cm² for devices with 2 nm and 10 nm of BCP (I), respectively. The emerging peak at 504 nm and the reduction of the efficiency for a thick BCP (I) are due to inefficient exciplex emission,^{126,138} which is originated from radiative transition of excited excitons in BCP (I) to the ground state of the m-MTDATA molecules. The radiative rate of the exciplex is slow and inefficient because of the weak overlap in wavefunctions between the excited BCP (I) and ground state m-MTDATA molecular.

Figure 5.3 shows the change in emission spectra with applied voltage for the optimized device with 2 nm BCP (I) and 20 nm BCP (II). There is a slight increase in exciplex emission as the voltage increases, resulting in lower efficiency. The inset of Figure 5.3 shows the change in the CIE coordinates for the optimized device with applied voltage. The optimized device shows a deep pure blue close to the deepest blue of the National Television System Committee (NTSC) standard with CIE coordinates of $x = 0.14$ and $y = 0.08$.¹⁹ Moreover, there is only a slight variation in CIE coordinates when the applied voltage changes from 5 V ($x = 0.1659$, $y = 0.0772$) to 10 V ($x = 0.1747$, $y = 0.1059$).

Figure 5.3 Normalized EL spectra for various applied voltage of the optimized device. Inset shows the variation of the CIE coordinate for various applied voltage.

Figure 5.4 Spectral of m-MTDATA (PL), BCP (PL), and m-MTDATA/BCP (EL). Inset shows the EQE versus current density for device with structure of m-MTDATA/BCP.

To verify the exciplex emission at the m-MTDATA/BCP (I) interface, we conducted another experiment with a structure of ITO/ m-MTDATA (50 nm)/ BCP (50 nm)/ Mg:Ag. Figure 5.4 shows the photoluminescence (PL) spectra of the m-MTDATA, BCP and the EL spectra of the device. It is clear that the EL spectrum does not resemble any of the constituent materials, indicating that the emission occurred via exciplex at the m-MTDATA/BCP interface. The inset of Figure 5.4 shows the EQE of the exciplex emission. Due to the weak overlap between the excited BCP exciton wavefunction with that of the ground state m-MTDATA molecule, exciplex radiative emission is inefficient; explaining the drops in efficiency

for device with thick BCP layer (Figure 5.2). The maximum EQE for the exciplex emission is only 0.2% (inset in Figure 5.4).

5.4. Summary

In summary, we have introduced an exciton confining structure which was used to realize a more efficient blue emission from NPB. The device with 2 nm and 20 nm of BCP (I) and BCP (II), respectively, shows the best performance with improved efficiency and luminance. A 25% of improvement was achieved with absolute an EQE of 1.38%. Further improvement can be done by utilizing a different cathode such as LiF/Al to inject more electrons, optimizing the thickness of the HIL and ETL for optimum output coupling, incorporating better emitter, HBLs and ETL. The color coordinate of our OLED is close to that of the deepest blue specified by the NTSC standard, and insensitive to applied voltage. The appearance of exciplex emission was also observed at m-MTDATA/BCP interface. The exciplex emission is responsible for the reduced efficiency in OLED with thick BCP (I) layer.

Multilayer approach for multicolor emission

6.1. Introduction

White organic light-emitting diodes (WOLEDs) have attracted interest of many due to its potential application in display and general illumination.¹³⁹

Various techniques have been reported in optimizing the efficiency and color purity of WOLED.^{13,25,39,139-147} Among those techniques, electrophosphorescence is the most effective since it is possible to achieve 100% of internal quantum efficiency.^{25,39,140,141}

An alternate approach was reported recently by utilizing highly efficient red, green, and blue materials,¹⁴⁵ where a WOLED with efficiency as high as 3% photon/electron was obtained with good color purity without doping. A more traditional approach was to use fluorescent dopant, Ko *et al.* reported a WOLED with efficiency of 1.97% photon/electron by utilizing red emission from dopant DCM, green from Alq₃ and blue from 1,7-diphenyl-4-biphenyl-3,5-dimethyl-1,7-dihydrodipyrzolo[3,4-*b*;4',3'-*e*]pyridine (PAP-ph). However, doping is still required.¹⁴⁶ To eliminate the doping process, Tsuji *et al.* deposited an ultrathin layer of DCM to harvest the red emission.¹⁴⁷ However, their WOLED could only reach ~ 1000 cd/m².

In this chapter, we shall report other alternatives of two undoped WOLEDs employing the most commonly used fluorescent materials by multilayer approach. A

maximum brightness of 4500 cd/m² and external quantum efficiency of 0.89% photon/electron (2 cd/A) were achieved.

6.2. Experimental

To produce a saturated white light, we utilized NPB emitting at 420 nm as the blue emitter, Alq₃ emitting at 532 nm as the green emitter and exciplex of m-MTDATA/Alq₃ (emission at 600 nm) or 0.1 nm of DCM (emission at 620 nm) as the red emitter.

6.3. Results and discussion

Figures 6.1(a) and (b) show the schematic of the two WOLEDs, which consist of ITO /m-MTDATA (30 nm)/ Alq₃(I) (X nm)/ NPB (20-X nm)/ BCP (30 nm)/ Alq₃(II) (20 nm)/ Mg:Ag for device A [Figure 1(a)], and ITO/ NPB (30-Y nm)/ DCM (0.5 nm)/ NPB (Y nm)/ Alq₃(I) (X nm)/ NPB (20-X nm)/ BCP (30 nm)/ Alq₃(II) (20 nm)/ Mg:Ag for device B [Figure1 (b)], where X and Y are variables in thickness that are used to tune the color.

Devices A and B minimize the non-radiative emission from the Förster process, which may reduce the overall radiative emission rate, by utilization of two different sources of excitons [Figs. 6.1(a) and (b)] in harvesting blue and green emissions from NPB and Alq₃, respectively. Only red emission is attained via exciplex at m-MTDATA/Alq₃ interface (Device A) and the non-radiative Förster energy transfer from Alq₃ to DCM (Device B).

For device A, the thickness of Alq₃(I) is the only variable used to tune the color. Figures 6.2(a) and (b) show the current density (J) and luminance (L) as functions of voltage (V), respectively for device A with various thicknesses of Alq₃(I) from 0, 7, 10, to 15 nm. It can be seen that for a fixed current density, the voltage initially increases with Alq₃(I) thickness, and then drops for thick Alq₃(I). This is because for very thin thickness, Alq₃(I) layer blocks hole injection to NPB (see chapter 5), however as the thickness of Alq₃(I) increases further (NPB thickness reduces), electrons start to tunnel from NPB, therefore compensating the increase of electric field in Alq₃-NPB layer and thus reducing the voltage. The increase in luminance with the increase of Alq₃(I) thickness is due to the increase of green emission. As green spectrum overlaps better with the photopic response, the total luminance of the greener device increases.

Figure 6.3(a) shows the corresponding emission spectrum of device A with various thicknesses of Alq₃(I). For comparison, the emission spectrum from pure Alq₃ is also included in Figure 6.3(a). Without Alq₃(I), only NPB emission was recorded, indicating that excitons were formed only at the NPB/BCP interface. This agrees to a study conducted previously, where a NPB layer thicker than 20 nm is capable of blocking the electron completely, preventing exciton formation at m-MTDATA/NPB interface.¹²⁷ However as the thickness of the Alq₃(I) increases (thickness of NPB reduces), electrons start to accumulate at the m-MTDATA/Alq₃ interface. From Figure 6.3(a), it can be seen there is an increase in yellow emission, which was originated from Alq₃ and exciplex emission at the m-MTDATA/Alq₃ interface.⁹⁸ The presence of exciplex broadens the Alq₃ spectrum on the longer wavelength side [Figure 6.3(a)]. The inset of Figure 6.3(a) shows the EQE for device with various

Alq₃(I) thicknesses (X). It can be seen that the EQE drops from 0.85 to 0.21% photon/electron (about 4 times) as exciplex emission appears. The low quantum-yield of exciplex emission has been reported previously.¹²⁶

Figure 6.1 (a) and (b) are the band diagrams for devices A and B, respectively. Electron-hole recombination is indicated by arrows. Blue and green emissions originate from NPB 50 nm away from the cathode and Alq₃ about 60 nm away from the cathode respectively, for both devices A and B. Red emission comes from either exciplex (device A) or DCM (device B) about 70 nm away from the cathode.

Figure 6.2 Current density (a) and luminance (b) as functions of voltage for device A with various thicknesses of $\text{Alq}_3(\text{I})$ layer. The symbols in (a) apply to (b) as well.

Figure 6.3(b) shows the CIE coordinates of the WOLEDs for various Alq₃(I) thicknesses, where the coordinates for blue emission from NPB, green emission from Alq₃ and yellow emission from the exciplex-Alq₃ are also drawn. It can be seen that the CIE coordinate shifts almost linearly from blue NPB to yellow exciplex-Alq₃ emission. The best white was obtained for the device with X = 10 nm, whose CIE color coordinate (x, y) = (0.31, 0.35) is the closest to the equal-energy white [(x, y) = (0.33, 0.33)]. For the optimized device, the color coordinate slightly varies with voltage, changing from (x, y) = (0.31, 0.35) at 7 V to (x, y) = (0.31, 0.39) at 11 V. The inset of Figure 6.3(b) shows the normalized emission spectra of the optimized device at various voltages. We can see that there is a slight increase in yellow emission as the voltage increases, indicating an increase in electron accumulation at m-MTDATA/Alq₃ interface, i.e. electron tunneling at NPB/BCP interface increases faster with voltage than hole tunneling at m-MTDATA/Alq₃(I) interface. This can be caused by two factors: 1) different electric-field dependences of the electron mobility in the NPB and hole mobility in Alq₃ (I), 2) different energy barriers at the NPB/BCP interface (for electrons) and the m-MTDATA/Alq₃ (I) interface (for holes). Carrier mobility in organic semiconductor follows the Poole-Frenkel behavior of $\propto \exp(\gamma\sqrt{E})$, where $\gamma = \beta\left(\frac{1}{kT} - \frac{1}{kT_0}\right)$ is the Poole-Frenkel factor and β and T_0 are constants. The dissimilar field dependence of the mobility will lead to different electron and hole flow rates with the increase in voltage. Secondly, different energy barriers will also lead to different electron and hole fluxes toward the two recombination zones. These two factors cause a shift in recombination region (color shift-shape and peak position shift) as the voltage increases.

In spite of the very good white color produced, the EQE of the device is relatively low. For the optimum white device with $X = 10$ nm, the luminance reached 1100 cd/m^2 at current density of 270 mA/cm^2 .

The low efficiency of device A is inevitable due to the usage of exciplex emission, which is an inefficient process.¹²⁶ To obtain more efficient WOLED, we explored red color from fluorescent material DCM in device B. For device B, there are two parameters [X and Y in Figure 1(c)] that can be used to tune the relative content of red, green and blue. To optimize the thickness of NPB separating DCM and $\text{Alq}_3(\text{I})$ [Y in Figure 6.1(c)], we fabricated OLEDs with a structure of ITO/ NPB (30- Y)/ DCM (0.5 nm)/ NPB (Y)/ Alq_3 (70 nm)/ Mg:Ag, where Y was varied from 15, 10, 5 to 2 nm, respectively.

Figure 6.4 shows the emission spectra for devices with various Y 's. As the thickness of the NPB (Y) reduces, more excitons transfer their energy from Alq_3 to DCM layer via the non-radiative Förster process, increasing the contribution of the red emission. It can be seen that the peak of the emission spectrum shifts from 532 nm to 588 nm as the NPB thickness reduces. The inset (a) shows the CIE coordinates of the corresponding devices. The straight line extrapolating from blue NPB to the white [$(x, y) = (0.33, 0.33)$] in inset (a) touches the coordinate of device with $Y = 5$ nm, indicating the best mixing to obtain white. The inset (b) of Figure 6.4 shows the EQE for devices with various Y 's. Device with very thin NPB separation layer is shown to be inefficient. The reduction of efficiency is due to exciton quenching by the DCM layer.¹⁴⁷ For WOLED consideration, the device with $Y = 5$ nm with the best color mixing, also presents relatively good EQE of 0.91 % photon/electron at a current density of 200 mA/cm^2 .

Figure 6.3 (a) Emission spectra and (b) CIE color coordinates of device A with various Alq₃ (I) thicknesses biased with various voltages. Pure Alq₃ emission spectrum is also drawn in (a). The CIE coordinates of equal-energy white, Alq₃ emission and Alq₃-exciplex are also indicated in (b). The insets in (a) and (b) show the EQE and emission spectra at various applied voltage for device A with X = 10 nm, respectively. The symbols in (a) apply to (b) as well.

Figure 6.4 Emission spectra for devices with a structure of ITO/ NPB (30-Y nm)/ DCM/ NPB (Y nm)/ Alq₃/ Mg:Ag for various Y's. Insets (a) and (b) show the CIE color coordinate and EQE for the devices with various Y's, respectively.

Figures 6.5(a) and (b) show the current density (J) and luminance (L) versus voltage (V), respectively for device B with Y = 5 nm [Figure 6.1(c)] but various Alq₃(I) thicknesses from 4, 7, 10 to 15 nm. Similar trends with device A were observed.

Figure 6.6(a) shows the emission spectra of devices in Figure 6.5. Similar to device A, there is an increase in yellow emission as X increases due to the shift of electrons accumulation from NPB to Alq₃. Figure 6.6(b) shows the CIE coordinates for devices with various Alq₃(I) thicknesses. The best white is the one with 10 nm Alq₃(I) which shows a CIE coordinate of (x, y) = (0.32, 0.38) at 8 V. The CIE coordinate changes with voltage from (x, y) = (0.30, 0.34) at 5 V to (x, y) = (0.33, 0.4) at 12 V. The inset of Figure 6.6(b) shows the normalized emission spectrum as a

function of voltage for the optimized device with $X = 10$ nm. It can be seen that the contribution of the yellow emission increases with voltage. Device B shows a worse color-shift than device A. The large increase of the exciton formation with the increase of voltage at m-MTDATA/Alq₃ interface in device A is compensated by the poor radiative emission rate that resulted in less yellow-shift. Although the change in color is more prominent, device B shows much better efficiency and luminescence which reached 0.89 % photon/electron (2 cd/A) and 4500 cd/m² respectively at a current density of 270 mA/cm² [inset Figure 6.6(a)], which is also much better than undoped DCM based WOLED reported before.¹⁴⁷ For illumination application, the CCT ought to be between 3000 and 7500 K.¹⁴⁸ Devices A and B exhibit CT of 6631 and 7160 K respectively under a bias of 7 V.

Figure 6.5 Current density (a) and luminance (b) as functions of voltage for device B with $Y = 5$ nm and various thicknesses of Alq₃(I) layer. The symbols in (a) apply to (b) as well.

Figure 6.6 (a) Emission spectra and (b) CIE color coordinates for device B with Y = 5 nm but various Alq₃(I) thicknesses biased with various voltages. The equal-energy white is also indicated in (b). The insets in (a) and (b) show the EQE and emission spectra at various applied voltage for the device with X = 10 nm, respectively. The symbols in (a) apply to (b) as well.

It is worth mentioning that although not the best reported WOLED, devices A and B are undoped devices exploiting emission from the most commonly used OLEDs materials (Alq_3 and NPB). Our structures reduce complexity of device fabrication and produce moderate external quantum yield. With our structure, further improvement can be achieved by utilizing more efficient emitting materials, or if necessary, doping.

As a final remark, although the $\text{Alq}_3(\text{I})$ layer is used to transport hole, it should not degrade the device's lifetime. As shown previously that cationic Alq_3 species are unstable and cause device degradation.¹⁰⁸ However, since electrons are also introduced at the $\text{Alq}_3(\text{I})$ layer, cationic species are eliminated. The presence of electrons in the layer neutralizes the unstable species, hence improve the lifetime.

6.4. Summary

In summary, we have reported two undoped WOLED structures. Device A utilized an exciplex emission for red and device B harvests a more efficient red emission from an ultrathin layer of DCM. The maximum EQE and luminance of device B are 0.89% photon/electron (2 cd/A) and 4500 cd/m^2 at a current density of 270 mA/cm^2 , respectively. The relatively good EQE was achieved by utilizing two sources of excitons which minimize the non-radiative cascade energy transfer process to obtain white.

Observation of excitonic quenching by long-range dipole-dipole interaction in sequentially doped organic phosphorescent host-guest system

7.1. Introduction

Given the maturity of liquid crystal display technology, the recent rise of OLED is almost impossible without the discovery of electrophosphorescence.¹³ Phosphorescence boosts efficiency by four times compared to that of the normal fluorescence OLEDs, by harvesting the normally spin-forbidden triplet state which accounts for three quarters of all excitons formed in the device⁴⁰. Utilizing phosphorescence, device with internal quantum efficiency approaching 100% has been reported.¹⁴ The current state-of-the-art phosphorescent OLED utilizes various different layers which function separately as carriers transport, carriers and excitons blocker, and emitting layer (EML).

The EML is normally formed by a host-guest system formed by co-evaporating a small amount of guest molecule in the matrix of host material. Most excitons are formed in the matrix host which then transfers the energy to the guest molecule where final emission takes place. Host-guest system minimizes aggregation of guest molecules so as to enable high quantum yield. It is generally accepted that in a host-guest system, concentration quenching occurs because of molecule aggregation. As concentration of guest molecule increases, a drop in quantum efficiency is followed

by a red-shift in the emission spectrum, characteristics of aggregate state.¹⁴⁹⁻¹⁵¹ However it is still not clear whether molecules aggregation alone is responsible for concentration quenching.

Here we investigated the mechanisms responsible for concentration quenching in phosphorescent host-guest system, utilizing a specially designed OLED devices with EML consisting of a few repeating cells, similar to a multiple quantum well structure. Each cell consists of a sequentially deposited host and guest materials. Figure 7.1 shows the comparison between the conventionally fabricated devices (random doping) with our specially designed multiple quantum well-like structure (sequential doping). Variation of the thickness of the guest layer in each cell enables the study of the effect of molecule aggregation to the quantum efficiency. On the other hand, variation of the thickness of host layer leads to the observation of a new long range quenching mechanism which will be discussed in this chapter.

7.2. Experimental

We employed NPB as the hole transporting layer, CBP as the host, Ir(ppy)₃ as the guest, BCP as the hole blocking layer, and Alq₃ as the electron transporting layer. Since excitons are formed at both NPB/CBP and CBP/BCP interfaces,³⁹ the guest was evaporated at these interfaces to harvest the excitons.

Figure 7.1 Phosphorescence OLED fabricated with sequential doping with N cells (a) and random doping (b). In sequential doping emission layer is defined by series of repeatable thin layer of guest and host materials. In random doping, guest molecules are dispersed in matrix of host.

7.3. Results and Discussion

For the first set of experiment, six cells were evaporated as the EML. Devices with a structure of ITO/ NPB (50 nm)/ [Ir(ppy)₃ (x nm)/ CBP (5 nm)] 6 cells/ Ir(ppy)₃ (x nm)/ BCP (20 nm)/ Alq₃ (30 nm)/ Mg:Ag, with x varied from 0.5, 1.0, 1.5, to 2.0 nm, were studied. Figure 7.2 (a) shows the normalized emission spectrum for devices with various guest layer thicknesses. As the thickness of the Ir(ppy)₃ layer increases, the emission peak shifts from 512 nm [0.5 nm Ir(ppy)₃ cells] to 524 nm [2 nm Ir(ppy)₃ cells]. The inset of Figure 7.2(a) shows the EQE for devices with various thicknesses of Ir(ppy)₃. Devices with Ir(ppy)₃ thickness smaller than 1 nm are capable to produce an EQE as high as 8.78 % photons/electron at a current density of 50 $\mu\text{A}/\text{cm}^2$. This value is comparable to that of the device fabricated by random doping utilizing NPB, CBP, and BCP.¹⁵² The EQE drops to 5.9% photons/electron for the device with 2 nm of Ir(ppy)₃ layer.

Included also in inset of Figure 7.2 (a) is the EQE of device fabricated using random doping method with Ir(ppy)₃ : CBP ratio of 6 wt% for comparison. It can be seen that EQE drops faster with current density for devices fabricated by sequential doping. This is due to an additional triplet-polaron (T-P) annihilation¹⁵³ in sequential doping as current passes through the Ir(ppy)₃ layers (see section 2.7.3). Moreover, in the thin layer structure of Ir(ppy)₃, the Ir(ppy)₃ molecules are more closely packed, biexcitonic T-T annihilation may rise as well, especially under large current injection (see section 2.7.5).¹⁰³

The reduction in efficiency and the red-shift of the emission peak with increasing Ir(ppy)₃ thickness [Figure 7.2 (a)] suggest the presence of an aggregate state, similar to that reported previously.^{149,154} Different from a molecular state, an aggregate state

is formed when two molecules are positioned close to one another. An aggregate state requires an overlapping between the wave functions of two molecules, hence their excited state has much longer lifetime, i.e. lower quantum yield.¹⁵¹

Besides long excited lifetime, an aggregate state also has a significantly different absorption spectrum compared to that of the monomer.¹⁴⁹ However, the time-resolved PL study of bulk film of Ir(ppy)₃ showed an excited state with shorter lifetime.¹⁶ The absorption spectrum of the bulk film of Ir(ppy)₃ was also found to be the same as that of the dispersed solution.^{155,156} Furthermore, device with bulk Ir(ppy)₃ layer as EML shows a much lower EQE of 0.6% photons/electrons, despite the almost similar emission spectrum to that of 2 nm of Ir(ppy)₃ cells as EML [Figure 7.2 (a)]. These facts suggest that molecule aggregation is not the main culprit behind the excitons quenching in the bulk material.

To further understand the quenching mechanism, we conducted another experiment where the thickness of the host was varied. Devices with a structure of ITO/ NPB (50 nm)/ [Ir(ppy)₃ (1 nm)/ CBP (y nm)] 6 cells/ Ir(ppy)₃ (1 nm)/ BCP (20 nm)/ Alq₃ (30 nm)/ Mg:Ag, with y varied from 2, 3, 5, 7, to 10 nm, were studied. Figure 7.2 (b) shows the EQE of devices with various CBP thicknesses. It can be seen that the EQE increases initially with the increase of CBP thickness peaking at 5 nm, then drops for further increase in CBP thickness. The drops in EQE for device with CBP thicker than 5 nm can be attributed to incomplete energy transfers from CBP to Ir(ppy)₃ molecule, however the very low EQE (< 2% photons/electrons) of devices with CBP thickness less than 5 nm signifying excitonic quenching. It is also noticed that besides having a lower value, the curve of EQE as a function of current density

for devices with thin CBP also resembles that of bulk film of Ir(ppy)₃ [Inset of Figure 7.2(a)].

The normalized emission spectra for devices with various CBP thicknesses are shown in the inset of Figure 7.2 (b), where no significant change can be observed, except for devices with CBP of 10 nm, indicating no increase in aggregate state. The small red-shift observed for device with 10 nm of CBP layer can be understood from the weak microcavity effect, as the total thickness of the EML reaches 67 nm.¹⁵⁷

The lack of appearance of the aggregate peak for devices with thin CBP layer suggests that other quenching mechanism is involved. The structures are only differed in thickness of CBP layer that separates the Ir(ppy)₃ layers, hence the excitonic quenching can only come from the increased interaction between the emitting Ir(ppy)₃ molecules. However, as the Ir(ppy)₃ layers are separated by several CBP molecules (20 - 50 Å), the only known process that applies in such range is the long range Förster (dipole-dipole) energy transfer.⁵⁶ Long range Förster energy transfer occurred when the absorption spectrum of an acceptor molecule overlaps with the emission spectrum of a donor molecule, provided an allowed state transition. Since the absorption and emission spectra of the Ir(ppy)₃ molecule overlap significantly,¹⁵⁵ energy transfers between Ir(ppy)₃ molecules are possible. However energy transfer among excited electronic states of Ir(ppy)₃ molecules would not explain the reduced efficiency, since in principle, it will not add any new nonradiative decay pathway. To explain the observed excitonic quenching, we need to revisit the nonradiative processes.

Figure 7.2 (a) Normalized emission spectrum for device with various Ir(ppy)_3 thicknesses. Also included, spectrum from device fabricated using random doping, (b) EQE for devices with various thickness of CBP with six cells as emission layer. Inset in (a) shows EQE versus current density for devices in (a); Inset in (b) shows the normalized emission spectrum for devices in (b).

Figure 7.3 shows the Jablonski diagram of the photophysical processes including Förster energy transfer. Due to a strong spin-orbit coupling, the rate of the intersystem crossing (ISC) in this system becomes large, hence luminescence is dominated by phosphorescence corresponding to a transition from the excited triplet state (T_1) to the singlet ground state (S_0). The nonradiative transition is occurred by ISC from T_1 to the higher energy vibrational-mode of the S_0 referred as S_0^v . Then, vibrational relaxation (VR) from S_0^v to S_0 occurs thermally. In the presence of another molecule nearby, it is possible that T_1 transfers its energy to the excited triplet state of the adjacent molecule (T_1') via Förster process. Meanwhile, due to a strong spin-orbit coupling, T_1 will also be coupled to the adjacent vibrational-mode ($S_0^{v'}$), i.e. a T_1 - $S_0^{v'}$ transition, which is similar to the Förster process. The T_1 - $S_0^{v'}$ will introduce a new nonradiative decay pathway which will result in reduction of the quantum efficiency. Assuming that the T_1 - S_0 , T_1 - S_0^v - S_0 , T_1 - T_1' and T_1 - $S_0^{v'}$ occurred at rates of K_r , K_{nr} , K_F and K_{Fnr} , respectively, the quantum efficiency can be written as

$$\eta = \frac{K_r + \eta K_F}{K_r + K_{nr} + K_{Fnr} + K_F}, \quad (7.1)$$

from which, η can be rewritten as

$$\eta = \frac{K_r}{K_r + K_{nr} + K_{Fnr}}. \quad (7.2)$$

Eqs. (7.1) and (7.2) show that only the T_1 - $S_0^{v'}$ interaction and not the T_1 - T_1' interaction (which is the commonly known Förster process) affects the EQE. In our case as CBP thickness reduces, the nonradiative transition (T_1 - $S_0^{v'}$) K_{Fnr} increases, resulting in the decrease in EQE of the device. The increase in overall recombination rates due to T-S Förster process agrees well with the reduced PL decay lifetime of

bulk layer Ir(ppy)₃ conducted previously.¹⁶ In other words, T-S Förster energy transfer is the main reason of excitons quenching for the case of bulk Ir(ppy)₃, not the molecules aggregation.

Recently, it has been shown that phosphorescent material with large Stokes' shift exhibit less quenching in the bulk,²⁴ which can be understood due to less inter-molecular Förster process.

Biexcitonic annihilation may be eliminated from the rationale behind the efficiency drops for device with thin layer of CBP for the following reason. Biexcitonic annihilation (triplet-triplet interaction) causes the efficiency to roll-off with the increase in the current (excitons) density. From Figure 7.2(b), it can be seen that devices with thin layer of CBP do not show an increase in the roll-off of EQE compared to that with optimized CBP thickness. Instead, the quenching is occurred only at low current density, when the biexcitonic annihilation is small.

Another possible quenching mechanism needs to be considered is defect impurities. Direct exciton diffusion to these non-radiative quenching states may reduce the quantum efficiency of the OLED. Previously, it has been suggested that an increase in guest concentration will introduce more defect impurities within the emission layer, which will lead to exciton quenching.¹⁵⁸ In our case, the reduction of the host thickness increases the probability of the exciton to impact the impurities sites in the guest layers, which will lead to reduction of the quantum efficiency. However, the same is true when the thicknesses of the guest layers increase. From Figure 7.2 (a) and (b) it can be seen that, increasing the guest thickness only slightly reduces the quantum efficiency, in contrast to the impact of host thickness reduction which sharply reduces the efficiency. To be more specific, device with thinner host

thickness of 3 nm (nearly half of the optimum 5 nm host thickness) would have the same or better quantum efficiency than device with guest thickness of 2 nm (double the optimum 1 nm guest thickness), assuming quenching arises from defect impurities. However, on the contrary, device with 2 nm of guest layer shows much better efficiency with much red-shifted emission spectrum. Therefore, we can exclude the argument that exciton quenching is mainly due to possible direct diffusion toward non-radiative quenching states.

One may argue that the reason of the efficiency reduction for device with CBP layer smaller than 5 nm is due to thinner EML, which has shown to be an important parameter affecting the efficiency.¹⁵⁹ To eliminate this factor, we conducted another set of experiment where the thickness of the CBP layer was varied [Ir(ppy)₃ is fixed at 1 nm] while keeping total thickness of the organic layer fixed, therefore the structures studied consist of different number of cells. The EQE plots are shown in Figure 7.4 (a). It can be seen that, similar to the results from Figure 7.2 (b), the efficiency drops significantly as the CBP thickness reduces. Emission spectrum also shows no significant change, indicating no increase in aggregation state [Figure 7.4 (b)]. These confirm that the drops in efficiency for device with thin layer of CBP is caused by the increased interaction among Ir(ppy)₃ molecules, not the thinner emission region.

Figure 7.3 The proposed simplified Jablonski diagram of photophysical processes in the presence of other Ir(ppy)₃ molecules nearby. The radiative transition is indicated by straight arrows (F = fluorescence, P = phosphorescence), nonradiative process by wavy and dotted arrows (IC = internal conversion, ISC = intersystem crossing, VR = vibrational relaxation).

To discuss the long-range quenching mechanism quantitatively, we plotted the EQE versus CBP thickness at a low current density of $50 \mu\text{A}/\text{cm}^2$ [A low current density of $50 \mu\text{A}/\text{cm}^2$ was chosen to minimize other excitonic quenching such as the T-T and T-P annihilations, which become more significant at high current densities] in the inset of Figure 7.4 (a). It is known that the rate of the long range Förster process (K_{Fnr}) is proportional to R^{-6} for two-molecules interaction⁵⁶ and R^{-4} for molecule-planar layer interaction¹⁶⁰ where R is the distance between the donor and acceptor, i.e. the CBP thickness approximately. Hence, according to Eq (7.2), the $\text{EQE} \propto [1 + (R_{\text{Fnr}2D} / R)^4]^{-1}$, where $R_{\text{Fnr}2D}$ is the modified 2D nonradiative Förster radius which is related to the nonradiative Förster radius (R_{Fnr}) by $R_{\text{Fnr}2D} = (\sigma \pi R_{\text{Fnr}}^6)^{1/4}$,¹⁶¹ where σ is the molecular surface density of the guest layer.

It can be seen from the inset of Figure 7.4 (a), the data obtained experimentally (square) show a sharp increase in EQE for CBP thickness larger than 3 nm, which agrees well to the fitting curve (solid line) with a 2D Förster-type decaying rate (R^{-4}). This further verifies that the excitonic quenching occurred for devices with thin layer of CBP are enabled by the long range dipole-dipole interaction. From the fitting, the modified 2D nonradiative Förster radius is found to be around 3.8 nm. Assuming that the molecular surface density of the 1 nm Ir(ppy)₃ guest layer is approximately $\sigma \approx 1 - 0.6^2 \text{ nm}^{-2}$.¹⁶² The nonradiative Förster radius (R_{Fnr}) can be approximated to be 2.0-2.3 nm. This value is comparable to the calculated value of 1.8 nm for Ir(ppy)₃ based on spectrum overlap.¹⁶³ It is worth mentioning that device with bulk layer of Ir(ppy)₃, i.e. with R approaches the inter-molecular distance, EQE still show a respectable value of 0.6 % (shown in Figure 7.4(a) as $R = 0$).

Figure 7.4 (a) EQE for devices with various thickness of CBP with same total thickness of emission layers, (b) Normalized emission spectrum for devices in (a). Inset in (a) shows EQE versus CBP thickness at current density of 50 $\mu\text{A}/\text{cm}^2$ (squares) and the fitting curve (solid line) utilizing the Förster-type quenching rate, with a modified 2D nonradiative Förster radius of around 3.8 nm. The symbols in (a) apply to (b) as well.

For completeness, we also investigated the effect of thickness of emission region, with optimized cell parameter, to the device performance. Another set of experiment was conducted where we varied the numbers of cells for device with the optimized cell. Device with a structure of ITO/ NPB (50 nm)/ [Ir(ppy)₃ (1 nm)/ CBP (5 nm)] N cells/ Ir(ppy)₃ (1 nm)/ BCP (20 nm)/ Alq₃ (30 nm)/ Mg:Ag, with N varied from 1, 2, 4, 6, to 8, were studied. Figure 7.5 (a) shows the J-V and L-V curves for devices with various numbers of cells. For a fixed value of voltage, the current density increases as the number of cells reduces due to thinner structures. The luminance plots also follow similar trend as the current density. The normalized emission spectrum for devices with various numbers of cells is shown in Figure 7.5 (b). Devices with less than six cells exhibit an increase in NPB emission peaking at 420 nm, because of the poor carrier and excitons confinement.¹⁵⁹ The EQE is shown in the inset of Figure 7.5 (b). Devices with less than six cells are inefficient. EQE saturates for devices with cell number more than six. This agrees with the fact that thin layer of EML has poor carrier and exciton confinement. Device with six cells shows current and power efficiency of 31 cd/A and 24 lm/W, respectively, at a luminance of 15 cd/m².

Figure 7.5 (a) Current density (J) and Luminance (L) versus voltage for devices with different number of cells. (b) Normalized emission spectrum for devices in (a). Inset in (b) shows EQE versus current density for devices in (a). Symbols in (a) also apply in (b).

7.4. Summary

In summary, we studied the quenching mechanism in the host-guest system for phosphorescent OLED. A specially designed OLED structure with EML resembling that of the multiple quantum well was fabricated. Besides appearance of molecule aggregate state, we also observed for the first time a long range (Förster process) self-quenching in Ir(ppy)₃ phosphorescent molecule. The Förster process is allowed due to a significant overlap of emission and absorption spectrum of Ir(ppy)₃ molecules. Hence, to eliminate such a long range quenching effect, molecular synthesis should aim for phosphorescent materials with large Stokes' shift.

Sequential doping approach for fluorescent devices

8.1. Introduction

Doping has been generally used to increase the EQE for phosphorescent¹³ and fluorescent⁵ OLED devices performed by co-evaporating the host and dopant material; doping enables isolation of emitting-molecule to reduce the aggregation effect in solid state.⁴⁴ Precise control of the evaporation rates of both host and dopant materials is crucial to ensure optimal performance. However, it is not an easy task considering day-to-day repeatability.¹⁶⁴ Uniform deposition rate of organic materials is difficult to achieve because the organic materials are typically thermal insulators. In a conventional evaporation boat, only those organic materials in contact with the resistively heated boat are heated, creating pockets in the source that occasionally collapse under gravity, resulting in rapid changes in deposition rate.¹⁶⁵ For fluorescent OLED, repeatability is further hindered by the very low optimum doping concentration (~0.5%) which is difficult to control over a long time.⁵

In chapter seven, we have used the sequential doping to investigate the quenching mechanism in phosphorescent materials. Here we shall utilize the sequential doping method to fabricate two fluorescent, red and blue, OLEDs. The EML consists of a few repeating cells, similar to a multiple quantum well structure. Provided that layer thickness is easier to control than deposition rate, sequential doping should render

better control on device performance and day-to-day repeatability than the conventional doping (co-doping or random doping). Besides, this technique utilizes three independent parameters, host and dopant thickness in the cell and the number of cells, to allow a full range optimization on device performance. By controlling the thickness of host and guest of a single cell, devices with better performance compared to those made via co-evaporation method are reported.

8.2. Highly efficient red fluorescent OLED

8.2.1. Introduction

In this section we shall investigate red fluorescent OLED fabricated by sequential doping, where host and dopant materials are sequentially deposited as cells. We shall show that aggregation state can be minimized by depositing a very thin layer (0.1 nm) of dopant materials. We also studied the possible quenching mechanism responsible for the very low (if not zero) efficiency of pure fluorescent thin film. Our study on quenching mechanism enables better understanding of fluorescent materials in a hope to achieve simple yet highly efficient multilayer undoped OLEDs.

8.2.2. Experimental

Here we employed NPB as the hole transporting layer, Alq₃ as the host, DCM as dopant, and BCP as the HBL and also the ETL.

Assuming a Lambertian emission pattern, we calculated the EQE from the luminance, current density and EL spectrum. All measurements were carried out at room temperature under ambient atmosphere without any encapsulation.

8.2.3. Results and Discussion

Figure 8.1 (a) and (b) show the architecture of the fluorescent OLED fabricated using sequential doping and co-evaporation technique, respectively. In co-evaporation, dopants are randomly dispersed in the matrix of host molecules. By keeping the doping concentration low ($\sim 0.5\%$), almost all dopant molecules are isolated from one another, preventing the formation of aggregation state. By doing so, device with high EQE can be realized.¹⁶⁴ In sequential doping, similar isolation effect can be achieved by separating the dopant molecules with host layers. However, as dopants are deposited as a thin layer, aggregation effects are unavoidable but can be minimized.¹⁴⁹

To optimize device efficiency, we fabricated devices with a structure of NPB/[DCM (x nm)/ Alq₃ (5 nm)] (6 cells)/ DCM (x nm)/ BCP, where x was varied from 0.1, 0.2, 0.3, 0.5, 1, 1.5, to 2.0 nm. Figure 8.2 (a) shows the current density and luminance versus voltage curves for devices with various x 's. It can be seen that the current density shifts toward higher voltage as the thickness of DCM increases. This is due to a thicker structure and the likeliness of carrier trapping as current pass through the DCM molecules.⁵ The luminance plots show similar trend with the current density.

Figure 8.1 Schematic diagram of fluorescent OLED fabricated with sequential doping with *N* cells (a) and co-evaporation method (b).

Figure 8.2 (b) shows the normalized emission spectra for devices in Figure 8.2 (a). The emission peak shifts from 604 nm (0.1 nm of DCM) to 664 nm (2 nm of DCM).¹⁶⁶ The inset of Figure 8.2 (b) shows the EQE of the respective devices. It can be seen that the EQE drops from 1.45 % to 0.2 % photons/electron at a current density of $250 \mu\text{A}/\text{cm}^2$ for devices with DCM thicknesses of 0.1 nm and 2.0 nm, respectively. The large red-shift and reduction in EQE for devices with thicker DCM layer suggest the appearance of aggregation state.¹⁴⁹ Different from molecular states, aggregation states are formed when two molecules are positioned close to one another. The interaction between the molecules introduces new states different from those of the isolated molecules. Since it requires an overlap between two different molecular states, an excited aggregation state has a much longer lifetime, hence it has a much lower quantum yield.¹⁴⁹ Device with 0.1 nm of DCM layer shows the best EQE with an emission spectrum similar to that of the device fabricated by random doping with optimized doping concentration.⁵

Figure 8.2 (a) J-V and L-V curves for devices with various DCM thicknesses (six cells). (b) Normalized emission spectra for devices in (a). Inset in (b) shows EQE versus current density for devices in (a). Symbols in (a) also apply in (b).

To further optimize the cell, devices were fabricated with a structure of NPB/[DCM (0.1 nm)/ Alq₃ (y nm)] (6 cells)/ DCM (0.1 nm)/ BCP, where y was varied from 3, 6, 7, 8, 10, 15, to 20 nm. Figure 8.3 (a) shows the current density and luminance versus voltage curves for devices with various y's. It can be seen that the current density shifts toward higher voltage as the thickness of Alq₃ increases. This is due to a thicker structure. The luminance plots show similar trend with the current density.

Figure 8.3 (b) shows the emission spectrum for devices with various Alq₃ thicknesses. It can be seen that all devices show similar emission spectrum. The inset of Figure 8.3 (b) shows the EQE of the respective devices. EQE increases with the Alq₃ thickness and saturates for thickness larger than 15 nm. Also shown in the inset of Figure 8.3 is the EQE for device with a pure of Alq₃ layer of 30 nm. It can be seen that the maximum EQE for DCM device is more than three times higher (3.38 % photons/electron) than that of pure Alq₃ one (1.08 % photons/electron) at a current density of 50 $\mu\text{A}/\text{cm}^2$. To our knowledge, this is the highest reported EQE for DCM based fluorescent OLED.^{5,167} The linear relationship between EQE and current density in the log-log plot can be attributed to an increased biexcitonic quenching with the increase of current density.¹⁶⁸ In sequential doping, the current passes through the thin layers of DCM. In addition to singlet-singlet annihilation (biexciton quenching), the existence of free carriers in DCM may introduce another current density dependent loss. A particular quenching mechanism is the singlet-polaron annihilation process.¹⁶⁸

Figure 8.3 (a) J-V and L-V curves for devices with various Alq_3 thicknesses (six cells). (b) Normalized emission spectra for devices with various thicknesses of Alq_3 (six cells). Inset in (b) shows the corresponding EQE. Symbols in (b) also apply in (a).

The decrease in EQE for device with Alq₃ thickness less than 15 nm signifies excitonic quenching. As the structures only differ by the thickness of the Alq₃ layer that separates the DCM layers, and as no aggregation state appears (see Figure 8.3), the excitonic quenching can only come from the increased interaction between the emitting DCM molecules. Since DCM layers are separated by a number of Alq₃ molecules (30-100 Å), the only known energy transfer mechanism that apply in such range is the Förster process.⁵⁶ The long range Förster energy transfer occurs when the absorption spectrum of an acceptor molecule overlaps with emission spectrum of a donor molecule, provided the state transition is allowed (see chapter 7). Since the absorption and emission spectrum of the DCM molecule overlap significantly,¹⁶⁹ energy transfers between DCM molecules are possible.

Figure 8.4 (a) shows the Jablonski diagram of the photophysical processes including Förster energy transfer. Luminescence (fluorescence) corresponds to a spin allowed transition from the excited state (S_1) to the ground state (S_0). The radiationless transition involves internal conversion (IC) from S_1 to the higher energy vibrational-mode of the S_0 referred as S_0^v . Then, vibrational relaxation (VR) from S_0^v to S_0 occurs thermally. In the presence of another molecule nearby, it is possible that S_1 transfers its energy to the excited state of the adjacent molecule (S_1') via Förster process. Meanwhile, there is also another vibrational-mode ($S_0^{v'}$) that may involve in the process, i.e. a S_1 - $S_0^{v'}$ transition, which is similar to the Förster process. The S_1 - $S_0^{v'}$ transition will introduce a new radiationless decay pathway which will result in reduction of the quantum efficiency. Assuming that the S_1 - S_0 , S_1 - S_0^v - S_0 , S_1 - S_1' and S_1 - $S_0^{v'}$ occurred at rates of K_r , K_{nr} , K_F and K_{Fnr} respectively, the quantum efficiency can be written as

$$\eta = \frac{K_r + \eta K_F}{K_r + K_{nr} + K_{Fnr} + K_F}, \quad (8.1)$$

from which, η can be rewritten as

$$\eta = \frac{K_r}{K_r + K_{nr} + K_{Fnr}}. \quad (8.2)$$

In our case, as Alq₃ thickness reduces, the radiationless transition ($S_1 \rightarrow S_0^{v'}$) K_{Fnr} increases, resulting in the decrease in EQE of the device.

For a complete understanding of the excitonic quenching, we need to consider the overall radiationless Förster interaction within the planar guest layer and between the guest layers. Assuming the guest molecules in the planar layer are homogeneously distributed in a 2D square lattice with inter-molecular separation of a , the summation of the radiationless Förster interaction within the planar guest layer (2D) can be written as:

$$K_{Fnr2D} = \int_a^\infty \frac{1}{\tau} \left(\frac{R_{Fnr}}{r} \right)^6 \sigma 2\pi r dr = \frac{2\pi\sigma R_{Fnr}^6}{\tau} \int_a^\infty \frac{r dr}{r^6} \quad (8.3)$$

where τ is the exciton lifetime, R_{Fnr} is the radiationless Förster radius, and σ is the surface density of the guest layer (for the case of square lattice, $\sigma = a^{-2}$). The overall radiationless Förster interaction within the guest layer is therefore:

$$K_{Fnr2D} = \frac{\pi}{2\tau} \left(\frac{R_{Fnr}}{a} \right)^6 \quad (8.4)$$

On the other hand, the overall interactions between the guest layers (3D) can be written as:

$$K_{Fnr3D} = 2 \times \frac{2\pi\sigma R_{Fnr}^6}{\tau} \int_0^\infty \frac{r dr}{(r^2 + R^2)^3} = \frac{\pi\sigma R_{Fnr}^6}{\tau} \left(\frac{1}{R^4} \right) \quad (8.5)$$

where R is the distance between the guest layers, the factor 2 is included to consider both neighboring layers. The overall Förster process is the summation of the 2D and 3D terms,

$$K_{Fnr} = \frac{\pi}{2\tau} \left(\frac{R_{Fnr}}{a} \right)^6 + \frac{\pi}{\tau} \frac{R_{Fnr}^2}{a^2} \left(\frac{R_{Fnr}}{R} \right)^4 \quad (8.6)$$

The quantum efficiency then becomes

$$\eta = \frac{K_r}{K_r + K_{nr} + K_{Fnr}} = \frac{\eta_\infty}{1 + \left(\frac{R_{Fnr2D}}{R} \right)^4} \quad (8.7)$$

where the maximum quantum efficiency (η_∞) is given by

$$\eta_\infty = \frac{K_r}{K_r + K_{nr} + \frac{\pi}{2\tau} \left(\frac{R_{Fnr}}{a} \right)^6} \quad (8.8)$$

and the modified 2D radiationless Förster radius is

$$R_{Fnr2D} = \left(\frac{1}{\eta_\infty} \right)^{1/4} \left(\frac{\pi R_{Fnr}^6}{a^2} \right)^{1/4} \quad (8.9)$$

Eq. 8.7 shows that the efficiency drops as the thickness of the host layer (R) reduces.

In Figure 8.4 (b), we plotted the EQE versus the Alq₃ thickness at a low current density of 50 $\mu\text{A}/\text{cm}^2$ [A low current density of 50 $\mu\text{A}/\text{cm}^2$ was chosen to minimize other excitonic quenching such as the singlet-singlet (see section 2.7.1), singlet-polaron (see section 2.7.3), and singlet-heat (see section 2.7.4) annihilations, which become more significant at high current densities]. It can be seen that the data obtained experimentally (square) fits well with Eq. 8.7, indicating that the excitonic quenching occurred for devices with thin layer of Alq₃ are enabled by the long range

dipole-dipole interaction. From the fitting, the modified 2D radiationless Förster radius is around 6.5 nm.

Estimation of the radiationless Förster radius can be done using Eq 8.9 by incorporating the modified 2D radiationless Förster radius obtained from the fitting. The internal quantum efficiency of the DCM molecule is taken to be 0.55¹⁷⁰ (notice that the Förster radius has a weak dependence with the quantum efficiency $\propto (\eta_{\infty})^{1/6}$). To estimate the intermolecular spacing of the DCM layer, we assume that 0.1 nm of DCM layer corresponds to 0.1 monolayer of DCM. Assuming that a monolayer square lattice of DCM has intermolecular spacing of 1 nm, the intermolecular spacing of 0.1 monolayer can be estimated as $a = 1 \text{ nm} \times \frac{1}{\sqrt{0.1}}$. Further assuming that two molecules may be closely spaced forming aggregate (dimer), the intermolecular spacing may ranges between 3-6 nm. Therefore using Eq. 8.9, the radiationless Förster radius is $R_{\text{Fnr}} = 3.6\text{-}4.5 \text{ nm}$

The radiative Förster radius is given by

$$R_F^6 = \frac{9}{8\pi} \frac{c^4}{n^4} \kappa^2 \int \frac{E_D(\omega) \phi_A(\omega)}{\omega^4} d\omega \quad (8.10)$$

where c is the speed of the light, n is the refractive index of the organic material, κ is the orientation factor, E_D is the normalized molecular donor emission spectrum, and ϕ_A is the molecular acceptor absorption cross section.⁴⁴ Assuming that only a fraction of the spectral overlap (Eq. 8.10) corresponds to the radiationless Förster transfer, the radiationless and radiative Förster radius should be in the same order due to the R^6 relation.

The R_F value of guest-host system of DCM-Ir(ppy)₃ is 5.0 nm.¹⁷⁰ This value is calculated for a maximum spectrum overlap between the emission Ir(ppy)₃ and absorption of DCM. In DCM-DCM system, the spectrum overlap can be estimated to be 1/10 of the maximum spectrum overlap.¹⁶⁹ This means that the R_F value for the DCM-DCM system can be estimated to be

$$R_{F(DCM-DCM)} = \left(\frac{1}{10} \right)^{1/6} R_{F(Ir(ppy)_3-DCM)} = 3.4 \text{ nm} \quad (8.11)$$

This value is comparable with the radiationless Förster radius obtained from the fitting of the experimental data.

The excitonic quenching within the planar DCM guest layer can be estimated using Eq. 8.4. Assuming that the inter-spacing of DCM molecules within the planar layer is 6 nm, we have:

$$\frac{K_{Fnr2D}}{K_r} = \frac{\pi}{2} \left(\frac{R_{Fnr}}{a} \right)^6 = 0.052 \quad (8.12)$$

This means that the excitonic quenching within the planar guest layer is miniscule and therefore can be neglected.

Figure 8.4 (a) The proposed simplified Jablonski diagram of photophysical processes in the presence of other DCM molecules nearby. The radiative transition is indicated by straight arrows, radiationless process by wavy arrows. (b) shows EQE versus Alq₃ thickness at current density of 50 $\mu\text{A}/\text{cm}^2$ (squares) and the fitting curve (solid line) utilizing the Förster-type quenching rate, with $R_{Fnr2D} = 6.5$ nm.

From the fitting and analysis above, the Förster radius was found to be around 3.4 nm. The Förster radius for DCM device is larger than that for Ir(ppy)₃-based phosphorescent OLED utilizing CBP as the host (2 nm) in Chapter 7. This indicates that the dipole-dipole interaction between the DCM molecules is more significant than that of Ir(ppy)₃. Together with the more significant appearance of aggregation state [Figure 8.2 (b)], the larger Förster radius explain why DCM based fluorescent OLED requires a very low doping concentration of about 0.5% compared to that of Ir(ppy)₃ based phosphorescent OLED (7%).¹⁶ Another reason for such a thick host in fluorescent OLED is that a long-range Förster process is responsible for the energy transfer from host to guest molecule, while phosphorescence occurs via short-range Dexter process.

For devices with Alq₃ thicknesses of 15 nm or more, the active emitting regions spans from 50 to 140 nm from the cathode. However, previous experimental results have shown that emission from distance larger than 100 nm from cathode resulted in destructive interference for wavelength of 550-600 nm.¹⁵⁷ This means that our device should have lower EQE due to the interference effect. However, as shown in the inset of Figure 8.3 (b), the EQE is maximized instead for devices with Alq₃ thickness larger than 15 nm. This can only occur if those DCM layers located at distance larger than 100 nm from thr cathode do not contribute to light emission (redundant), or only those DCM layer near cathode contributes to emission.

To investigate this matter, we conducted another series of experiment where the number of cells was varied. We studied the structure of NPB/ [DCM (0.1 nm)/ Alq₃ (15 nm)] (N cells)/ DCM (0.1 nm)/ BCP, where N was varied from 2, 3, 4, 5, to 6. Figure 8.5 (a) and (b) show respectively the current density versus voltage curve and

the normalized emission spectra for devices with various numbers of cells. It can be understood that the operating voltage decreases with less cells due to reduced layer structure. From the emission spectrum, it can be seen that the two-cell device shows an increase in Alq₃ emission. No significant change in emission spectrum was observed for devices with more than three cells. Inset of Figure 8.5 (b) shows the EQE for those devices in (a). The EQE of the two-cell device is slightly lower than the rest, which show almost the same EQE. The appearance of Alq₃ emission and slight drops in EQE for the two-cell device shows incomplete energy transfer from Alq₃ molecule to DCM molecule. This is due to inadequate numbers of DCM molecules available for emission. The three-cell device shows the best performance with current and power efficiency of 6.6 cd/A and 4.2 lm/W, respectively, at a luminance of 3.3 cd/m². At a higher luminance of 1000 cd/m² [with the CIE coordinates of (x, y) = (0.58, 0.41)], the current efficiency drops to 3.1 cd/A, which seems smaller than that reported by Xie *et al.*¹⁶⁷ However, the spectrum in Xie's paper is much greener (with slight emission from Alq₃) compared to ours.

It is worth mentioning that the device structure has the potential for further optimization, such as the usage of LiF¹³⁰ or CsF¹⁷¹ cathodes, hole⁴² (or electron)¹²-blocking layer, corrugated substrate,¹³¹ microcavity¹⁷² and/or utilization of higher efficiency dopant¹⁶⁴ in order to further reduce the operating voltage and increase the EQE of the device.

Figure 8.5 (a) J-V curves for devices with different numbers of cells. (b) Normalized emission spectra for devices in (a). Inset in (b) shows EQE versus current density for devices in (a). Symbols in (a) also apply in (b).

8.3. Highly efficient blue fluorescent OLED

8.3.1. Introduction

We have reported red fluorescent OLED fabricated by sequential doping, which relies on thickness rather than rate control, where host and guest materials are sequentially deposited as cells. Here, we report on a blue OLED with sequential doping. Besides achieving a high efficiency close to the conventional doping method, devices with different emission spectra can be realized without altering the efficiency by simply varying the thickness of the guest layer. This capability is unique to sequential doping as both the thicknesses of guest and host layers can be controlled separately. In contrast, the conventional doping only allows one parameter, the doping concentration, to be varied. It is the purpose of this section to highlight this unique feature of sequential doping.

The inset of Figure 8.6 (a) shows the architecture of the blue fluorescent OLED fabricated using sequential doping. In co-evaporation, guests are randomly dispersed in the matrix of host molecules. By keeping the doping concentration low ($\sim 0.1\text{-}5\%$), almost all guest molecules are isolated from each other, preventing the formation of aggregate states. By doing so, a device with high EQE (2.8% photons/electron) can be realized. In sequential doping, a similar isolation effect can be achieved by separating the guest molecules with host layers. However, as guests are deposited as a thin layer, aggregation effects are unavoidable but can be minimized.

8.3.2. Experimental

Here we employed NPB as the HTL, CBP as the host, BCzVBi as guest, and BCP as the HBL and Alq₃ as the ETL. Measurement and characterization are the same with those of section 8.1.

8.3.3. Results and Discussion

For the first step of optimization, we varied the thickness of the host layer while fixing the guest layer thickness. We fabricated devices with a structure of NPB/[BCzVBi (0.5 nm)/ CBP (x nm)] (6 cells)/ BCzVBi (0.5 nm)/ BCP/Alq₃, where x was varied from 3, 5, 7, 10 to 15 nm. Figure 8.6 (a) shows the current density and luminance versus voltage curves for devices with various values of x. As expected, the current density drops with the increase of the CBP thickness, as thicker structure leads to a higher operating voltage. The luminance also follows the trend of the current density.

The emission spectra for various devices at a current density of 5 mA/cm² are shown in Figure 8.6 (b). The inset of Figure 8.6 (b) shows the external quantum efficiency (EQE) of the respective devices in Figure 8.6 (a). A maximum EQE of 2.8 % photons/electron was obtained for a device with 7 nm of CBP layer. The EQE is comparable to that of OLED fabricated by the conventional doping method using the same materials.³⁹ Current and power efficiency reach 4.5 cd/A and 2.3 lm/W, respectively, at a current density of 100 μ A/cm² for the optimized device. Devices with CBP thickness larger than 7 nm, besides having a lower efficiency, also emit an additional peak at 420 nm, as shown in Figure 8.6 (b). This indicates that the efficiency loss originates from an incomplete energy transfer from the host to the

guest molecules, which leads to the host emission [The emission peak corresponds to NPB emission. This occurs because the excess excitons in CBP transfer their energy to NPB layer]. In contrast, the device with thin layers of CBP and a similar lower EQE, show no sign of host emission. This suggests that the exciton quenching occurs via an escalating interaction among guest layers, which may introduce another non-radiative recombination pathway (chapter eight). Interaction between the active BCzVBi layers can be activated by dipole-dipole coupling (Förster process) type interaction, due to its long range capability.⁵⁶ However unlike the known Förster process which involves the electronic state of the excited donor and ground acceptor, the process occurring here is between the excited donors and the vibrational mode of the acceptor (see chapter eight). This is because the known Förster process would not result in efficiency loss, while the later introduces a new non-radiative decay channel. As the thickness of the CBP is reduced, the active layers of BCzVBi become closer to one another resulting in the increase of the non-radiative energy transfer rate between the active layers.

Figure 8.6 (a) Current density and luminance versus voltage for devices with various CBP thicknesses. (b) Normalized emission spectrum for the device in (a). The inset in (a) shows the architecture of the blue OLED fabricated by the sequential doping method. The inset in (b) shows EQE versus current density for the devices in (a). Symbols in (a) also apply in (b).

In addition to the variation of the host thickness, we also varied the thickness of the guest layer. It is found that a variation of guest thickness is able to shift the emission spectrum without degrading the device EQE. We fabricated devices with a structure of NPB/ [BCzVBi (y nm)/ CBP (7 nm)] (6 cells)/ BCzVBi (y nm)/ BCP/Alq₃, where y was varied from 0.1, 0.5, 1, 1.5 to 2 nm. Figure 8.7 (a) shows the current density and luminance versus voltage curves for devices for various values of y . The operating voltage slightly shifts toward higher values with the increase of BCzVBi thickness, which illustrates that the guest material alters the current transport. The luminance curves on the other hand do not show much change, except for a BCzVBi thickness of 2 nm. Maximum luminance for device with 2 nm and 0.1 nm of BCzVBi is 8165 cd/m² and 3697 cd/m², respectively. Current and power efficiency reach 5.3 cd/A and 2.5 lm/W, respectively, at a current density of 100 μ A/cm² for a device with 2 nm of BCzVBi layer. This seemingly indicates that the device with thicker guest layer emits light more efficiently. However, as we will see later, the increase in luminance is accompanied by a shift in the emission peak. The shift of the emission spectrum to longer wavelengths resulted in the seemingly better device performance. In Table 8.1, we summarized the performances of the device with various thicknesses of BCzVBi. Table 8.1 also tabulates the equivalent guest concentration by conventional doping which produces a similar emission spectrum with that fabricated by the sequential doping method. Details of the calculation are explained later in the paper.

Table 8.1. Summary of performances for devices with various BCzVBi thicknesses

Thickness of BCzVBi (nm)	EQE (%) @ $J=100 \mu\text{A}/\text{cm}^2$	Current Efficiency (cd/A) @ $J=100 \mu\text{A}/\text{cm}^2$	Power Efficiency (lm/W) @ $J=100 \mu\text{A}/\text{cm}^2$	Operating voltage @ $J=100 \mu\text{A}/\text{cm}^2$	CIE (x,y)	Fraction of Aggregate (f)	Peak of Emission Spectrum (nm)	Corresponding conventional doping concentration
0.1	1.4	1.9	1	5.9	0.15,0.17	0	472	0.005-0.01% (monomer)
0.5	2.6	4.5	2.3	6.2	0.15,0.24	0.4	478	0.625-1.25%
1.0	2.5	4.7	2.3	6.3	0.16,0.29	0.7	482	5-10%
2.0	2.5	5.3	2.5	6.8	0.18,0.34	1	488	40-80%

Figure 8.7 (b) plots the emission spectrum for devices in Figure 8.7 (a). The emission peak shifts from 472 to 488 nm for thicknesses of BCzVBi of 0.1 to 2 nm, respectively. In term of CIE coordinate, it shifts from deep blue $(x,y) = (0.15,0.17)$ to slightly greenish blue $(x,y) = (0.18,0.34)$. As the photopic response is higher at a green wavelength (Chapter 3), a device that emits slightly greener would have higher luminance value compared to that of pure blue. This explains why the device with thick BCzVBi appears to have a higher luminous efficiency. In Figure 8.8, we plotted the EQE for all devices in Figure 8.7. Except for the device with 0.1 nm of BCzVBi, the EQE shows almost the same value irrespective of the guest thickness with a maximum EQE of 2.8 % photons/electron. This indicates that the aggregate state does not alter the EQE. The device with 0.1 nm of BCzVBi exhibits lower EQE because of the inadequate number of guest molecules available for emission. From the emission spectrum, it can be seen clearly that the device with 0.1 nm BCzVBi has an additional peak at 420 nm, which shows an incomplete host-guest energy transfer.

The shift in emission spectrum is obviously related to the aggregation of the BCzVBi molecules. Molecule aggregation may shift the emission wavelength by a few different mechanisms, the solid state solvation effect,¹⁵⁴ increase in local order,¹⁵⁸ and increase in electronic aggregate state (dimer or excimer).⁴⁴ Here, we discuss the likeliness of each mechanism to explain the observed spectrum shift.

Figure 8.7 Current density and luminance versus voltage for devices with various BCzVBi thicknesses. (b) Normalized emission spectrum for device in (a), fitting data shown in square are obtained from a linear combination of monomer and aggregate emissions with $f = 0.7$.

Figure 8.8 EQE for devices with various thicknesses of BCzVBi with six cells as emission layer. Inset shows the logarithmic plot of emission peak and fraction of aggregation (f) versus BCzVBi thickness.

The solid state solvation effect occurs due to an increase in the local electric field (permittivity) of the thin film, which results in a wavelength shift.¹⁵⁴ Provided that the host and guest molecules have different dipole moments, a variation of the concentration of either molecule would change the local electric field, hence the permittivity. In other words, an emission shift is expected if either the host or the guest layer thickness changes, i.e. an increase in thickness of the guest layers has a similar effect, though weaker, with reduction of host thickness. However, for our case, a spectrum shift is only observed for devices with a variation of the guest layer.

A variation of the host thickness only changes the EQE of the device, but does not change in emission spectrum. Hence, the solid state solvation effect can be eliminated from the rationale behind the spectrum shift.

An alternative explanation of the emission shift is the increase in local order due to thicker structure of the active molecules. In the literature, an increase in local order resulted in a logarithmic shift in the emission spectrum with the size of the order-domain.¹⁵⁸ Order-domain is defined as the average area of molecular aggregate where molecules are correlated by the dipole-dipole interaction. For our case the thickness of the guest layer corresponds linearly to the dimension of the order-domain. In the inset of Figure 8.8, we plotted the peak energy (emission spectrum) as a function of guest layer thickness. A logarithmic shift is clearly observed. This signifies that the shift in the emission spectrum is due to an increase in the local order of the active molecules. Based on this model, we can calculate the corresponding guest concentration for a device fabricated by conventional doping which produces a similar emission spectrum to that fabricated by sequential doping. As mentioned above, the shift in emission spectrum is caused by the increase in the order-domain. In conventional doping, the size of the order-domain (R) is related with the doping concentration (η) by $R^3 \propto \eta$.¹⁵⁸ Assuming that the emission of the device with 1 nm of BCzVBi (with peak emission at 482 nm) corresponds to the conventional doping concentration of 5-10%,^{140,173,174} we can extrapolate the corresponding guest doping concentration by conventional doping for devices with other thicknesses of BCzVBi proportionally (Table 8.1). The emission from the device with a BCzVBi layer of 0.1 nm can be considered as monomer emission due to its low corresponding guest concentration of 0.005-0.01% for conventional doping.

Another way to understand the shift in the emission spectrum is the following: we divide the emission spectrum into two separate entities, one of which is pure monomer emission ($g_{Monomer}(\lambda)$), and the other emission of a purely aggregate electronic state ($g_{Aggregate}(\lambda)$) (such as dimers or excimers),

$$g(\lambda) = (1 - f)g_{Monomer}(\lambda) + fg_{Aggregate}(\lambda) \quad (8.13)$$

where f is the fraction of the aggregate emission. As the thickness of the guest layer increases, an increase in the fraction (f) of aggregate emission is expected. The fitting of emission spectrum as combination of monomer and aggregation [we assumed pure monomer (aggregate) emission for the devices with 0.1 (2.0) nm of BCzVBi] is shown as square in Figure 8.7(b), where a good fit is achieved. In the inset of Figure 8.8, we also plotted the fraction of aggregate (f) as a function of guest thickness. The fraction of aggregate emission increases and eventually saturates with the increase of the guest layer thickness. This is reasonable, as at a certain guest thickness, the emission spectrum should not shift any more.

Both models, the local order and electronic aggregate, are able to fit well with the data obtained in the experiment. This coincidence may occur only if the dipole-dipole coupling is weak and the aggregate peak only slightly red-shifts compared to that of the monomer. The exact origin of the emission shifts, however, remains inconclusive; it can be either the local order or electronic aggregate, or both.

In the picture of local order, the drop in efficiency with an increase in order-domain is usually discussed in terms of material impurity.¹⁵⁸ For our case, the absence of efficiency loss for thick guest layers that is accompanied by an emission shift indicates that the purity of the BCzVBi is very high. Our discussion on electronic

aggregate state indicates that the dimer or excimer of the BCzVBi molecule has a high photo-yield relatively to the monomer.⁴⁴

It is worth mentioning that the device structure has the potential for further optimization, such as the usage of LiF/Al or CsF/Al cathodes and the reduction in the number of cells in order to further reduce the operating voltage and the complexity of the device.

8.4. Summary

In this chapter we reported two highly efficient fluorescent OLEDs by sequential doping methods. Sequential doping provides an alternative for the commonly used co-doping technique. We have introduced a sequential doping method for efficient red fluorescent OLED. Device with EQE of 3.38 % photons/electron has been produced, the highest reported for DCM based OLED. The excitons quenching in the thin layers of DCM was not mainly due to the appearance of aggregation state, but to the presence of inter-molecule energy transfer among DCM molecules, i.e. by long range Förster process between the DCM molecules in different layers. The Förster process is allowed due to a significant overlap of emission and absorption spectrum of DCM molecules; hence to eliminate quenching effect, molecular synthesis should aim for fluorescent materials with large Stokes' shift. The number of cells is also found to be an important parameter determining devices performance. A device with three cells is enough to achieve the maximum EQE.

We have also fabricated a blue OLED with the sequential doping method. A device with EQE of 2.8% photons/electron is reported, similar to that achieved by the conventional doping method. A variation of guest thickness is shown to shift the

emission spectrum without sacrificing the EQE. The mechanism which governs the emission shift is concluded to be due to either the local order or electronic aggregate, or both, but not the solid state solvation effect.

Conclusions and recommendation for future works

9.1. Conclusions

OLED has shifted from a laboratory experiment to an industrial platform for futuristic display technologies. OLED is a device that utilizes various organic layers to convert electrical energy into light. Every organic layer serves a different function to optimize each single process involves in light production. Inevitably, multilayer structure is almost ubiquitous in OLED design. In this thesis, we tempted, using multilayer structures to optimize every aspect of photon production in OLED.

The role of CuPc, as HIL or HBL, has been controversial. The first is a study of the effect of addition of CuPc and role of oxygen plasma treatment on the performances of OLED. We observe that CuPc can act as hole injection or blocking layer, depends on the oxygen content at the CuPc-NPB interface, i.e. depend on oxygen plasma treatment. When large oxygen diffuse to the CuPc-NPB interface, CuPc serve as a hole blocking due to broadening in the interface density of state. On the other hand when there is lack of oxygen diffusion to the interface, CuPc act to improve the hole current due to it high hole mobility and lower injection barrier from ITO to the CuPc layer.

Our second study is on the insertion of a thin HBL between the hole-injection and hole transporting layers to improve the performance of OLED. In a typical OLED

structure, the hole current is much larger than the electron current. This causes imbalance in the flux of carrier, which means some holes escape the recombination and contribute to loss. Addition of a HBL between the hole-injection and hole-transporting layers serves to reduce the hole current. The current efficiency was improved by almost 30% for devices with 3 nm of BCP or 2 nm blocking-Alq₃ layers inserted between the hole-injection and hole-transporting layers. Variation of HTL thickness was observed to render different result for devices with BCP and blocking-Alq₃ as HBL. In devices with BCP blocking layer, the voltage reduces with reduction of NPB thickness, while the current efficiency remains unchanged. However, in devices with Alq₃ blocking layer, besides reduction in voltage, the current efficiency also decreases with reduction of HTL thickness. For devices with blocking-Alq₃ layer, as the HTL thickness reduces less than 20 nm, the electron starts to leak to the blocking-Alq₃ HBL results in the inefficient exciplex emission.

In OLED, excitons can easily diffuse to the adjacent layer due to the large exciton diffusion length. If the adjacent layer has lower bandgap and lower quantum yield, excitons are readily to be quenched. To confine the excitons within the emission layer and minimize excitons loss through diffusion, we utilize layers with large bandgap to sandwich the emission layer. Significant improvement in device performance was reported with 25% of improvement in EQE (1.38%).

We also design two multilayer structures to produce white emission. To do this we design the emission layer such that the excitons are formed in two different places, one for blue emission, and the other for green (or orange) emission. The device is capable to achieve almost perfect white color with moderate EQE. The maximum EQE and luminance are 0.89% photon/electron (2 cd/A) and 4500 cd/m² at a current

density of 270 mA/cm², respectively. Considering that no-doping method was used, our structures show rather good performances.

To achieve high performances, OLED structure normally incorporates a host-guest system (doping) in the emission layer. Host-guest system minimizes aggregation of guest molecules so as to enable high quantum yield. When the doping concentration increases, the guest molecules start to aggregate and results in drop in EQE. Beside lower EQE, aggregation of molecule also produces emission which is red-shifted that the monomer. In OLED, aggregation was always considered as the culprit behind this concentration quenching. We discovered that besides molecule aggregation, a new long range quenching mechanism involving a Förster-like dipole-dipole interaction between the guest molecules also responsible for the concentration quenching. Our quantitative analysis shows that the efficiency as a function of host layer thickness follows the characteristics of the long range Förster process. The long range Förster process is found to be the dominant quenching mechanism and determined by the overlap between the emission and absorption spectra of the guest molecules. Based on our finding, it is possible to eliminate concentration quenching by minimizing the emission and absorption spectra overlap of the guest molecules, providing guidance for chemical synthesis. Moreover, according to our finding, it is possible to develop highly efficient OLED that do not rely on the host-guest system, hence a much more simplified and controllable fabrication process.

In some cases, co-doping method suffers from repeatability issue, since it involves precision control of evaporation rate of two or more types of organic materials at the same time. To solve this problem, we introduce a new design for host-guest system, the sequential doping. Instead of co-evaporating the host and guest materials at the

same time, they are deposited in a sequential manner, like the multiple quantum well. This structure relies on thickness control rather than rate control as that in co-evaporation case. The sequential doping technique also enables realization of devices emitting different spectrum without degrading the power and current efficiency.

9.2. Recommendation for future works

Recent technology news says that SONY is going to introduce the world thinnest OLED television in December of 2007, indicating the OLED technology is maturing, and is becoming more engineering-oriented. A big question now for OLED researcher is that “Is there any science left for future study?”

As discussed in chapter two, OLED suffers from various bi-excitonic quenchings that limit the performance of the device under high current operation, which is also the main obstacle in achieving electrically pumped organic lasers.¹⁷⁵ Although the mechanisms for this current-dependent exciton annihilation are known, few studies can be relied on. The lack of microscopic understanding of various biexcitonic annihilations, such as the singlet-singlet, singlet-polaron, triplet-triplet, and the singlet-triplet annihilations, make it difficult to eradicate the problems. Recently, an enlightening study on the triplet-triplet annihilation mechanism was reported.¹⁷⁶ It was suggested that the triplet-triplet annihilation can be eliminated by minimizing the spectral overlap between triplet-ground state emission and triplet-triplet vibrational mode absorption. Future works should focus on understanding detail physics of the various others biexcitonic quenching in organic semiconductor.

A complete understanding of carrier injection and transportation in organic semiconductor is important to further improve the performance of the OLED. In the

literature, various mechanisms have been attributed to carrier injection and transportation in organic semiconductor, but a consistent and convincing theory that applicable for general cases is still lacking.⁷⁵ A consistent theory could also be valuable for development of the other fields such as the organic TFT and photovoltaic devices. Future works should attempt to achieve a complete understanding of carrier injection and transportation in organic semiconductor.

Our study on excitonic quenching in phosphorescent material in chapter seven suggests that the concentration quenching can be eliminated by minimizing the overlap between the emission and absorption spectra of the guest molecules. Therefore development of new phosphorescent materials with a large Stoke's shift is important and desirable. Phosphorescent material which suffers no concentration quenching, will significantly reduce the complexity of the OLED structure, where no guest-host system is required.

Sequential doping has shown its potential as an alternative for co-doping method (chapter eight). Besides its usefulness for applications that require ultra low doping concentration, it is also able to achieve what co-doping could not, such as devices emitting different spectrum without degrading the EQE. We only showed two applications of sequential doping; future works could extend sequential doping to other applications such as white OLEDs, photovoltaic devices, etc.

Recently, a new method to achieve a highly efficient OLED, termed the extrafluorescence, was introduced.¹⁷⁷ Instead of harvesting the spin-forbidden triplet excitons, the spin orientation of the injected carrier was altered to minimize the formation of triplet exciton. Others have also suggested of using a manganite

electrode to inject spin-polarized carriers into the device.^{178,179} These techniques are interesting and should be further investigated in the future.

About 80% or so of the light produced in the organic semiconductor is absorbed by the cathode-organic surface plasmon mode and waveguide. In the literature, various techniques have been applied to extract the trapped light, such as the usage of corrugated substrates,¹⁸⁰ photonic crystals,¹⁸¹ microcavity,¹⁷² incorporation of microlens,¹⁸² etc. However, these solutions increase the complexity of the device and suffer from angular dispersion. Future study may focus on introducing a simple structure design to extract these trapped modes with angular dispersion eliminated or minimized.

Refereed journal publications

1. **Divayana Y**, Sun XW, Chen BJ, Lo GQ, Jiang CY, Kwong DL and Sarma KR, “Bandgap engineering in Alq₃- and NPB-based organic light-emitting diodes for efficient green, blue and white emission ” *Solid State Electronics* 51, 1618, Nov 5 2007.
2. **Divayana Y** and Sun XW, “Sequentially doped blue electrofluorescent organic light-emitting diodes” *Org. Electron.* 9, 136, Oct 30 2007.
3. **Divayana Y** and Sun XW, “Observation of excitonic quenching by long-range dipole-dipole interaction in sequentially doped organic phosphorescent host-guest system”, *Phys. Rev. Lett.* 99, 143003, Oct 5 2007. Also selected for the October 15, 2007 issue of *Virtual Journal of Biological Physics Research*.
4. **Divayana Y**, Sun XW, Chen BJ, Lo GQ, Jiang CY, Kwong DL and Sarma KR, “Undoped White Organic Light-Emitting Diodes Utilizing Two Sources of Excitons” *Jpn. J. Appl. Phys.* 46 (8A), 5164, Aug 6 2007.
5. **Divayana Y** and Sun XW, “Efficient electrofluorescent organic light-emitting diodes by sequential doping”, *Appl. Phys. Lett.* 90 (20), 203509, May 14 (2007).
6. **Divayana Y**, Sun XW, Chen BJ, and Sarma KR, “Improved organic light-emitting device with tris-(8-hydroxyquinoline) aluminium inserted between hole-injection layer and hole-transporting layer”, *J. Phys. D: Appl. Phys.* 40 (1): 183-186, Jan 7 2007.
7. **Divayana Y**, Sun XW, Chen BJ, Lo GQ, Jiang CY, and Sarma KR, “Efficient blue organic light-emitting device based on N,N'-di(naphth-2-yl)-N,N'-

- diphenyl-benzidine with an exciton-confining structure” *Appl. Phys. Lett.* 89 (17), 173511, Oct 23 2006.
8. **Divayana Y**, Chen BJ, and Sun XW, “Comment on "Singlet-singlet and singlet-heat annihilations in fluorescence-based organic light-emitting diodes under steady-state high current density" [Appl. Phys. Lett. 86, 213506 (2005)] ”, *Appl. Phys. Lett.* 88 (9), 096101, Feb 27 2006.
 9. **Divayana Y**, Chen BJ, Sun XW, and Sarma KR, “Organic light-emitting devices with a hole-blocking layer inserted between the hole-injection layer and hole-transporting layer” *Appl. Phys. Lett.* 88 (8), 083508, Feb 20 2006.
 10. **Divayana Y**, Chen BJ, Sun XW, Wong TKS, Sarma KR, and Hu X, “Hole injection or blocking? The role of CuPc in Alq(3)-based organic light-emitting devices ”, *J. Cryst. Growth* 288 (1), 105-109, Feb 2 2006.
 11. Chen BJ, Sun XW, **Divayana Y**, and Tay BK, “Improving organic light-emitting devices by modifying indium tin oxide anode with an ultrathin tetrahedral amorphous carbon film”, *J. Appl. Phys.* 98 (4), 046107, Aug 15 2005.

Conference presentations

1. **Divayana Y**, Sun XW, and Chen BJ, “Multilayer Approach for Efficient Multicolor Organic Light-emitting Diodes”, in *Proc. of the 10th Asian Symposium on Information Display*, Singapore, Aug 2007.
2. **Divayana Y** and Sun XW, “Highly efficient electrophosphorescent and electrofluorescent organic light-emitting diodes by sequential doping”, in *Proc. of the International Conference on Materials for Advanced Technologies 2007*, Singapore, Jul 2007.
3. **Divayana Y**, Sun XW, Chen BJ, Lo GQ, Jiang CY, Kwong DL and Sarma KR, “Optimizing the interference effect for high-efficient undoped white organic light-emitting diodes”, in *Proc. of the Asia Display 2007*, Shanghai, China, Mar 2007.
4. **Divayana Y**, Sun XW, Chen BJ, Lo GQ, and Sarma KR, “Improved organic light-emitting devices with tunable IV by inserting a hole-blocking layer between hole-injecting layer and hole-transporting layer”, in *Proc. of the 36th European Solid-State Device Research Conference*, Montreux, Switzerland, Sept 2006.
5. **Divayana Y**, Chen BJ, Sun XW, Wong TKS, Sarma KR, and Hu X, “The role of CuPc in organic light-emitting diodes”, in *Proc. of the International Conference on Materials for Advanced Technologies 2005*, Singapore, Jul 2005.

Bibliography:

- ¹ Z. Kafafi, *Organic Electroluminescence* (Taylor and Francis, Boca Raton, 2005).
- ² J. Kalinowski, *Organic Light-Emitting Diodes. Principles, Characteristics, and Processes* (Marcel Dekker, New York, 2005).
- ³ W. E. Howard, in *Scientific American Magazine*; Vol. 290 (2004), p. 76-81.
- ⁴ C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **11**, 913 (1987).
- ⁵ C. W. Tang, S. A. VanSlyke, and C. H. J. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- ⁶ J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature* **347**, 539 (1990).
- ⁷ A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burn, A. B. Holmes, and A. Kraft, *Appl. Phys. Lett.* **61**, 2793 (1992).
- ⁸ S. A. VanSlyke, C. H. Chen, and C. W. Tang, *Appl. Phys. Lett.* **69**, 2160 (1996).
- ⁹ S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock, and J. C. Scott, *Appl. Phys. Lett.* **70**, 2067 (1997).
- ¹⁰ L. S. Hung, C. W. Tang, and M. G. Mason, *Appl. Phys. Lett.* **70**, 152 (1997).
- ¹¹ J. Kido and T. Matsumoto, *Appl. Phys. Lett.* **73**, 2866 (1998).
- ¹² M. Pfeiffer, S. R. Forrest, K. Leo, and M. E. Thompson, *Adv. Mater. (Weinheim, Ger.)* **14**, 1633 (2002).
- ¹³ M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature* **395**, 151 (1998).
- ¹⁴ C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 5048 (2001).
- ¹⁵ M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Nature* **403**, 750 (2000).
- ¹⁶ C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000).
- ¹⁷ E. Balasubramaniam, Y. T. Tao, A. Danel, and P. Tomasik, *Chem. Mater.* **12**, 2788 (2000).
- ¹⁸ L. H. Chan, H. C. Yeh, and C. T. Chen, *Adv. Mater. (Weinheim, Ger.)* **13**, 1637 (2001).
- ¹⁹ Y. H. Kim, D. C. Shin, S. H. Kim, C. H. Ko, H. S. Yu, Y. S. Chae, and S. K. Kwon, *Adv. Mater. (Weinheim, Ger.)* **13**, 1690 (2001).
- ²⁰ K. Okumoto and Y. Shirota, *Appl. Phys. Lett.* **79**, 1231 (2001).
- ²¹ M. Kinoshita, H. Kita, and Y. Shirota, *Adv. Funct. Mater.* **12**, 780 (2002).
- ²² C. C. Wu, Y. T. Lin, H. H. Chiang, T. Y. Cho, C. W. Chen, K. T. Wong, Y. L. Liao, G. H. Lee, and S. M. Peng, *Appl. Phys. Lett.* **81**, 577 (2002).
- ²³ S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.* **83**, 569 (2003).
- ²⁴ R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li, and M. E. Thompson, *Appl. Phys. Lett.* **83**, 3818 (2003).

- 25 B. W. D'Andrade, R. J. Holmes, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **16**, 624 (2004).
- 26 X. Gong, W. Ma, J. C. Ostrowski, G. C. Bazan, D. Moses, and A. J. Heeger, Adv. Mater. **16**, 615 (2004).
- 27 T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S. C. Lo, and P. L. Burn, Appl. Phys. Lett. **82**, 4824 (2003).
- 28 Y. Kawamura, S. Yanagida, and S. R. Forrest, J. Appl. Phys. **92**, 87 (2002).
- 29 J. P. J. Markham, S. C. Lo, and S. W. Magennis, Appl. Phys. Lett. **80**, 2645 (2002).
- 30 T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, and J. C. Sturm, Appl. Phys. Lett. **72**, 519 (1998).
- 31 S. C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, and I. D. W. Samuel, Adv. Mater. **14**, 975 (2002).
- 32 Z. G. Liu and H. Nazare, Synth. Met. **111**, 47 (2000).
- 33 R. H. Jordan, A. Dodabalapur, M. Strukelj, and T. M. Miller, Appl. Phys. Lett. **68**, 1192 (1996).
- 34 B. W. D'Andrade, M. E. Thompson, and S. R. Forrest, Adv. Mater. **14**, 147 (2002).
- 35 C. H. Chen and H. F. Meng, Appl. Phys. Lett. **86**, 201102 (2005).
- 36 T. Y. Chu, J. F. Chen, S. Y. Chen, and C. H. Chen, Appl. Phys. Lett. **89**, 113502 (2006).
- 37 J. H. Jou, Y. S. Chiu, C. P. Wang, R. Y. Wang, and H. C. Hu, Appl. Phys. Lett. **88**, 193501 (2006).
- 38 B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson, and S. R. Forrest, Adv. Mater. **14**, 1032 (2002).
- 39 Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, Nature **440**, 908 (2006).
- 40 M. A. Baldo, D. F. O'Brien, M. E. Thompson, and S. R. Forrest, Phys. Rev. B **60**, 14422 (1999).
- 41 H. Kanno, R. J. Holmes, Y. Sun, S. K. Cohen, and S. R. Forrest, Adv. Mater. **18**, 339 (2006).
- 42 L. S. Liao, K. P. Klubek, and C. W. Tang, Appl. Phys. Lett. **84**, 167 (2004).
- 43 G. Parthasarathy, G. Gu, and S. R. Forrest, Adv. Mater. **11**, 907 (1999).
- 44 M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2 ed. (Oxford University Press, Oxford, 1999).
- 45 J. B. Birks and D. J. Dyson, Proc. Roy. Soc. (London) A **275**, 135 (1963).
- 46 L. D. Landau and E. M. Lifshitz, *Quantum mechanics (course of theoretical physics v.3)*, 3 ed. (Butterworth-Heinemann, Oxford, 1977).
- 47 D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, and D. M. Whittaker, Nature **395**, 53 (1998).
- 48 T. Förster, Angew. Chem. internut. Edit. **8**, 333 (1969).
- 49 D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, D.-K. Fu, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, Appl. Phys. Lett. **70**, 1644 (1997).
- 50 M. Klessinger and J. Michl, *Excited states and photochemistry of organic molecules* (VCH Publishers, New York, 1995).
- 51 P. M. Morse, Phys. Rev. **34**, 57.

52 M. A. Baldo, Thesis, Princeton University, 2001.
 53 M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).
 54 R. Englman and J. Jortner, Mol. Phys. **18**, 145 (1970).
 55 D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
 56 T. Förster, Discuss. Faraday Soc. **27**, 7 (1959).
 57 H. Nakanotani, H. Sasabe, and C. Adachi, Appl. Phys. Lett. **86**, 213506
 (2005).
 58 M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000).
 59 S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, and G. Wegner,
 Phys. Rev. Lett. **97**, 143903 (2006).
 60 D. Cahen, A. Kahn, and E. Umbach, in *Materials Today* (2005), p. 32.
 61 C. Shen, A. Kahn, and I. G. Hill, in *Conjugated Polymer and Molecular*
Interfaces, edited by W. R. Salaneck, K. Seki, A. Kahn, and J. J. Pireaux
 (Marcel Dekker, Inc, New York, 2002).
 62 A. Kahn, N. Koch, and W. Gao, J. Poly. Sci. B: Poly. Phys. **41**, 2529 (2003).
 63 I. G. Hill and A. Kahn, J. Appl. Phys. **88**, 4515 (1999).
 64 A. Rajagopal and A. Kahn, J. Appl. Phys. **84**, 355 (1998).
 65 I. G. Hill, A. Rajagopal, A. Kahn, and Y. Hu, J. Appl. Phys. **73**, 662 (1998).
 66 H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. **11**, 605 (1999).
 67 I. G. Hill, J. Schwartz, and A. Kahn, Org. Electron. **1**, 5 (2000).
 68 C. Shen, A. Kahn, and J. Schwartz, J. Appl. Phys. **89**, 449 (2001).
 69 P. S. Bagus, V. Staemmler, and C. Woll, Phys. Rev. Lett. **89**, 096104 (2002).
 70 X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W. R. Salaneck,
 and J. L. Bredas, J. Am. Chem. Soc. **124**, 8131 (2002).
 71 N. Koch, E. Zojer, A. Rajagopal, J. Ghijsen, R. L. Johnson, G. Leising, and J.
 J. Pireaux, Adv. Funct. Mater. **11**, 51 (2001).
 72 A. Rajagopal, C. I. Wu, and A. Kahn, J. Appl. Phys. **83**, 2649 (1998).
 73 I. G. Hill and A. Kahn, J. Appl. Phys. **84**, 5583 (1998).
 74 I. G. Hill, D. Milliron, J. Schwartz, and A. Kahn, Appl. Surf. Sci. **166**, 354
 (2000).
 75 J. C. Scott, J. Vac. Sci. Technol. A **21**, 521 (2003).
 76 I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).
 77 A. J. Campbell, D. D. C. Bradley, J. Laubender, and M. Sokolowski, J. Appl.
 Phys. **86**, 5004 (1999).
 78 P. R. Emtage and O'Dwyer, Phys. Rev. Lett. **16**, 356 (1966).
 79 J. C. Scott and G. C. Malliaras, Chem. Phys. Lett. **299**, 115 (1999).
 80 D. Emin, Advances Physics **24**, 305 (1975).
 81 T. Holstein, Annals of Physics **8**, 325 (1959).
 82 T. Holstein, Annals of Physics **8**, 342 (1959).
 83 A. Miller and E. Abrahams, Phys. Rev. **20**, 745 (1960).
 84 R. A. Marcus, J. Chem. Phys. **24**, 966 (1955).
 85 R. H. I. Young, Philosophical Magazine B **72**, 435 (1995).
 86 U. Wolf, V. I. Arkhipov, and H. Bassler, Phys. Rev. B **59**, 7507 (1999).
 87 V. I. Arkhipov, U. Wolf, and H. Bassler, Phys. Rev. B **59**, 7514 (1999).
 88 S. Barth, U. Wolf, H. Bassler, P. Muller, H. Riel, H. Vestweber, P. F. Seidler,
 and W. Riess, Phys. Rev. B, 8791 (1999).
 89 H. Ishii and K. Seki, IEEE Trans. Electron Devices **44**, 1295 (1997).

90 I. Hill, A. Rajagopal, A. Kahn, and Y. Hu, Appl. Phys. Lett. **73**, 662 (1998).
 91 M. A. Baldo and S. R. Forrest, Phys. Rev. B **64**, 085201 (2001).
 92 M. Stoßel, J. Staudigel, F. Steuber, J. Blassing, J. Simmerer, and A.
 Winnacker, Appl. Phys. Lett. **76**, 115 (2000).
 93 W. D. Gill, J. Appl. Phys. **43**, 5033 (1972).
 94 D. H. Dunlap, P. E. Parris, and V. M. Kenkre, Phys. Rev. Lett. **77**, 542 (1996).
 95 P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A.
 Cronin, and M. E. Thompson, J. Appl. Phys. **79**, 7991 (1996).
 96 S. C. Jain, A. K. Kapoor, W. Geens, J. Poortmans, R. Mertens, and M.
 Willander, J. Appl. Phys. **92**, 3752 (2002).
 97 S. T. Lee, Y. M. Wang, X. Y. Hou, and C. W. Tang, Appl. Phys. Lett. **74**, 670
 (1999).
 98 K. Itano, H. Ogawa, and Y. Shirota, Appl. Phys. Lett. **72**, 636 (1998).
 99 C. C. Wu, C. I. Wu, J. C. Sturm, and A. Kahn, Appl. Phys. Lett. **70**, 1348
 (1997).
 100 G. Wyszecki and W. S. Stiles, *Color Science. Concepts and Methods,*
Quantitative Data and Formulae, 2 ed. (John Wiley & Sons, Inc., 1982).
 101 E. Tutiş, D. Berner, and L. Zuppiroli, J. Appl. Phys. **93**, 4594 (2003).
 102 B. J. Chen, X. W. Sun, Y. Divayana, and B. K. Tay, J. Appl. Phys. **98**, 046107
 (2005).
 103 D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys.
 Lett. **74**, 442 (1999).
 104 B. J. Chen, X. W. Sun, T. K. S. Wong, X. Hu, and A. Uddin, Appl. Phys. Lett.
87, 063505 (2005).
 105 B. Massenelli, D. Berner, M. N. Bussac, F. Nuesch, and L. Zuppiroli, Appl.
 Phys. Lett. **79**, 4438 (2001).
 106 I. G. Hill and A. Kahn, J. Appl. Phys. **86**, 2116 (1999).
 107 H. Vestweber and W. Riess, Synth. Met. **91**, 181 (1997).
 108 H. Aziz, Z. D. Popovic, N. X. Hu, A. M. Hor, and G. Xu, Science **283**, 1900
 (1999).
 109 Z. D. Popovic, H. Aziz, N. X. Hu, A. M. Hor, and G. Xu, Synth. Met. **229**,
 111 (2000).
 110 Z. D. Popovic and H. Aziz, IEEE J. Quantum Electron. **8**, 362 (2002).
 111 S. M. Tadayyon, H. M. Grandin, K. Griffiths, P. R. Norton, H. Aziz, and Z. D.
 Popovic, Org. Electron. **5**, 157 (2004).
 112 V. I. Arkhipov, E. V. Emelianova, and H. Bassler, J. Appl. Phys. **90**, 2352
 (2001).
 113 E. Gautier, A. Lorin, J. M. Nunzi, A. Schalchli, J. J. Benattar, and D. Vital,
 Appl. Phys. Lett. **69**, 1071 (1996).
 114 T. D. Anthopoulos and T. S. Shafai, Appl. Phys. Lett. **82**, 1628 (2003).
 115 A. K. Hassan and R. D. Gould, J. Phys.: Condens. Matte. **1**, 6679 (1989).
 116 V. I. Arkhipov, P. Heremans, E. V. Amelianova, and H. Bassler, Phys. Rev. B
71, 045214 (2005).
 117 A. R. Hosseini, M. H. Wong, Y. Shen, and G. G. Malliaras, J. Appl. Phys. **97**,
 023705 (2005).
 118 Y. Shen, K. Diest, M. H. Wong, B. R. Hsien, D. H. Dunlap, and G. G.
 Malliaras, Phys. Rev. B **68**, 081204 (2003).

119 C. C. Wu, C. I. Wu, J. C. Sturm, and A. Kahn, Appl. Phys. Lett. **70**, 1348
 (1997).
 120 M. B. Khalifa, D. Vaufrey, and J. Tardy, Org. Electron. **5**, 187 (2004).
 121 J. G. Simmons, J. Appl. Phys. **34**, 2581 (1963).
 122 C. Qiu, H. Chen, M. Wong, and H. S. Kwok, IEEE Trans. Electron. Devices
48, 2131 (2001).
 123 B. Ruhstaller, T. Beierlein, H. Riel, S. Karg, J. C. Scott, and W. Riess, IEEE
 J. Quantum Electron. **9**, 723 (2003).
 124 Y. F. Liew, F. Zhu, S. J. Chua, and J. X. Tang, Appl. Phys. Lett. **85**, 4511
 (2004).
 125 J. C. Scott, G. G. Malliaras, W. D. Chen, J. C. Breach, J. R. Salem, S. B.
 Sachs, and C. D. E. Chidsey, Appl. Phys. Lett. **74**, 1510 (1999).
 126 C. Giebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, J. Appl. Phys.
85, 608 (1999).
 127 S. T. Zhang, Z. J. Wang, J. M. Zhao, Y. Q. Zhan, Y. Wu, Y. C. Zhou, X. M.
 Ding, and X. Y. Hou, Appl. Phys. Lett. **84**, 2916 (2004).
 128 D. Troadec, G. Veriot, and A. Moliton, Synth. Met. **127**, 165 (2002).
 129 L. S. Hung, L. R. Zheng, and M. G. Mason, Appl. Phys. Lett. **78**, 673 (2001).
 130 L. S. Hung, C. W. Tang, M. G. Mason, P. Raychaudhuri, and J. Madathil,
 Appl. Phys. Lett. **78**, 544 (2001).
 131 Y. J. Lee, S. H. Kim, J. Huh, G. H. Kim, Y. H. Lee, S. H. Cho, Y. C. Kim, and
 Y. R. Do, Appl. Phys. Lett. **82**, 3779 (2003).
 132 A. P. Kulkarni, A. P. Gifford, C. J. Tonzola, and S. A. Jenekhe, Appl. Phys.
 Lett. **86**, 061106 (2005).
 133 M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, Appl. Phys. Lett. **79**,
 156 (2001).
 134 Y. Kijima, N. Asai, and S. I. Tamura, Jpn. J. Appl. Phys. **38**, 5274 (1999).
 135 C. C. Tsou, H. T. Lu, and M. Yokoyama, J. Cryst. Growth **289**, 168 (2006).
 136 G. Yu, X. Xu, Y. Liu, Z. Jiang, S. Yin, Z. Shuai, D. Zhu, X. Duan, and P. Lu,
 Appl. Phys. Lett. **87**, 222115 (2005).
 137 P. Andrew and W. L. Barnes, Science **306**, 1002 (2004).
 138 D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, D. K. Fu, T. M.
 Swager, A. G. MacDiarmid, and A. J. Epstein, Appl. Phys. Lett. **70**, 1644
 (1997).
 139 B. W. D'Andrade and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **16**, 1585
 (2004).
 140 H. Kanno, Y. Sun, and S. R. Forrest, Appl. Phys. Lett. **89**, 143516 (2006).
 141 Y. Zhang, G. Cheng, Y. Zhao, J. Hou, and S. Liu, Appl. Phys. Lett. **86** 011112
 (2005).
 142 X. Gong, S. Wang, D. Moses, G. C. Bazan, and H. J. Heeger, Adv. Mater.
 (Weinheim, Ger.) **17**, 2053 (2005).
 143 J. Thompson, R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli, and R. Cingolani,
 Appl. Phys. Lett. **79**, 560 (2001).
 144 R. S. Deshpande, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. **75**, 888
 (1999).
 145 S. J. Yeh, H. Y. Chen, M. F. Wu, L. H. Chan, C. L. Chiang, H. C. Yeh, C. T.
 Chen, and J. H. Lee, Org. Electron. **7**, 137 (2006).

146 C. W. Ko and Y. T. Tao, Appl. Phys. Lett. **79**, 4234 (2001).
 147 T. Tsuji, S. Naka, H. Okada, and H. Onnagawa, Appl. Phys. Lett. **81**, 3329
 (2002).
 148 X. Xu, G. Yu, C. Di, Y. Liu, K. Shao, L. Yang, and P. Lu, Appl. Phys. Lett. **89**
 123503 (2006).
 149 R. Farchioni and G. Grosso, *Organic Electronic Materials* (Springer, Berlin,
 2001).
 150 J. B. Birks, Rep. Prog. Phys. **38**, 903 (1975).
 151 T. M. Wu, D. W. Brown, and K. Lindenberg, Phys. Rev. B **47**, 10122 (1993).
 152 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest,
 Appl. Phys. Lett. **75** (1999).
 153 C. Adachi, M. A. Baldo, and S. R. Forrest, J. Appl. Phys. **87**, 8049 (2000).
 154 C. F. Madigan and V. Bulovic, Phys. Rev. Lett. **91**, 247403 (2003).
 155 K. A. King, P. J. Spellane, and R. J. Watts, J. Am. Chem. Soc. **107**, 1431
 (1985).
 156 T. Tsuboi and M. Tanigawa, Thin Solid Films **438**, 301 (2003).
 157 S. K. So, W. K. Choi, L. M. Leung, and K. Neyts, Appl. Phys. Lett. **74**, 1939
 (1999).
 158 M. A. Baldo, Z. G. Zoos, and S. R. Forrest, Chem. Phys. Lett. **347** 297 (2001).
 159 B. W. D'Andrade and S. R. Forrest, J. Appl. Phys. **94**, 3101 (2003).
 160 J. Hill, S. Y. Heriot, O. Worsfold, T. H. Richardson, A. M. Fox, and D. D. C.
 Bradley, Phys. Rev. B **69**, 041303 (2004).
 161 S. R. Scully, P. B. Armstrong, C. Edder, J. M. J. Frechet, and M. D. McGehee,
 Adv. Mater. **19**, 2961 (2007).
 162 J. C. Ribierre, A. Ruseckas, K. Knights, S. V. Staton, N. Cumpstey, P. L.
 Burn, and I. D. W. Samuel, Phys. Rev. Lett. **100**, 017402 (2008).
 163 Y. Kawamura, J. Brooks, J. J. Brown, H. Sasabe, and C. Adachi, Phys. Rev.
 Lett. **96**, 017404 (2006).
 164 C. T. Chen, Chem. Mater. **16**, 4389 (2004).
 165 S. R. Forrest, Nature **428**, 911 (2004).
 166 J. Jakabovic, O. Lengyel, J. Kovac, T. C. Wong, C. S. Lee, and S. T. Lee,
 Appl. Phys. Lett. **83**, 1295 (2003).
 167 Z. Y. Xie, L. S. Hung, and S. T. Lee, Appl. Phys. Lett. **79**, 1048 (2001).
 168 M. A. Baldo, R. J. Holmes, and S. R. Forrest, Phys. Rev. B **66**, 035321 (2002).
 169 V. G. Kozlov, G. Parthasarathy, P. E. Burrows, V. B. Khalfin, J. Wang, S. Y.
 Chou, and S. R. Forrest, IEEE J. Quantum Electron. **36**, 18 (2000).
 170 B. W. D'Andrade, M. A. Baldo, C. Adachi, J. Brooks, M. E. Thompson, and
 S. R. Forrest, Appl. Phys. Lett. **79**, 1045 (2001).
 171 M. Y. Chan, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, Chem. Phys.
 Lett. **374**, 215 (2003).
 172 H. Peng, J. Sun, X. Zhu, X. Yu, M. Wong, and H. S. Kwok, Appl. Phys. Lett.
88, 073517 (2006).
 173 C. Hosokawa, H. Higashi, H. Nakamura, and T. Kusumoto, Appl. Phys. Lett.
67, 3853 (1995).
 174 Y. Kishigami, K. Tsubaki, Y. Kondo, and J. Kido, Synth. Met. **153**, 241
 (2005).
 175 M. A. Baldo, R. J. Holmes, and S. R. Forrest, Phys. Rev. B **66**, 035321 (2002).

- 176 W. Staroske, M. Pfeiffer, K. Leo, and M. Hoffmann, Phys. Rev. Lett. **98**,
197402 (2007).
- 177 M. Segal, M. Singh, K. Rivoire, S. Difley, T. Van Voorhis, and M. A. Baldo,
Nat. Mat. **6**, 374 (2007).
- 178 I. Bergenti, V. Dediu , E. Arisi, T. Mertelj, M. Murgia, A. Riminucci, G.
Ruani, M. Solzi, and C. Taliani, Org. Electron. **5**, 309 (2004).
- 179 E. Arisi, I. Bergenti, V. Dediu , M. A. Loi, M. Muccini, M. Murgia, G. Ruani,
C. Taliani, and R. Zamboni, J. Appl. Phys. **93**, 7682 (2003).
- 180 D. K. Gifford and D. G. Hall, Appl. Phys. Lett. **81**, 4315 (2002).
- 181 Y. R. Do, Y. C. Kim, Y. W. Song, C. O. Cho, H. Jeon, Y. J. Lee, S. H. Kim,
and Y. H. Lee, Adv. Mater. (Weinheim, Ger.) **15**, 1214 (2003).
- 182 S. Moller and S. R. Forrest, J. Appl. Phys. **91**, 3324 (2002).