Efficiency optimization of organic light-emitting diodes

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EFFICIENCY OPTIMIZATION OF ORGANIC LIGHT-EMITTING DIODES

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2014

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Efficiency Optimization of Organic Light-emitting Diodes

Summary

Interest in Organic light-emitting diode (OLED) technology was extensive lately, because of the unique advantages compared to its inorganic counterpart and other technologies. With extensive research of more than two decades, OLED has advanced from pure laboratory research and stepped into the commercial world, however, due to current limitation in efficiency, yield and cost, OLED technology has still a long way to go to be a dominant force in display and lighting market.

This thesis focuses on the optimization of OLED through improvement of the internal and external efficiencies. Firstly, high-efficiency green emission phosphorescent OLED with much better roll-off of efficiency was demonstrated. Replacing N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) with 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA) as hole transporting (HTL) and electron blocking layer (EBL) not only eliminates the exciton quenching by relocating the exciton formation zone from the EBL/ emissive layer interface to the hole blocking layer (HBL)/ emissive layer interface, which avoid exciton quenching by the lower triplet NPB, it also broadens the exciton formation with much more uniform exciton distribution profile within emissive layer, which is very useful to suppress triplet-triplet annihilation, reducing the efficiency roll-off.

Secondly, a graded host approach was employed to achieve higher efficiency red phosphorescent OLED with lower roll-off. The graded host is a combination of two hosts with opposite charge transport abilities (i.e. n-type and p-type respectively), whose concentration fades towards the other emissive layer/ blocking layer interface. Due to the unipolar transport nature of most host material, the exciton formation region was commonly located at the emissive layer/ blocking layer interface, the narrow

Efficiency Optimization of Organic Light-emitting Diodes

exciton formation zone has detrimental effects on the efficiency at higher current injection level. The use of graded host layer allows self-balanced charge transport within emissive layer; the gradual reducing host composition relocates the recombination zone away from the interface, which helps reduce the exciton quenching such as triplet-triplet annihilation, where two triplet excitons interact and result in only one triplet.¹

Lastly, to further improve the efficiency of OLED, an external outcoupling technique was employed to extract portion of the light trapped (wave-guided) in the glass substrate which is also known as substrate mode. The outcoupling layer was fabricated by imprinting a layer of ZnO nanopillars arrays with varying pitches at the back side of the glass substrate. By studying the outcoupling characteristics of different pitched ZnO nanopillars, we achieved an efficient non-lambertian emission with much improved extraction efficiency. The angular emission characteristic of an OLED was changed significantly with the pitch of ZnO nanopillar, the optimized device shows a much wider angular distribution with peak luminous intensity observed at 40° viewing angle. Both the theoretical fitting and simulation confirm that the improved extraction was achieved by diffraction and higher extraction probability around the pillars due to light incident on the vertical walls.

Efficiency Optimization of Organic Light-emitting Diodes

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Efficiency Optimization of Organic Light-emitting Diodes

Contents

Summary i

Acknowledgements iii

List of figures viii

Chapter I 1

Introduction to organic light-emitting diode 1

1.1. Background 1

1.2. Advantages of OLED technology in display and lighting 3

1.3. Basic definition and configuration of OLED 7

1.4. History of OLED development 10

1.5. Objectives and achievements 12

1.6. Thesis organization 13

Chapter II 15

Review of OLED physics 15

2.1. Organic semiconducting materials 15

2.1.1. Organic semiconductors 16

2.1.2. Advantages and disadvantages of organic semiconductors 19

2.2. Charges injection and transport 21

2.2.1. Injection from electrode 22

2.2.2. Transport within organic material 25

2.2.3. Electrical doping 29

2.3. Excitons 32

Efficiency Optimization of Organic Light-emitting Diodes	
2.3.1.	Classification of excitons 33
2.3.2.	Quenching of excitons 35
2.4.	Energy transfer between molecules..... 37
2.5.	Light generation via fluorescence and phosphorescence 40
2.6.	Light extraction 42
2.7.	Summary 47
Chapter III 49	
Experiment setup and OLED characterization 49	
3.1.	Experimental setup 49
3.1.1.	Preparation of Indium Tin Oxide (ITO) substrate 49
3.1.2.	OLED deposition system 50
3.2.	Characterization of OLED 52
3.2.1.	Human eye response 53
3.2.2.	Chromaticity 53
3.2.3.	Terminologies used in OLED characterization..... 55
Chapter IV 58	
The study and optimization of triplet distribution and the performance of phosphorescent OLEDs 58	
4.1.	Introduction 58
4.2.	Experimental details..... 60
4.3.	Results and discussions 62
4.3.1.	Electrical and optical performance 62

Efficiency Optimization of Organic Light-emitting Diodes	
4.3.2.	Verification of device S1 performance 66
4.3.3.	Exciton distribution analysis..... 67
4.3.4.	Hole only devices..... 73
4.3.5.	Exciton quenching analysis via triplet-triplet annihilation 74
4.4.	Conclusion..... 76
Chapter V 77	
Optimization of the efficiency of red phosphorescent OLED via charge balance by self balanced charge transport..... 77	
5.1.	Introduction of EML optimization 77
5.2.	Experimental: devices fabrication and characterization..... 78
5.3.	Results and discussions 80
5.4.	Conclusion..... 89
Chapter VI..... 91	
The Study of OLEDs outcoupling using imprinted submicron-size zinc oxide pillar arrays..... 91	
6.1.	Introduction 91
6.2.	Experimental details..... 93
6.3.	Results and discussions 96
6.3.1.	Electrical results and efficiency analysis..... 96
6.3.2.	Angular emission characterization..... 99
6.3.3.	Efficiency over all angles..... 102
6.3.4.	Simulation..... 103

Efficiency Optimization of Organic Light-emitting Diodes	
6.4. Conclusion.....	106
Chapter VII	107
Conclusion and future challenges	107
7.1. Conclusion.....	107
7.2. Future challenges.....	108
Publications.....	110
Bibliography	113

Efficiency Optimization of Organic Light-emitting Diodes

List of figures

Fig. 1- 1 Carbon dioxide emissions by fuel type from 1990 to 2035 ⁶	2
Fig. 1- 2 Comparison between OLED and LCD displays ⁸	4
Fig. 1- 3 OLED display revenue forecast ¹⁰	5
Fig. 1- 4 Schematic structure of a bottom emitting OLED	7
Fig. 1- 5 types of OLED	9
Fig. 1- 6 commonly used organic materials in OLEDs	10
Fig. 1- 7 (a) bilayer OLED structure developed by Tang et al. (b) PLED configuration by Burroughes et al.	11
Fig. 2- 1 Schematic representation of sp ¹ , sp ² and sp ³ hybridization process	17
Fig. 2- 2 Schematic representation of π -bonds and σ -bond ²³	17
Fig. 2- 3 formation of anti-bonding and bonding states.....	19
Fig. 2- 4 Effects of contact barrier height in determining the electrical characteristics ³⁵ (a) energy band structure, (b) current-electric field curve fitted using F-N tunneling theory.	23
Fig. 2- 5 Log scale representation of typical J-V curve of OLED ⁶¹	27
Fig. 2- 6 Working principle of (a) N and (b) P doping in an organic material	30
Fig. 2- 7 Energy diagram measured by UPS/XPS for ITO and top: undoped ZnPc, bottom: doped ZnPc. ⁶⁹	31
Fig. 2- 8 Conductivity of ZnPc film with varying F4-TCNQ doping ratio. ⁶⁹	32
Fig. 2- 9 Representation of singlet and triplet spin configurations. ⁷⁸	34
Fig. 2- 10 (a) Device energy band structure and (b) resulted quantum efficiency ⁸⁰	36
Fig. 2- 11 Electronic transition of Forster and Dexter energy transfer mechanisms modified from Ref ⁹¹	38
Fig. 2- 12 Modified Jablonski energy diagram ⁹⁴	41

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 13 Light escape cone, modified based on Ref ⁹⁵	43
Fig. 2- 14 Light paths within OLED	45
Fig. 3- 1 Schematic plot of patterned ITO strips	49
Fig. 3- 2 OLED deposition system	51
Fig. 3- 3 human eye response for different wavelength.....	53
Fig. 3- 4 (a) color matching function (b) CIE chromaticity diagram.....	55
Fig. 4- 1 Device structure and energy bands for S1, S2 and S3.	61
Fig. 4- 2 (a) Current density versus voltage (J-V) and (b) luminance versus current density (L-J) for devices S1, S2 and S3.	63
Fig. 4- 3 (a) EQE with fitting and current efficiency versus current density and (b) power efficiency versus current density for devices S1, S2 and S3.	65
Fig. 4- 4 EQE, voltage and power efficiency (inset) of devices with NPB thickness of 40nm, 50nm, 60nm and 70 nm, respectively at current density of 0.1 mA/cm ²	66
Fig. 4- 5 Average triplet exciton distribution profile within CBP host for devices E1, E2 and E3.....	68
Fig. 4- 6 Emission spectrum of (a) E1, (b) E2, and (c) E3 at the current density of 0.22 mA/cm ² when the sensing layer was placed at X=0, 5 nm, 10 nm, and 15 nm.	70
Fig. 4- 7 J-V characteristics for devices (a) E1 with NPB as HTL (b) E2 with NPB/ TCTA as HTL and (c) E3 with TCTA as HTL.....	72
Fig. 4- 8 J-V characteristics of hole-only devices H1, H2 and H3.	73
Fig. 5- 1 (a) Device structure with layer compositions, (b) layer structure of graded EML with uniformly varying host concentration and fixed dopant concentration, and (c) proposed energy diagram with HOMO-LUMO values available in the literature.	80

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 5- 2 (a) Electroluminescence spectra for the devices with TCTA host, TPBI host and graded mixed hosts of TCTA and TPBI (G-host) and (b) L-J-V performance of the three devices.....	82
Fig. 5- 3 Sensing spectrum extracted from device with host of (a) TCTA only, (b) TPBI only and with (c) graded host, respectively, (c) exciton density within the different host materials.	85
Fig. 5- 4 Plot of (a) CE-J and (b) PE and EQE-J for OLED with TCTA host, TPBI host and the graded mixed hosts of TCTA and TPBI (G-host). Inset of (a) Normalized CE-J.	86
Fig. 5- 5 Transient PL of EML consisting of TPBI, TCTA and graded TCTA: TPBI as host, respectively.....	88
Fig. 5- 6 Comparison of PE - J and EQE - J between the D-host and G-host devices.	89
Fig. 6- 1 (a) PRINT process used to fabricate ZnO nanopillar array and (b) schematic illustration of the OLED stacks with ZnO nanopillar array at the back side of glass...	95
Fig. 6- 2 Patterns of the ZnO nanopillar array with pitch of (a) 400nm (b) 500 nm (c) 650 nm and (d) 800 nm, respectively measured by SEM.	96
Fig. 6- 3 (a) L-V and (b) CE-J characteristics of the reference device and devices with grating period of 400nm, 500nm, 650nm and 800nm. Inset: (a) normalized emission spectra for respective device (b) J-V curves.	98
Fig. 6- 4 (a) Normalized angular distributions of the reference device and device with different pitches. (b) Fitting of the angular distribution.	100
Fig. 6- 5 (a) EQE – J and (b) PE - J. Inset: Diffraction grating with the presence of ZnO nanopillar arrays.	103
Fig. 6- 6 Intensity field distribution with propagation of (a) reference OLED, (b) OLED with ZnO nanopillar array. (c) Experimental results of light extraction	

Efficiency Optimization of Organic Light-emitting Diodes

enhancement ratio with respect to fill factor in comparison with Lumerical FDTD
simulation and fitting result using diffraction theory. Inset of (b): zoom-in image of
field distribution..... 105

Chapter I

Introduction to organic light-emitting diode

Organic light-emitting diode (OLED) was recognized as the next-generation display and lighting technology due to its advantages like high efficiency, low power consumption, potential of low cost and large area processing capability, etc..^{2,3} OLED can be fabricated on top of a great variety of substrates such as thin metal foil, glass and even plastic films unlocks enormous possibilities for novel applications.^{4,5} An interactive transparent display mounted on the wall, dinner table or windows from science fiction movies or a 60 inch TV in millimeter thickness and can be folded into our pocket are among the gadgets made possible in the near future with OLEDs.

This chapter will provide the readers the basics of OLEDs. Section 1.1 illustrates the background and importance of OLED technology. Section 1.2 depicts the advantages of OLED in display and lighting applications. Section 1.3 describes the basic definition and configuration of OLED. Section 1.4 briefly introduces the history of the development of OLED; while section 1.5 shows the organization of this thesis.

1.1. Background

Accompanying the development of the global economy, the demand and generation of electricity have increased 2.3% in average annually from the year 2007 and it will remain so until the year 2035.⁶ Electricity is mainly used for industries and household consumptions. At the same time, energy consumption and carbon dioxide emission, also known as the greenhouse gas, increase significantly, deteriorating the environment. Fig. 1-1 shows the increasing trend of carbon dioxide emission by

Efficiency Optimization of Organic Light-emitting Diodes

different type of fuels from 1990 to 2035 forecasted by U.S. Energy information Administration.⁶ The greenhouse gas emission is mainly contributed by the use of energy to meet human needs, such as transportation, entertainment, commercial and residential activities. Ever since the beginning of industrial revolution, the burning of fuels (such as Coal, liquid, etc.) has been the major source of energy generation, the consumption of energy is the main culprit of greenhouse gas emission.⁷ Electricity consumption in both display and general lighting take a significant portion of the total energy consumption, improving the general efficiency of the display and lighting equipment thus can have a huge impact on the environment. Therefore, high efficiency and low cost display and lighting technologies are utmost essential.

Fig. 1- 1 Carbon dioxide emissions by fuel type from 1990 to 2035 ⁶

Despite of the environmental issues, our daily chore is surrounded by electrical powered appliances, such as lighting equipment, computer, mobile phone, TV and music player, etc. The requirements for low power, light and flexible display and

Efficiency Optimization of Organic Light-emitting Diodes

lighting systems have been driving the advancement of the current existing technology. OLED technology aims to replace liquid crystal display (LCD) with more efficient, lighter weight, higher resolution and brighter displays.

1.2. Advantages of OLED technology in display and lighting

There have been intensive researches focused on OLEDs in the past two decades. Owing to its potential of low cost, high efficiency and design flexibility, etc., OLED is regarded as the next generation display and lighting technology. In the following paragraphs, the advantages of OLED technology will be described in detail.

Although LCD technology still dominates the current display market, its limitation in colour saturation, contrast ratio, weight, efficiency and response time remain to be a big drawback for the technology. OLED display, particularly active-matrix OLED display (AMOLED) can offer several key advantages compared to the LCD technology:

The first one is the superior picture quality. As illustrated by Fig. 1-2 below, OLED can provide the audience with more vivid colours, nearly 180° viewing angle and much higher contrast ratio. The refresh rate of OLED display can be thousands of times faster than that of LCD.⁸

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 1- 2 Comparison between OLED and LCD displays⁸

Another advantage of OLEDs is its potential to achieve very high quantum efficiency. Nearly 100% internal quantum efficiency (IQE) of OLED can be achieved by using phosphorescent dopants.⁹ Furthermore, OLED is emissive, it does not need backlight to function, and it will produce the desired color itself. In contrast, LCD needs the color filter to filter the white backlight to produce the desired red, green and blue components. Therefore, in LCD, significant fraction of optical energy is wasted due to the filtration. Hence, OLED displays are expected to be more efficient and power saving than LCDs.

Moreover, OLED displays are much thinner and lighter than the current existing LCDs in the market. This is the inherent advantage of OLED owing to its structural characteristic. The average thickness of the organic component of OLED is around 100nm, which implies that the total thickness and weight of the OLED displays are limited by the substrate. Thus, it is understandable that the thickness of the OLED display can be made as thin as a piece of glass or even plastic. However, there is a popular type of display in the market currently named light-emitting diode (LED)

Efficiency Optimization of Organic Light-emitting Diodes

display, different from LCD TVs which use fluorescent back lighting, LED TVs employ more energy efficient and smaller size LEDs, however, the use of LEDs as back lighting units still makes the LED TVs significantly thicker and energy inefficient as compared to the self-emissive OLED TVs. Although the price of the large-area OLED display in market is relatively expensive today, it will drop dramatically in the future as the technology matures and mass production is carried out. Eventually, compared to other flat panel display (FPD) technologies, OLED display will be more cost effective since it consists less components and its production involves fewer materials and steps.^{2,3}

With the above-mentioned advantages of OLED displays, it can be imagined that the OLED display panel market will grow tremendously in the future. As forecasted by the DisplaySearch in second quarter of 2009 (shown in Fig. 1-3), the world AMOLED display revenue will increase from US \$67 million in 2007 to more than US \$ 7 billion by 2016, from which we can see the great potential of OLED displays in FPD market.¹⁰

Fig. 1- 3 OLED display revenue forecast¹⁰

Efficiency Optimization of Organic Light-emitting Diodes

In the field of lighting, OLED also has several advantages compared to the conventional lighting source. Compared to conventional incandescent lighting bulb which works at an efficiency around 10 lm/W and fluorescent lamp with higher efficiency of 70 lm/W, white OLED lighting with efficiency approaching 100 lm/W has been demonstrated.¹¹ Moreover, OLED lighting panels are two-dimensional, they emit light with no glares and harsh shadows, therefore, OLED is an ideal illuminating source for indoor ambient lighting. This is quite different from other lighting techniques such as LED, which is a point light source and requires light distribution elements to produce flat panel lightings. There are many other advantages such as thin, flat and light weight as introduced in the next paragraph, the color of the OLED can also be electronically controlled, all those advantages make OLED an attractive alternative for general lighting equipment.

In terms of design and innovation, slimness and flexibility are also their advantages. By employing a thinner substrate, the thickness of OLED appliances could be made to less than 1 mm. As a matter of fact, the thinnest prototype for OLED display has been made to be 0.3mm in thickness.¹² With such a characteristic, OLED lighting panels could be placed directly on walls or ceiling, rather than hanging in the air for the case of light bulb. Furthermore, by employing flexible substrate such as plastics or thin metal foil, OLED equipment could be made flexible, this characteristics allows OLED panel to be tailored towards certain specific requirement. Although flexible OLED electronics have not massively entered the market, it is forecasted that it will increase rapidly from 2018 (market share of 1% in OLED market) and take up 12% of the total OLED market by the year 2023.¹³

Efficiency Optimization of Organic Light-emitting Diodes

1.3. Basic definition and configuration of OLED

Before going deeper into the thesis, the first question we would like to know is what is an OLED. OLED is a device which consists of thin organic layers stacking in between two electrodes fabricated on a supporting substrate such as metal foils, glass and plastics. The operation principle of an OLED is not complicated. When the device is driven by electrical power, charges are firstly injected from their respective electrodes into the adjacent organic layers, then driven by the electric field, the injected charges transport to the emissive layer, where they recombine to emit light. Fig. 1-4 below shows a typical bottom emitting multi-layer OLED device.

Fig. 1- 4 Schematic structure of a bottom emitting OLED

The device shown above contains two highly conductive electrodes, anode and cathode, for a typical bottom emitting OLED. The anode should be transparent or semi-transparent to allow efficient light extraction from the substrate. Furthermore, to facilitate the hole injection from the anode, the material selected for anode should have a high work function, while the work function of cathode has to be small enough for

Efficiency Optimization of Organic Light-emitting Diodes

efficient electron injection. However, most of the commonly used anode materials don't possess sufficient large work function, which results in insufficient hole concentration in the OLED operation. To overcome this problem, a hole injection layer (HIL) is chosen to decrease the barrier height for hole injection, the same is true for electron injection layer (EIL) for efficient electron injection. To facilitate charge transport within the organic layers, namely hole transport layer (HTL) and electron transport layer (ETL), they need to possess good hole and electron transport property, respectively. The emissive layer is the region where light generation takes place, a single layer of organic material or a host-guest composite system may be used. A good host material shall be ambipolar in charge transport, i.e. able to transport both electron and hole efficiently, the bandgap of the host material should be large enough to confine excitons into the guest dye, which typically have high photoluminescence (PL) efficiency, thus, high light output. To have high quantum efficiency, both charges and excitons need to be confined within the emissive layer. This requires either a hole blocking layer (HBL) having good hole and exciton blocking properties or/and an EBL possessing good electron and exciton blocking properties to be placed at the transport layer/ EML interface.

Based on the light emitting direction and position of electrodes, OLED can be classified into four different types:

- 1: Bottom-emitting OLED (BEOLED, Fig. 1-5 (a)), which emits light from bottom (substrate) side of OLED, the anode is also placed at bottom.
- 2: Inverted bottom-emitting OLED (IBEOLED, Fig. 1-5 (b)), light emission from bottom, reflective anode is placed on top of organic materials.

Efficiency Optimization of Organic Light-emitting Diodes

- 3: Top-emitting OLED (TEOLED, Fig. 1-5 (c)), light emits through top of the OLED, anode is placed on the substrate side.
- 4: Inverted top-emitting OLED (ITEOLED, Fig. 1-5 (d)), light emission through top of OLED, anode is also placed on the top.

Fig. 1- 5 types of OLED

The definition is quite straightforward. For a bottom-emitting OLED, the light emission is from the bottom (substrate) side, otherwise it is top-emitting OLED. When the cathode is placed directly above the substrate (bottom) side, the OLED is called inverted.

Fig. 1-6 shows the structures of some commonly used organic materials, for example, an electron transport material: Tri-(8-hydroxyquinoline) aluminum (Alq_3), hole blocking material: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), host

Efficiency Optimization of Organic Light-emitting Diodes

material: 4-4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP), material with good hole transport ability: N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB), material help hole injection: Phthalocyanine, copper complex (CuPc) and green phosphorescent emitting material: Tris (2-phenylpyridine) iridium (III) (Ir(ppy)₃). From the molecular structures of the organic materials listed below, we can find that they are all aromatic compound. This is due to the fact that not all organic materials are suitable to be used in OLED, only organic semiconductors with good charge transport properties can be used. More details into organic semiconductors will be introduced in Chapter 2.

Fig. 1- 6 commonly used organic materials in OLEDs

1.4. History of OLED development

The origin of OLED technology can be traced back to the year 1963, when the organic electroluminescence (EL) was first discovered in a layer of electrically driven anthracene film by M. Pope *et al.*¹⁴ However, the low efficiency of the devices

Efficiency Optimization of Organic Light-emitting Diodes

fabricated was the main reason impeding its further development. The thick organic layer resulted in high driving voltage (larger than 100V) and extremely low efficiency of the device.¹⁵ Interest in the field was little until 1987, when Ching W. Tang and Steve Van Slyke invented a double-layer EL device shown in Fig. 1-7 (a) in Eastman Kodak Company.¹⁶ This device is commonly recognized as the world first OLED. The fabrication was done by deposition of 60 nm of Alq_3 and 75 nm of diamine in a bilayer configuration, which facilitated the electron and hole transport and recombination. This device was relatively efficient with an external quantum efficiency (EQE) of nearly 1%, high brightness level with luminance larger than 1000 cd/m^2 and low operating voltage ($<10\text{V}$). While the the first conjugated polymer based LED (PLED) was fabricated by Burroughes *et al.* in 1990 as shown in Fig. 1-7 (b) below.¹⁷ Since then, tremendous interest and research have been aimed to this field of OLED and significant progress have been made in the improvement of device structure, performance and development of new materials.

Fig. 1- 7 (a) bilayer OLED structure developed by Tang et al. (b) PLED configuration by Burroughes et al.

Another big breakthrough after the initial development was using of dopant (fluorescent) material within the host matrix.¹⁸ Although the bilayer OLED developed by Tang *et al.* was quite efficient, an EQE of 1% is far from enough for applications.

Efficiency Optimization of Organic Light-emitting Diodes

His group employed a doped Alq₃ layer as the light emitting region and achieved a maximum EQE of 2.5%.¹⁸ The use of dopants was a big step, it not only led to an improvement of the device efficiency, but also reveals the possibility of multi-color emission. Continuous work in fluorescent dopants resulted in highly efficient fluorescence approaching their theoretical EQE limits of 5% and beyond.^{19,20} The next milestone was the incorporation of the phosphorescent emitting materials into the host matrix.²¹ In phosphorescent material, the incorporation of rare earth metal element in the molecule resulted in a large spin-orbital coupling that leads to rapid inter-system crossing between triplet and singlet states. Unlike fluorescence, which can only harvest singlet excitons, phosphorescence harvests both singlet and triplet excitons. Because of that, phosphorescence is inherently four times more efficient than fluorescence. Therefore, by employing phosphorescent dopants in OLED, efficient energy transfers between host and guest can take place, both singlet and triplet excitons can radiatively decay to the ground state. Therefore, all excitons can emit light by using phosphorescent material and achieving 100% internal quantum efficiency (IQE) is possible.^{9,22}

1.5. Objectives and achievements

The objective of this thesis is on the optimization of OLED efficiency through internal and external means.

Internally, by employing different HTL, we reported phosphorescent OLEDs with internal quantum efficiency near 100% with significantly reduced efficiency roll-off. Our best device reaches external quantum efficiency (EQE), current, and power efficiency of 22.0%, 69.0 cd/A, 76.1 lm/W respectively, with half current of 198.4 mA/cm². Furthermore, we employed the graded host as EML, which shows improved

Efficiency Optimization of Organic Light-emitting Diodes

quantum efficiency and power efficiency with significantly reduced efficiency roll-off as compared to the unipolar-host and double layer heterojunction host devices.

Externally, through applying a layer of zinc oxide periodic nanopillar arrays by pattern replication in non-wetting templates (PRINT) technique, we reported phosphorescent OLEDs with a substantially improved light outcoupling efficiency and a wider angular distribution. The best device showed a peak luminance efficiency of 95.5 ± 1.5 cd/A at 0° emission (external quantum efficiency - EQE of $38.5 \pm 0.1\%$, power efficiency of 127 ± 1 lm/W), compared to that of the reference device, which has a peak luminance efficiency of 68.0 ± 1.4 cd/A (EQE of $22.0 \pm 0.1\%$, power efficiency of 72 ± 1 lm/W).

1.6. Thesis organization

The organization of this thesis is described below:

Chapter I describes the background and motivation for OLED research, followed by a comprehensive review of the advantages of OLED technology in both display and lighting sectors. Furthermore, a brief introduction of OLED configuration and its development histories are presented.

In chapter II, to better understand the physics behind OLED technology, details of organic semiconductors are elaborated, the working principle of OLED such as the charge (electron and hole) injection and transport, the formation and harvest of excitons, light extraction, etc. are illustrated. To achieve high performance of the devices, both internal, like reduction in exciton quenching, and external techniques such as organic and substrate mode extraction are shown.

Efficiency Optimization of Organic Light-emitting Diodes

Chapter III depicts the basic experimental setup before organic material and metal deposition, which is very important since the substrate cleaning and plasma treatment are crucial to form high quality ITO surface condition. Furthermore, the basic terminologies used in OLED measurement are described.

Chapters IV, V and VI are the main body. In chapter IV, by studying the effects of different hole transport layers on the exciton distribution and quenching, the proper hole transport layer material was suggested to better confine charges and excitons. In chapter V, the efficiency optimization of OLED was achieved through changing the conductivity of emissive layer by doping the material with opposite polarity. Chapter VI illustrates the effect of using ZnO nanopillars as outcoupling layer. By using ZnO nanopillars with proper fill factor, the diffraction grating effect, hence the extraction efficiency was maximized. At last, chapter VII concludes the thesis.

Chapter II

Review of OLED physics

In previous chapter, we have briefly introduced the concept of OLED, its advantages and disadvantages in comparison with other display and lighting technologies. This chapter focuses on the physics of OLED from the basic of organic material to light generation and extraction processes. In Section 2.1, the definition of organic semiconductor and its formation are discussed, in section 2.2, various excited-states of organic semiconductors and their formation process are depicted. The energy transfer among difference molecules via excitonic process is illustrated in section 2.3, and the electrical properties such as charge injection and transport is shown in section 2.4, while section 2.5 and section 2.6 describe the light generation and extraction processes, respectively.

2.1. Organic semiconducting materials

Organic materials are defined as carbon-based chemical compounds. From this definition, organic covers a broad number of materials, from a simple hydrocarbon molecule to very complex polymer chains that contain a large number of carbon atoms bonded with other different atoms such as oxygen, hydrogen and even metallic atoms. Among so many different kinds of organic materials, organic semiconducting materials (which are also called conjugate materials) are particularly attractive to researchers owing to their semiconductor like properties.

Due to the many advantages in potential of low cost processing, unlimited choice of materials and design flexibility, organic semiconductors have attracted more and more attentions lately. However, organic semiconductors also have inherent problems.

Efficiency Optimization of Organic Light-emitting Diodes

Therefore, it is very important for us to overview of the physics of organic semiconductor.

2.1.1. Organic semiconductors

Organic semiconductor is defined as organic material that contains conjugate bonds, which is formed by alternating single and double carbon-carbon covalent bonds. To understand the formation of conjugate bonds, orbital hybridization has to be introduced first. Carbon, a group IV element, is capable of forming four covalent bonds with other elements; it has a ground state electronic configuration of $1s^2 2s^2 2p^2$. When carbon forms covalent bonds with other chemical element such as hydrogen, the electrons may form sp^1 , sp^2 or sp^3 configuration, this process is referred to hybridization process. The details of the hybridization process are illustrated using Fig. 2-1.

To form conjugate bonds, three of the four valence electrons of a carbon atom are hybridized to form three sp^2 orbitals (σ -bonds), leaving one electron to form a loose p_z orbital in a direction which is vertical to the surface formed by the carbon atoms. While the π -bonds is formed by the overlapping of the p_z orbitals between adjacent carbon atoms. Fig. 2-2 shows the formation of the σ -bonds and π -bonds by sp^2 hybridization, which uses Ethane as an example. The charge transport property of organic semiconductors is due to the delocalized π electrons, which are able to migrate via π -bond.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 1 Schematic representation of sp^1 , sp^2 and sp^3 hybridization process Fig. 2- 2 Schematic representation of π -bonds and σ -bond²³

Efficiency Optimization of Organic Light-emitting Diodes

Similar to the energy band formation of inorganic semiconductors, organic semiconductors also possess conduction band and valence band like orbitals which are commonly known as LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital), respectively. If two carbon atoms are close enough, their energy levels interact and split to form the anti-bonding and bonding orbitals. The overlap of the σ electrons results in the formation of σ - σ^* levels, while π electrons interaction and overlap open the π - π^* levels. With more carbon atoms involved, the electrons interactions lead the formation of discontinued band. Since π electrons are loosely bonded, they have much smaller bonding energy compared to that of the σ -bond, and the strength of π -bond is much weaker. Thus the σ -electrons have more probability to occupy the space between the nuclei. In other word, σ -orbitals are more effectively overlapped than that of the π electrons. Therefore, the splitting of the σ -orbitals is broader, resulting in position of the anti-bonding and bonding orbitals as illustrated in Fig. 2-3. The π -bonding molecular orbital lies above the energy level of the σ -bonding molecular orbital, while the π anti-bonding molecular orbital (π^*) lies below the position of σ anti-bonding level (σ^*). Most commonly, HOMO and LUMO are referred to π and π^* levels, respectively. Therefore, the properties of π -bond is very critical in determining the optical and electrical characteristics of organic semiconductors.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 3 formation of anti-bonding and bonding states

2.1.2. Advantages and disadvantages of organic semiconductors

Organic semiconductors largely retain their molecular properties because of the weak intermolecular force (van der waals force, typically 10^{-3} eV - 10^{-2} eV) compared to the intra-molecular force (2 eV-4 eV). Due to this distinct feature, there are some advantages and disadvantages when compared to inorganic semiconductors.

First, let's focus on the advantages of organic semiconductors. The first advantage of organic semiconductor comes to our mind is their diversity. Since there are unlimited possible combination between carbon atoms and other elements, not only we can have unlimited choices of material, by controlling the chemical elements (or moiety) added to the organic molecules, we can also modify the molecular chemical properties and tailor them for specific applications. For example, by adding heavy metal atoms into the organic material, the material then can possess the ability to harvest triplet excitons.²⁴⁻²⁶ One of the most attractive features of organic

Efficiency Optimization of Organic Light-emitting Diodes

semiconductors is their advantage of large area processing possibility and low manufacturing cost. Although there are significant differences in fabrication method between polymer and small molecular organic materials, for example, solution methods, such as ink-jet printing and spin-coating techniques are employed in polymer devices fabrication, while vacuum sublimation is commonly used for small molecular organic devices. Their manufacturing costs are significantly lower than that for inorganic semiconductor, which typically requires ultra-high vacuum and temperature. Another important advantage of organic semiconductors is their mechanical flexibility, which is very useful in novel flexible electronics.²

There are, however, some disadvantages for organic semiconductors. Firstly, because of the weak intermolecular interaction, organic semiconductors are typically “soft materials”, i.e. have low melting point and low glass transition temperature. Therefore, devices based on organic semiconductors might have low thermal stability, crystallization may occur, reducing the performance of the devices.²⁷⁻³⁰ Furthermore, organic materials are very prone to moisture, which limit the lifetime and stability of organic electronics.³⁰ Unlike inorganic semiconductors, where electrons are free to move in conduction band, only weakly bonded pi electrons can move in LUMO level inside organic semiconductor. Thus, they normally have low mobility, which may result in high operating voltage and low efficiency. Moreover, organic materials also have inherent structural defects and impurities, limiting the performance of organic devices. Despite the above-mentioned disadvantages, organic materials are still promising for future electronics, while the current limiting factors will be eliminated in the near future. For example, the lifetime and stability of organic devices can be improved by synthesis material with high thermal stability,³¹ insertion of nanocomposite buffer layer²⁷ and by exploring appropriate encapsulation technique.³²

Efficiency Optimization of Organic Light-emitting Diodes

2.2. Charges injection and transport

Unlike inorganic semiconductor, where electrons are able to migrate freely in the conduction band within the crystal, the electrons inside the organic semiconductor are localized, only the loosely bonded π electrons are able to move within the molecule. For a device point of view, the current density flowing through the semiconductor material is given by:³³

$$J = ne\mu E \quad \text{Eq. 2.1}$$

Here E is the external field applied; μ stands for the mobility, which is electric field dependent; e stands for electronic charge and n stands for the density of charge. Therefore, besides the electric field factor, both the charge density and the carrier mobility affect the electrical characteristic of the material. However, compared to inorganic semiconductor materials, organic semiconductors typically have much lower charge density. The expression of the intrinsic carrier density inside a semiconductor material is given by:

$$n_i = N_o e^{\left(-\frac{E_{gap}}{2kT}\right)} \quad \text{Eq. 2.2}$$

N_o : effective density of states, E_{gap} : bandgap of semiconductor. For a common inorganic semiconductor material such as Si, substitute the value of bandgap energy (1.12 eV) and the density of state (10^{19} cm^{-3}) into Eq. 2-2, the intrinsic charge density is approximately on the order of 10^{10} cm^{-3} . In contrast, for a purified organic semiconductor, such as Alq_3 (Tri-(8-hydroxyquinoline) aluminum), substitute in the bandgap energy (2.7 eV) and density of state (10^{21} cm^{-3}),³⁴ the calculated intrinsic carrier concentration is in the order of 10^{-2} cm^{-3} , which is far smaller compared to the intrinsic charge density in Si. Although the above calculation is only a quantitative measure and it doesn't indicate the true values, it can still reflect the fact that organic

Efficiency Optimization of Organic Light-emitting Diodes

semiconductor materials have low intrinsic charge concentration. According to Eq. 2-1, low charge concentration means organic semiconductor device possesses low current density, hence, poor electrical behavior. In order to overcome such inherent limitation of organic semiconductor material, external processes such as charge injection from adjacent electrode and material doping can be used to increase the charge density.

It is already known from previous analysis that organic materials are electrical insulator under low electric field and there is hardly any free-charge present in a purified organic material without chemical doping. However, very high current density up to several amperes per square centimeter can be achieved in OLED during device operation and this is attributed to the effective charge injection and transport from electrode and within organic layers, respectively.

2.2.1. Injection from electrode

Charge injection from an adjacent electrode is very important in determining the efficiency of an OLED. To have high efficiency performance, low energetic barrier heights for both electron and hole injections in an OLED are necessary to achieve balanced electron-hole flow. While the barrier height between metal and organic semiconductor is governed by the energy level difference between the HOMO/ LUMO level of the organic material and the work-function of the electrode. Therefore, interfacial energy structure is very important for efficient operation of OLED.

Charge injection from metal/organic interface can be either by thermal injection or Fowler-Nordheim tunneling injection, or combination of both. The figure below shows the effect of contact barrier height on the electrical behavior of OLED with structure metal/organic/metal.³⁵ The left figure shows the energy band alignment,

Efficiency Optimization of Organic Light-emitting Diodes

the barrier height between metal and organic layer with different choice of metal shows a relation: ITO<Ag<Cr.

Fig. 2- 4 Effects of contact barrier height in determining the electrical characteristics³⁵

(a) energy band structure, (b) current-electric field curve fitted using F-N tunneling theory.

The right figure shows the current behavior fitted using F-N tunneling theory.³⁶

$$I \propto E^2 \times \exp\left(-\frac{k}{E}\right) \quad \text{Eq. 2.3}$$

Here E is the external electric field, $E=V/d$. If one organic interface is assumed to be triangular barrier, k is given by:³⁷

$$k = \frac{8\pi\sqrt{2m^*\phi^3}}{3qh} \quad \text{Eq. 2.4}$$

Here ϕ stands for the barrier height for tunneling, m^* is the effective mass of the charge, h is Planck's constant, q is the electronic charge.

From the F-N tunneling equation and Fig. 2-4 (b), it is clearly indicated that lower tunneling barrier will result in larger electrical current under electrical bias. At low

Efficiency Optimization of Organic Light-emitting Diodes

electrical bias, however, all three fitting lines in (b) deviate from the experimental value, which Parker attributed to the thermionic emission.³⁵

Thermionic emission, which is also known as Richardson-Schottky (RS) emission, was first discovered by Richardson and modified by Schottky subsequently by taking the effect of electric field into account. The thermionic emission current density can be expressed by:³⁸

$$J = AT^2 \times \exp\left(\frac{-\phi q}{kT}\right) \quad \text{Eq. 2.5}$$

Here A : the modified Richardson constant which can be obtained experimentally,³⁹ ϕ : the barrier height (taking into account the electric field effect), while T is the temperature.

From both the F-N tunneling theory and the thermionic emission theory, the barrier height is an important factor in calculating the injection current. Therefore, in order to increase the current injected into the organic layer, contact that resulted in lower barrier height shall be used. For example, to ensure high charge injection, the anode electrode shall possess a deep work function, so that the band offset between the HOMO of the adjacent organic layer and the work function of anode is minimized, while the cathode material shall have a smaller work function such that the band offset between cathode and the LUMO of the organic layer shall be small enough. However, most of the work function of the anode doesn't lie deep enough. For example, ITO, which is the most widely used anode material in OLED, its work function is only 4.7 eV,⁴⁰ while the HOMO level of some commonly used hole transport layer (such as NPB, TCTA, etc.) range from 5.5 eV to 6 eV,⁴¹ the large energy barrier makes hole injection electrically unfavorable. Meanwhile, since the LUMO value of some commonly used electron transport materials (Alq₃, Bphen, etc.) ranges between 2 eV

Efficiency Optimization of Organic Light-emitting Diodes

to 3 eV,^{34,42} the cathode material should have low work function close to that of the LUMO's. Unfortunately, metals with shallow work function tend to be unstable and reactive.⁴³ For example, Mg and Li will react with O₂ when exposed to atmosphere. Therefore, chemically stable metal like Al and Ag, are chosen as cathode materials. Again, due to the relatively high work function of the both metals,⁴³ large barrier heights exist to hurdle electron injection. To overcome these problems, significant research efforts were dedicated in the field of charge injection enhancement in the past two decades. Plasma treatment of ITO using Chlorine,^{44,45} oxygen,⁴⁶ UV ozone⁴⁷, CO₂/H₂O₂,⁴⁸ CF₄,⁴⁹ etc. were employed to improve the ITO surface properties. Furthermore, the plasma treatment can efficiently decrease the oxygen vacancy density on the ITO surface, increase its work function and decrease the barrier for hole injection. Alternative, the insertion of a thin buffer layer can dramatically increase electron or hole injection. Researchers found that by inserting a thin buffer layer such as MoO₃,^{50,51} NiO,⁵² CuPc,⁵³ CuF₂,⁵⁴ etc., the energy barrier between ITO and HTL can be reduced significantly. Whilst using thin layer of LiF,⁵⁵ Liq,⁵⁶ CsF,⁵⁷ etc. as electron injection material, electron injection were largely improved. The deep reason to enhance charge injection from both electrodes is to realize Ohmic contact and reduce or even eliminate the dependence of the device performance on the contact limit.

2.2.2. Transport within organic material

In molecular level, the transport of charge (electron or hole) involves ionizing and deionizing molecules. For example, when an electron moves from one neutral molecule site to another, it creates two charged states, namely, a negatively charged radical ion and a positively charged radical ion. These newly created ionic states are stabilized by polarization energy in material solid. Different from the energy band

Efficiency Optimization of Organic Light-emitting Diodes

formation in a molecular crystal, in disordered organic semiconductor, weak dipole-dipole interaction in molecular level results in Gaussian density of states expressed by the following shape function:⁵⁸

$$\sigma^2 = x \left(\frac{7.04P}{a^2 \epsilon_r} \right)^2 + \sigma_o^2 \quad \text{Eq. 2.6}$$

Here x is the fraction of dipole molecules, σ stands for the width of the density of states, while a represents the intermolecular distance, σ_o is the width without dipole interaction, P stands for the dipole and ϵ_r for dielectric constant. Therefore, when describing the charge transport of a disordered organic material, we have to take the polarization effect into account. Classified by the difference in order degree, the transport mechanism of charge carriers in organic materials can be described using either band-transport model or polaron-hopping model.⁵⁹

The band-transport model describes the case where charges within organic material are sufficiently delocalized; the resulting energy bands are similar to that of the inorganic semiconductors. However, because of the weak intermolecular interaction, the band width is very narrow (a few KT), while the the charge carrier mean free path is much larger than the intermolecular distance. The mobility of this kind of organic semiconductor can reach up to $10 \text{ cm}^2/\text{Vs}$ at room temperature.⁵⁹ In this model, the mobility of organic semiconductor decreases with increasing temperature due to the lattice distortion created by increasing thermal energy.

The polaron-hopping model describes the other case when the mobility of the organic material is very small (around $10^{-3} \text{ cm}^2/\text{Vs}$ or less) and the mean free path of the charge is comparable to intermolecular distance.⁵⁹ In this case, the charge carrier will stay in one molecule for most of the time and hop to neighbouring molecules when obtained sufficient energy. In this model, the charge mobility will increase

Efficiency Optimization of Organic Light-emitting Diodes

dramatically with increasing temperature due to thermal assisted hopping rate increases. Since most organic materials are amorphous, it's expected that the transport of charge is mainly due to the charge hopping between molecules.

In device level, once the charges are injected into the organic layer, they either drift or hop towards the other electrode under the influence of external field. When the external field is very small, typically less than 0.1 MV/cm (for a OLED with 100nm organic layer thickness, the voltage is less than 1 V),⁶⁰ the amount of injected charges is much less compared to the intrinsic charge density (approximately 1 cm^{-3}), the current conduction follows Ohmic characteristic as illustrated in region A by Fig. 2-5.

Fig. 2- 5 Log scale representation of typical J-V curve of OLED⁶¹

When a much larger electric field is applied (typically beyond 0.5 MV/cm), the amount of injected charges is much larger than the intrinsic thermally generated charges, then the space charges are formed in the organic layer, the charge conduction now is not governed by electrode properties, instead, it depends on the bulk transport

Efficiency Optimization of Organic Light-emitting Diodes

properties of the organic. If the organic film is trap free, the injected charges will drift under the influence of external field, assume the diffusion current is negligible compared to drift current, then the current flow is given by Eq. 2.1.

By combining the Poisson's equation:

$$ne = \varepsilon\varepsilon_0 \frac{dE}{dx} \quad \text{Eq. 2.7}$$

The following equation is obtained:

$$J = \varepsilon\varepsilon_0\mu E \frac{dE}{dx} \quad \text{Eq. 2.8}$$

Integrating with respect to the distance to electrode/ organic interface:

$$Jx = \frac{1}{2} \varepsilon\varepsilon_0\mu [E(x)]^2 \quad \text{Eq. 2.9}$$

Substitute Eq. 2.9 into the voltage equation below:

$$V = \int_0^d E dx \quad \text{Eq. 2.10}$$

We obtain the famous Mott-Gurney equation:⁶²

$$J_{SCLC} = \frac{9}{8} \varepsilon\varepsilon_0\mu \frac{V^2}{d^3}$$

Here d is the organic layer thickness, V stands for the applied voltage. The charge conduction in this region is regarded as space-charge limited current, since carrier transport now is determined by the space charge effect. The carrier mobility in organic layer, however, is not a constant, but follows the Poole-Frenkel behaviour:⁶³

$$\mu = \mu_o \exp(\beta\sqrt{E}) \quad \text{Eq. 2.11}$$

Efficiency Optimization of Organic Light-emitting Diodes

Here E : the applied field, μ_0 : zero field mobility, β : Poole-Frenkel factor.

In reality, because of the structural defects and external impurities, organic material is usually not trap free and these traps will hinder current conduction. Therefore, when the external field (typical between 0.1 MV/cm to 0.5 MV/cm) is applied to the organic layer, the injected charges will first fill the traps rather than participating in current conduction. The current flow now is limited by trap density. Since the trapped charges do not contribute to transport, the current conduction level is generally less than the space-charge limited current model. If a higher electric field is applied, more charges are injected into organic layer, and more traps are filled. Gradually, this causes increasing effective carrier mobility, resulting in rapid increase of current, especially at very high field. For exponentially distributed trap density within the organic material bandgap, the trap charge limited current follows:⁶⁴

$$J_{TCLC} = K \frac{V^{m+1}}{d^{2m+1}} \quad \text{Eq. 2.12}$$

K stands for material dependent constant, $m = \frac{T_t}{T}$ with T_t being a temperature dependent parameter characterizing the trap distribution and T being the actual material temperature. The trap charge limited current model is describe in region B in Fig. 2-4, if the applied field is further increased, more charges are injected and traps are completely filled, then the current conduction recovered to SCLC case, which is shown in region C.

2.2.3. Electrical doping

To realize efficient charge injection (Ohmic contact) and transport, another alternative approach is to dope the charge transport layer. The working principle of doping is illustrated by Fig. 2-6.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 6 Working principle of (a) N and (b) P doping in an organic material

To achieve effective doping, charges (either electrons or holes) need to be transferred efficiently from dopant to matrix material. Therefore, for an efficient N dopant, its ionization potential needs to be positioned below the electron affinity of the organic matrix (Fig. 2-6 (a)). Some commonly used n dopants are Li,⁶⁵ Cs and Cs_2CO_3 ,⁶⁶ etc.. An effective P dopant shall have an electron affinity level lying below the HOMO of the matrix material (Fig. 2-6 (b)), $\text{F}_4\text{-TCNQ}$ ⁶⁷ and MoO_3 ⁶⁸ etc. are commonly used as P dopants.

Efficiency Optimization of Organic Light-emitting Diodes

To better illustrate how doping can facilitate charge injection, the energy diagram measured by UPS/XPS between ITO and undoped and doped ZnPc is shown below:⁶⁹

Fig. 2- 7 Energy diagram measured by UPS/XPS for ITO and top: undoped ZnPc,
bottom: doped ZnPc.⁶⁹

From the diagram we can clearly see that the depletion width inside the ZnPc layer is shorten from 15nm to less than 5nm upon doping F₄-TCNQ. The decrease of the space charge region is accompanied by the increasing band bending at the interface. Now holes can be injected into doped ZnPc layer more efficiently by tunneling according to Eq. 2.3. Furthermore, the doped ZnPc layer shows significantly increased

Efficiency Optimization of Organic Light-emitting Diodes

conductivity compared to pristine film, and its conductivity increases with doping concentration is illustrated in Fig. 2-8 below.⁶⁹ Here c_{dop} represents the molar doping concentration of F₄TCNQ in ZnPc layer. Therefore, the use of electrical doping can effectively increase the organic film's conductivity, which facilitates charge transport and reduces the applied voltage.

Fig. 2- 8 Conductivity of ZnPc film with varying F4-TCNQ doping ratio.⁶⁹

2.3. Excitons

Excitons are defined as coulomb interactive electron-hole pairs. An exciton is formed when the binding energy between the electron and the hole exceeds the thermal energy. The formation and recombination of excitons follows Langevin theory^{70,71} with exciton generation rate given by:

Efficiency Optimization of Organic Light-emitting Diodes

$$G = R \times n \times p \quad \text{Eq. 2.13}$$

Here n: electron density and p: hole density, R: recombination constant expressed by:

$$R = q \frac{\mu_n + \mu_p}{\varepsilon \varepsilon_0} \quad \text{Eq. 2.14}$$

ε : dielectric constant, μ_n , μ_p : the electron and hole mobility, respectively, q: elementary charge.

2.3.1. Classification of excitons

Since the formation of an exciton requires both electron and hole, it carries no net electric charge. According to the strength of the binding energy, three different types of excitons exist in crystalline solids, namely, Frenkel exciton, Wannier exciton and charge transfer exciton.⁷²⁻⁷⁴

The classification of exciton is determined by material properties, for example, if dielectric constant of a material is small, then a strong interaction exists between different charges, resulting in the residency of an exciton in one molecule. This type of exciton is called a Frenkel exciton.⁷² It typically has a large binding energy, approximately from 0.1 eV to 1 eV and the Bohr radius--the characteristic length between the electron and hole pair is very small (comparable to atomic spacing).^{72,75} For a material with a larger dielectric constant, such as inorganic semiconductor, the interaction between different charges is shielded by the electric field screening effect, the exciton formed in this type of material is called as Wannier-Mott (W-M) exciton⁷³. This type of exciton has a much larger Bohr radius ($\sim 100\text{\AA}$).⁷³ When polarons with opposite polarity are located in different adjacent molecules, they may form a charge transfer state / exciton, which has a Bohr radius comparable to the lattice constant.⁷⁴ Frenkel excitons and charge transfer excitons are typically generated in organic

Efficiency Optimization of Organic Light-emitting Diodes

semiconducting material, while W-M excitons are the characteristic excitons of inorganic material.

However, if we take the spin states of both electrons and holes into account, excitons can be further classified into singlet and triplet. A singlet is defined as exciton with no net spin, which means if one charge has spin up ($1/2$), the other one shall have spin down ($-1/2$). Therefore, according to Pauli exclusion principle,⁷⁶ the ground states of molecules contains all singlet. For excited state, however, since electrons occupied in different orbitals, non-zero spins may occur. Since each charge has two possible spin states, the electron-hole pair will have four possible states. Governed by Pauli's law, for any two-electron system, the total wave function shall be anti-symmetric, which is equivalent to say that if the spin function is symmetric, the spatial function has to be anti-symmetric, or vice versa. By definition, singlet exciton shall have anti-symmetric spin functions to allow net spin = 0. Thus, singlet has symmetric spatial function.⁷⁷ In contrast, triplet has symmetric spin function and anti-symmetric spatial function such that its net spin = 1. A schematic representation of the vector based singlet and triplet spins can be seen by Fig. 2-9 below. Here the black arrow indicates the spin direction of the electronic system, the red arrow shows the non-zero net spin of the triplet, while the red dot for the singlet illustrates the zero net spin state.⁷⁸

Fig. 2- 9 Representation of singlet and triplet spin configurations.⁷⁸

Efficiency Optimization of Organic Light-emitting Diodes

According to the quantum mechanics, all four states are formed in equal probability. Therefore, the ratio of the singlet and triplet in organic semiconductors will be 1:3.⁷⁹

2.3.2. Quenching of excitons

An exciton can be formed when an electron absorbs a photon and excited into LUMO state. However, the excited state is not stable, so exciton will return to ground state via radiative or non-radiative decay. The radiative transition will be described in section 2.5., while this section focuses on the non-radiative decay of exciton during OLED operation. An example illustrating one of the exciton quenching paths is described in Fig. 2-10, which shows the effect of electron transport layer on exciton quenching by Baldo *et al.*⁸⁰ Without the addition of BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) layer, the quantum efficiency was very small compared to that with 6 nm BCP layer inserted between CBP (4,4'-N, N'-dicarbazole-biphenyl) and Alq₃. This is because of the lower triplet energy of Alq₃ (T₁=2.0 eV) as compared to Ir(ppy)₃ (fac tris(2-phenyl-pyridinato-N,C^{2'}) iridium) (T₁=2.4 eV).^{1,81} The Ir(ppy)₃ triplet excitons will transfer their energy to the Alq₃ via Forster or Dexter energy transfer (more on next section). Since Alq₃ is a fluorescent material, according to the analysis in Section 2.3.1., triplet can't return to ground state due to spin selection rule. These excitons will decay non-radiatively through heat generation. After inserting the BCP layer, however, the Ir(ppy)₃ triplet energy will be confined within the emission region because of the higher triplet energy of BCP layer (T₁=2.5 eV).⁸¹ Thus, the triplets can decay radiatively and emit light.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 10 (a) Device energy band structure and (b) resulted quantum efficiency⁸⁰

Although using higher triplet energy charge confinement layer can reduce external quenching, it can't prevent the efficiency roll off as shown in Fig. 2-10 (b), which was caused by triplet-triplet annihilation due to high exciton density at large current injection level.¹ Similar to triplet-triplet annihilation, there are other current dependent losses causing efficiency roll-off such as singlet-triplet (S-T) annihilation, singlet-singlet (S-S) annihilation, singlet-polaron (S-P) annihilation, singlet-heat (S-H) annihilation, etc..^{1,82,83}

Efficiency Optimization of Organic Light-emitting Diodes

To solve the above-mentioned exciton quenching problems, more efforts need to be focused in reducing the triplet lifetime in phosphorescent material,⁸⁴ designing higher efficiency emitter with better thermal stability,²⁰ confining exciton in broader region to dilute exciton density by device structuring,^{85,86} synthesis of host material with better charge transport properties,⁸⁷ etc..

2.4. Energy transfer between molecules

To achieve high-efficiency excitonic radiative decay, fluorescent or phosphorescent dyes are employed to harvest singlet or triplet excitons. Upon exciton formation in host molecules, they either transfer their energy to the dye molecules via radiative,⁸⁸ or Förster⁸⁹ or Dexter⁹⁰ energy transfers.

Radiative energy transfer is also called photon re-absorption, which requires that the donor's emission spectra and the acceptor's absorption spectra are overlapped. During the radiative energy transfer process, the photon emitted through radiative exciton decay of the donor molecule is re-absorbed by the acceptor molecule, thus, the radiative energy transfer may occur over a long distance (>10nm) since only spectra overlapping is required. The probability of transfer is given approximately by:

$$P_{r,t} \propto [A]xJ \quad \text{Eq. 2.15}$$

Where $[A]$ is the concentration of the acceptor, x is the specimen thickness and J is the spectra overlap integral.

Both Förster and Dexter energy transfer mechanisms are non-radiative energy transfers. Fig. 2-11 illustrates the electronic transition process involved in Förster and Dexter energy transfers.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 11 Electronic transition of Förster and Dexter energy transfer mechanisms
modified from Ref⁹¹

Förster energy is a resonant energy transfer process. During the process, the donor returns to ground state nonradiatively, while the acceptor captures the energy and jumps to excited state. This process can occur with donor and acceptor molecules distance more than 10 nm, but shorter than the radiative energy transfer.⁸⁹ According to the Fermi's "golden rule", the transition rate between two different states is given by:

$$R = \frac{\rho}{h} < H' >^2$$

Eq. 2.16

ρ : effective density of states, h : Planck's constant, $< H' >$: donor and acceptor molecules matrix element. The Hamiltonian for the dipole-dipole interaction is given by:^{89,92,93}

Efficiency Optimization of Organic Light-emitting Diodes

$$H'(\vec{R}) = \frac{1}{4\pi\epsilon_r\epsilon_0 R^3} (\vec{\mu}_D \cdot \vec{\mu}_A - 3(\vec{\mu}_D \cdot \vec{R})(\vec{\mu}_A \cdot \vec{R})) \quad Eq. 2.17$$

Here, ϵ_r is the dielectric constant, $\vec{\mu}_D$ is the dipole of the donor, and $\vec{\mu}_A$ is the acceptor dipole moment, while $\vec{R}$ stands for the unit vector from donor to acceptor. From equation 2.17 and equation 2.16 and average over all possible directions, the Förster energy transfer rate can be simplified to:

$$K_{F,D-A}(R) = \left(\frac{1}{\tau_D}\right) \left(\frac{R_0}{R}\right)^6 \quad Eq. 2.18$$

τ_D is the donor lifetime without energy transfer, R is the distance between donor and acceptor molecules, R_0 is the Förster radius which depends on the spectra overlap of the donor and acceptor molecules and it is given by the equation below:

$$R_0^6 = 1.25 \times 10^{17} \frac{\vartheta_D}{n^4} \int F_D(\nu) a_A(\nu) \frac{d\nu}{\nu^4} \quad Eq. 2.19$$

Where F_D is the donor emission spectrum (area normalized to 1), ϑ_D is the quantum emission efficiency of the donor molecule, n is the refractive index, a_A stands for the acceptor's extinction coefficient.

Dexter energy transfer, on another hand, is an electron exchange process. For an Dexter energy transfer to happen, the donor and acceptor wave functions need to be overlapped. Thus, it occurs only for short distance (approximately 1 nm or less). The rate for Dexter transfer can be expressed by:^{90,92}

$$K_{D,D-A} = I_{orb} \cdot J e^{-2R_{DA}/L} \quad Eq. 2.20$$

J is the normalized spectral overlap integral, I_{orb} stands for the interaction of orbitals, L is the van der waal radius (Bohr radius), while R_{DA} represents the donor-acceptor distance.

Efficiency Optimization of Organic Light-emitting Diodes

Based on the above discussion, the photon re-absorption process is less likely to occur. This is because in the state of the art OLED configuration, the emitter molecules normally have the smallest bandgap energy, the photon emitted by the emitter molecules thus have less probability to be re-absorbed by the adjacent layers which have larger bandgap energy. While both Förster and Dexter energy transfers co-exist in the host-guest emissive layer, the Dexter process will dominate the energy transfer between donor and acceptor molecules if their distance is less than 1 nm. When their distance becomes larger than 2 nm, the Förster process will dominate the energy transfer due to its longer range of dipole-dipole interaction nature.

2.5. Light generation via fluorescence and phosphorescence

Exciton can decay to the ground state via two different processes: radiative and non-radiative decays. Radiative decay involves the emission of photons, which lead to the light generation, while non-radiative decay leads to the phonon generation, such as vibration, heat, etc. Fluorescence and phosphorescence are the two well-known processes in radiative decay, which are illustrated by using the Jablonski energy diagram in Fig. 2-12.⁹⁴

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 12 Modified Jablonski energy diagram⁹⁴

Fluorescence is a fast process which occurs in nanoseconds range. It is referred to the decay of singlet. As shown in the modified Jablonski energy diagram (Fig. 2-12), fluorescence occurs via three important process, which happens in different timescales. First, the molecules absorb external energy and are excited to higher vibrational level of excited state (S_1^n or S_2^n) via optical or electrical excitation. This process is very fast (10^{-15} s), since the higher order vibrational state is not stable. The exciton will quickly (about pico-seconds) relaxed to the zero order excited state (S_1^0) via internal conversion (if the initial state is S_2^n) and vibrational relaxation. Then light emission occurs when excitons return to the ground state in nano-second time scale.

Efficiency Optimization of Organic Light-emitting Diodes

Phosphorescence occurs over a longer period of time scale. Different from the fluorescence, phosphorescence refers to the radiative decay of triplet. When molecules are excited via optical or electrical stimulation, both singlet and triplet are created at the same time. According to Pauli's Exclusion principle, however, radiative decay of the excited state triplets to the ground state is energetically unfavorable. Fortunately, the transition can still happen with much longer time and slower rate as compared to fluorescence. This is because spin-orbital coupling mixes triplet states in some extent with singlet states, resulting a non-zero radiative decay rate of triplet. Thus, the molecules are able to emit light weakly for a longer period of time.

Because of the upper limit in the fraction of singlet exciton generation over all excitons, the maximum achievable internal quantum efficiency (IQE) of fluorescence is around 25%. To achieve 100% IQE, triplet excitons needs to be harvested radiatively. To realize triplet harvest, researchers introduced heavy metal atom such as Pt, Ir and Eu, etc. into organic emitter.^{21,22,84} Such that the spin-orbital coupling efficiency will be increased, resulting in effective mixing between singlet and triplet states. Due to the strong spin-orbital coupling, the triplet states now obtain some singlet properties and can decay to ground states radiatively. Therefore, due to its ability to harvest both excitons (singlet and triplet), phosphorescent dyes are widely used in OLED fabrication to realize the highest possible efficiency.

2.6. Light extraction

Light extraction from OLED is a very important issue, since only the extracted light is useful. However, due to the refractive index differences, light outcoupling efficiency is severely hindered by the total internal reflection (TIR) at the organic/glass and glass/ air interfaces for an OLED with glass substrate. If the emission rays are normal to the interfaces, most of the light can escape from the device. However,

Efficiency Optimization of Organic Light-emitting Diodes

the light rays will experience TIR if the incident angle at the interface is greater than the critical angle. For a semiconductor/ air interface illustrated in Fig. 2-13, to calculate the light escape ratio from the semiconductor into air, we assume the emission center is within the semiconductor, the incident angle at the interface is θ_i , the refracted angle to the air at the interface is θ_r . Based to snell's law, the following relation can be achieved:

$$n_s \sin \theta_i = n_{air} \sin \theta_r \quad Eq. 2.21$$

n_{air} is the refractive index of atmosphere, n_s is the refractive index of the semiconductor. The TIR critical angle can be calculated if $\theta_r = 90^\circ$.

Fig. 2- 13 Light escape cone, modified based on Ref⁹⁵

The critical angle for TIR is:

$$\theta_c = \sin^{-1} \frac{n_{air}}{n_s} \quad Eq. 2.22$$

The TIR angle defines the light escape cone, see (b) of Fig. 2-13, only the fraction of total emission within the cone shaped area could be extracted and becomes visible, while the fraction of light incident out of the cone will be total internal reflected. Assume the source emits light with power P_{in} and from a point within the

Efficiency Optimization of Organic Light-emitting Diodes

semiconductor, the total fraction of light escaped or light extraction ratio is calculated by the ratio of the surface area of the spherical cone to the total area of the sphere with radius r .

The spherical cone area can be determined by:

$$A_{cone} = \int_{\theta=0}^{\theta=\theta_c} 2\pi r^2 \sin \theta d\theta = 2\pi r^2 (1 - \cos \theta_c) \quad Eq. 2.23$$

For typical one-side emitting OLED, the total spectral power of the emitter will be in half of the sphere, which is $2\pi r^2$. Therefore, the power escaped into the air:

$$P_{escape} = P_{in} \frac{2\pi r^2 (1 - \cos \theta_c)}{2\pi r^2} = P_{in} (1 - \cos \theta_c) \quad Eq. 2.24$$

Because θ_c is general small, by expanding the term $\cos \theta_c$ into a power series and only keep the first order term and neglecting the higher order terms, the following equation can be obtained:

$$\frac{P_{escape}}{P_{in}} \approx \left(1 - \left(1 - \frac{\theta_c^2}{2} \right) \right) = \frac{\theta_c^2}{2} \quad Eq. 2.25$$

When θ_c is small, equation 2.22 can be approximated to $\theta_c \approx \frac{n_{air}}{n_s}$, substitute into equation 2.25 we get:

$$\frac{P_{escape}}{P_{in}} = \frac{1}{2} \frac{n_{air}^2}{n_s^2} \quad Eq. 2.26$$

For a conventional OLED with glass substrate ($n=1.5$), the condition is much more complicated, represented in Fig. 2-14 below:

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 2- 14 Light paths within OLED

Upon light generation from the emission layer, light ray will have to pass through three different interfaces in order to become useful light that is visible to us. According to the refractive index difference, light emitted by OLED is classified to three different mode:

The first one is air mode, illustrated by Ray 1 in Fig. 2-11, the light ray incident on the organic/ ITO interface with angle θ experience three different refractions and exits from glass/ air interface, until $\theta = \theta_{C1} = \sin^{-1} \frac{n_{air}}{n_{org}}$, where TIR occurs at the substrate/ air interface. Then light incident with an angle larger than θ_{C1} will trapped inside OLED structure. Assume the cathode is perfectly reflective and light is isotropic emission, referred to Eq. 2.24, the fraction of air mode is given by:

$$\eta_{out} = 1 - \cos \theta_{C1} \quad Eq. 2.27$$

Since the refractive index of organic materials mostly fall between 1.6 and 1.8,^{96,97} then the outcoupling efficiency: $0.17 < \eta_{out} < 0.22$.

Efficiency Optimization of Organic Light-emitting Diodes

If the emission angle increases further until $\theta = \theta_{C2} = \sin^{-1} \frac{n_g}{n_{ITO}}$, total internal reflection occur at glass/ ITO interface. Light with angle $\theta_{C1} < \theta < \theta_{C2}$ is trapped in glass substrate and is called substrate mode. The fraction of light trapped in glass is given by:

$$\eta_{glass} = \cos \theta_{C1} - \cos \theta_{C2} \quad Eq. 2.28$$

Here $n_g = 1.5$, $n_{ITO} = 1.8$, the light trapped in substrate mode: $0.23 < \eta_{glass} < 0.28$.

Light with emission angle larger than θ_{C2} is called ITO/ organic mode (or simply organic mode) since this portion of light is trapped in ITO/ organic layers. This fraction of light is given by:

$$\eta_{glass} = \cos \theta_{C2} \approx 0.55 \quad Eq. 2.29$$

Based on the above analysis, the amount of light extracted into the air is limited only around 20% of the total internally generated light. Most of light is trapped within substrate and organic layer, those trapped light will eventually lost inside OLED due to absorption. Therefore, the outcoupling of light from the substrate mode as well as organic mode attracts much interests. Various attempts have been made to improve the outcoupling efficiency, for instance, to help extract light trapped in substrate mode. Methods like substrate surface modification¹¹ and microlens arrays,⁹⁸ etc. are commonly used. Applying grating layer such as photonic crystals,^{99,100} low index grating,^{101,102} etc. at ITO/ organic interface or glass/ ITO interface were used to extract light trapped in ITO/ organic mode. With properly design of outcoupling layer, an efficiency enhancement factor of more than 3 was proposed.¹⁰¹

Efficiency Optimization of Organic Light-emitting Diodes

2.7. Summary

In this chapter, we have discussed the physics behind OLED and now we have better understanding on how to achieve efficient OLED, which needs to satisfy the following conditions:

1. Effective electron and hole injection from cathode and anode, respectively, this requires low barrier height for both carriers. To achieve low barrier height injection, we could either use proper contact material to match the energy level of the adjacent charge transport layer, or use a thin charge injection layer between electrode and transport layer. Alternative, electrical doping is also very effective in realize good charge injection.
2. Good charge transport, this requires the hole transport layer to possess good hole mobility, while electron transport to possess good electron transport properties.
3. Effective charge blocking layer to confine both charges and excitons within emissive region. To confine electrons, the LUMO of electron blocking layer needs to lie above the LUMO of emissive layer, to confine holes, the HOMO of hole blocking layer needs to lie below the HOMO of emissive layer. In contrast, the triplet energy of the blocking layer needs to be greater than the triplet energy of the emitter in order to confine excitons.
4. High internal quantum efficient, which requires good PL efficiency of the emitter, for example, by using efficient phosphorescent dopant, which enable the harvest of both singlet and triplet. Furthermore, both charges injected into the emission layer need to be balanced, otherwise excitons might be quenched by the excess charge particles.

Efficiency Optimization of Organic Light-emitting Diodes

5. High light extraction efficiency, this can be achieved by either internal method to outcouple the organic/ITO mode, or external method to extract glass mode, or the combination of both.

Chapter III

Experiment setup and OLED characterization

3.1. Experimental setup

3.1.1. Preparation of Indium Tin Oxide (ITO) substrate

Before organic material deposition, the Indium Tin oxide (ITO) coated glass substrates purchased commercially need to be patterned and cleaned. Fig. 3-1 illustrates a schematic plot of a patterned ITO strips employed in experiment:

Fig. 3- 1 Schematic plot of patterned ITO strips

Prior to the ITO patterning process is the ITO substrate cutting, the commercially purchased ITO substrate was firstly cut into smaller pieces with size of $3\text{cm} \times 3\text{cm}$, then normal Scotch tape was applied on the ITO surface. After the taping done, a sharp blade and metal ruler were used to pattern the tape into 3mm strips as ITO protection layer. Then the substrates were put into a tank filled with diluted Hydrochloric acid (HCL), Magnesium (Mg) powers were then put into the HCL tank

Efficiency Optimization of Organic Light-emitting Diodes

as catalyst. The ITO substrates can be taken out after 5 minutes of reaction, only the ITO under the protection tape was retained, while the ITO outside of the protection tape has been removed by HCL. The ITO pattern will be the same as shown in Fig. 3-1 after peeling off the protection tape.

After ITO patterned, the substrates are cleaned using detergent (DECON 90). Then the substrate are loaded into ultrasonic system for ultrasonication in Acetone and ethanol for half an hour, respectively. Then the substrates are rinsed in DI water and subsequently dried in oven. Before loading the substrate into the OLED deposition system, the substrates are treated using Oxygen plasma to remove surface residual contaminations. After all the preparation work is done, the substrates are loaded into the deposition chamber for organic and metal deposition.

3.1.2. OLED deposition system

The OLED deposition system we used is a multi-source organic molecular vapour deposition system, which is semi-automatic equipped with ten different source crucibles, which means that the system is capable of depositing ten different materials at the same time. Both the current through the coil heating the crucibles and the crucible temperature are accurately measured by sensors and displayed on the control panel. There are total three sets of shutters working together to achieve large area uniformity and abrupt interface. Right on top of each crucible is one set of the shutters through which opening and closing sequence controls the material deposition, while the big shutters between the crucibles and the substrates and the small ones under each substrate are operated in combination to isolate the substrate from the evaporated molecules. The deposition rate and thickness are monitored by a 6 MHZ gold crystal sensor (commercial available from INFICON) and a quartz oscillator combined with a frequency meter. There are total four crystal sensors mounted below the substrate

Efficiency Optimization of Organic Light-emitting Diodes

holders, which can be rotated at an adjustable speed. Furthermore, the material deposition rate can be monitored as accurately as 0.01 nm/s. The base vacuum during material deposition can reach 5×10^{-5} Pa (4×10^{-7} torr). More technical details on the OLED deposition system could be found at Shenyang Vacuum Technology Institute.¹⁰³

To fabricate OLED with desired pattern, two sets of masks are equipped with the system. Organic mask is used to deposit organic material onto the designated areas, while the metal mask is used in electrode deposition. The overlap between the deposited metal line and ITO strip marks the emission region.

Fig. 3- 2 OLED deposition system

Efficiency Optimization of Organic Light-emitting Diodes

3.2. Characterization of OLED

After OLED fabrication, the OLED is taken out of the deposition chamber and measured immediately, so that the material decay is minimized. The I-V characteristic of OLED was measured using YOKOGAWA GS610 source measurement unit, while the optical performance was measured using PhotoResearch PR705. The PR705 is one of the most sensitive optical measurement instrument provided by Photo Research Inc., it can accurately measure light level as low as 0.003 cd/m^2 within a wavelength range of 380 nm to 780 nm at a spectra accuracy of $\pm 2 \text{ nm}$, more technical details and specifications of the PR705 system can be found from Photo Research Inc..¹⁰⁴ To ensure the accuracy of the measurement, the lens of the PR705 has to be focused before the optical characterization process. To measure the electrical performance, the anode and cathode of the OLED device need to be connected properly to the source cables of the YOKOGAWA GS610 source measurement unit, once the applied minimum current, step and maximum current are set, the voltage for each individual current can be recorded automatically when start measurement button is on. When using the PR705 spectrometer to capture the optical performance, the OLED devices need to be mounted into a fixed stand with glass facing perpendicular to the lens of the the spectrometer, so that the lens can capture the emitted light from the planar OLED device. Once the OLED is turned on, the lens of the spectrometer has to be focused on the illuminating OLED (only need to focus once for the whole measurement), then the optical performance of the OLED such as luminance, photo radiance, etc. can be measured and recorded.

Different from the electrical performance, the measurement of optical performance, which is referred to photometry, is close related with human eye response.

Efficiency Optimization of Organic Light-emitting Diodes

3.2.1. Human eye response

Human eyes can sense color and brightness of light. There are two main photodectors responsible for color and intensity detection in human eyes, namely: rods and cones. According to their sensitivity to light, rods and cones are responsible to night (scotopic) and day (photopic) vision, respectively. Fig. 3-3 illustrates the photopic and scotopic response curves of human visions. The photopic curve is used in optical calculation since human are only capable of distinguish color in day vision.

Fig. 3- 3 human eye response for different wavelength

3.2.2. Chromaticity

The Commission internationale de l'éclairage (CIE) coordinates are commonly employed to depict the color of a light source. It was developed by International Commision on Illumination in 1931 and now it is the most popular system in lighting and display industry. In CIE coordinates, the tristimulus values X, Y, Z can be regarded as the fraction of primary colors (red, green and blue). The CIE has defined

Efficiency Optimization of Organic Light-emitting Diodes

three color matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$. The tristimulus values of a color with spectra power distribution $I(\lambda)$ can be calculated by the following equations:

$$\begin{aligned} X &= \int_{\infty}^0 I(\lambda) \bar{x}(\lambda) d\lambda \\ Y &= \int_{\infty}^0 I(\lambda) \bar{y}(\lambda) d\lambda \\ Z &= \int_{\infty}^0 I(\lambda) \bar{z}(\lambda) d\lambda \end{aligned} \quad \text{Eq. 3.1}$$

The chromaticity coordinates are:

$$\begin{aligned} x &= \frac{X}{X+Y+Z} \\ y &= \frac{Y}{X+Y+Z} \\ z &= \frac{Z}{X+Y+Z} \end{aligned} \quad \text{Eq. 3.2}$$

By convention, a specific color can be specified by x and y , since $z=1-x-y$, while the tristimulus value Y is used to describe the brightness (luminance) of a color. Fig. 3-4 below shows the three color matching function and the CIE chromaticity diagram:

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 3- 4 (a) color matching function (b) CIE chromaticity diagram

3.2.3. Terminologies used in OLED characterization

The terminologies used in OLED including:

Luminance power (flux in lumens) is the power detected by human eyes. It is a photometric unit since it depends on the human eye response to light of different frequency. Its expression is given by the following equation:

$$\phi=K_m \int \phi V(\lambda)d\lambda \tag{Eq. 3.3}$$

Here ϕ is the radiant power, $V(\lambda)$ stands for the human eye response, K_m is a constant, most commonly $K_m= 683 \text{ lm/W}$ for photopic response, while λ is the wavelength.

Luminous intensity (candela (cd)) is defined by luminous flux per solid angle, $I = \frac{d\phi}{d\omega}$. Therefore, a light source radiating a luminous intensity of 1 cd per solid angle has luminance power of 1 lm. While sometimes luminance is also employed to determine the brightness level, it is defined as the luminous intensity over 1 m^2 (also known as “nits”).

In OLED characterization, the **current efficiency** (luminous efficiency) is a parameter used to describe effectiveness of charge injection and utilization in OLED.

Efficiency Optimization of Organic Light-emitting Diodes

It is defined as the luminance flowing through the device per unit current density, given by the following equation:

$$\eta_c = \frac{L \left(\frac{\text{cd}}{\text{m}^2} \right)}{J \left(\frac{\text{A}}{\text{m}^2} \right)} \quad \text{Eq. 3.4}$$

Here J stands for the current density, expressed in A/m^2 . η_c is a measure of effectiveness of charge usage, to achieve the maximum current efficiency, all charges injecting from electrodes have to be transported to the EML and form radiative excitons, this requires that both electron and hole injection need to be balanced.

The **power efficiency** of the device is the fraction of optical power emitted to the total electrical power supplied to the OLED:

$$\eta_p = \frac{\text{luminous flux}}{\text{electrical power}} = \frac{L \cdot \pi}{V \cdot J} = \frac{\pi \cdot \eta_c}{V} \quad \text{Eq. 3.5}$$

Here, L is the luminance in cd/m^2 , V is the supply voltage in volt, J is the current density in A/m^2 , π is the solid angle for OLED device. Therefore, to have a high power efficiency, we need to achieve a high current efficiency under a small operating voltage.

EQE, which is defined as the number of photons extracted per injected electron, can be used to describe how efficiently charges are recombined, photons are emitted and extracted:

$$\eta_{ext} = \frac{\int \frac{I(\lambda)}{hc/\lambda} d\lambda}{I_{OLED}/q} \quad \text{Eq. 3.6}$$

Here, $I(\lambda)$ is the measured spectra intensity of the radiating source.

Efficiency Optimization of Organic Light-emitting Diodes

Apart from the above mentioned device parameters, sometimes **color rendering index** (CRI) and **color correlated temperature** (CCT) are also commonly used parameters in the classification of OLED quality, especially white OLED. The CCT of an OLED is the color temperature of a blackbody source which shows the same perceived color compared to the OLED. While CRI is a quantitative measurement of how effectively an OLED can reflect the true color of an object. Two different OLEDs having the same color coordinates are said to possess the same CCT, but they may be significantly different from each other upon reflection by the same object, which is measured by CRI. The value of CRI can be ranged between 0 and 100, 100 is referred to an ideal blackbody radiator, generally speaking, a light source with CRI above 80 is considered as high quality.

Upon understanding of the definitions and parameters above, we can evaluate the performance of the OLED devices.

Chapter IV

The study and optimization of triplet distribution and the performance of phosphorescent OLEDs

From the analysis in Chapter 2, to achieve stable high performance with low efficiency roll-off, an OLED needs to have balanced charge injection from both electrodes, good charge and exciton confinement and relatively broader exciton distribution zone such that the exciton mutual quenching can be minimized. In this chapter, different hole transport layers were used and their ability in charge injection into emissive layer and confining charges and excitons were experimentally analyzed.

4.1. Introduction

OLEDs, especially phosphorescent OLEDs (PHOLEDs) have attracted most attention due to their capability of reaching 100% internal quantum efficiency (IQE).⁸⁰ Because of their ability to harvest triplet excitons, phosphorescence is inherently four times as efficient as fluorescence, which can only harvest singlets. The emission layer of a PHOLED is made by effectively mixing a small fraction of emitter molecules within the host matrix. During the device operation, the excitons are firstly formed on the host molecules, then the exciton energies are transfer to the emitter molecules by Förster or/ and Dexter energy transfer as described in Section 2.4 in Chapter 2. Then the emitter molecules decay to ground state and emit light. Ever since the first report of PHOLEDs using *fac* tris(2-phenyl-pyridinato-N,C^{2'}) iridium (Ir(ppy)₃) as phosphorescent dye,⁸⁰ continuous efforts have been made to improve the external

Efficiency Optimization of Organic Light-emitting Diodes

quantum efficiency (EQE) from an initial value of 8% to more than 20% recently.^{3,80,105-107}

NPB (structure shown in Fig. 1-6) has been extensively used as HTL in OLED fabrication. Further studies on OLEDs with NPB used as HTL and CBP: Ir(ppy)₃ as EML revealed that the recombination zone was located near the HTL/ EML interface.^{108,109} However, such OLEDs were inefficient because of the lower triplet energy of NPB (which is 2.3 eV) in comparison to that of Ir(ppy)₃ (triplet energy of 2.4 eV).^{81,110} Therefore, material with larger triplet energy has to be employed at the EML/ transport layer interface to confine the excitons within the EML. Lee *et al.*¹¹⁰ studied the effect of HTL with high triplet energy on the efficiency of the OLED devices. Although high EQE was realized using high triplet hole transport material dimeric Phenylcarbazole (PHCZ2) and dimeric ethylcarbazole (ETCZ2), device with 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA) only resulted in a very low EQE of around 5.5%. Lee *et al.* attributed the low EQE to the reduction of hole injection from the anode.

Recently TCTA has been used as HTL due to its excellent hole mobility of around 10^{-4} cm²/V/s and high triplet energy of 2.7 eV.^{111,112} A host material, on the other hand, should have an ambipolar charge transporting capability, which will facilitate excitons recombination throughout the host layer, reducing the exciton concentration quenching.¹ This makes the TCTA not an ideal candidate for host layer due to its poor electron transport capability.¹¹² CBP on the other hand has ambipolar charge transporting capability with both hole and electron mobilities around 10^{-4} cm²/V.s at an applied field of 5×10^5 V/cm.¹¹² Moreover, the HOMO level of 6.1 eV and LUMO of 2.8 eV of CBP are almost ideal for host with relatively wide bandgap.

Efficiency Optimization of Organic Light-emitting Diodes

In this chapter, we use TCTA as the HTL and CBP as the host layer. Significant improvement was achieved compared to the control device that uses NPB as HTL. The EQE of the best device reaches $22.8 \pm 0.1\%$ with a maximum power efficiency (PE) of 85 ± 2 lm/W. The EQE roll-off was also significantly improved by using TCTA as the HTL. When the OLED is driven under higher current density of 22 mA/cm^2 , the best EQE is almost twice the efficiency of the control device. To our knowledge, this is one of the highest reported EQEs for CBP host without external light out-coupling. We found that the triplet exciton distribution is significantly altered and the half current is improved by almost 20 times with the usage of TCTA compared to the control device with NPB as HTL. The improvement in the device performance results from better exciton distribution and confinement in the emission layer.^{113,114}

4.2. Experimental details

Prior to OLED deposition, the etched ITO glass substrate was first cleaned using detergent and subsequently treated under ultrasonication in acetone and ethanol for half an hour, respectively. Then the ITO glass was further cleaned in deionized water and dried using nitrogen gun. Before loading ITO substrates into the deposition chamber, a three-minute oxygen-plasma was employed to remove excess moisture and residual organic contaminations. After plasma treatment, ITO substrates were transfer into OLED system for organic and metal electrode deposition.

Devices with the following configurations were fabricated:

S1, ITO/ MoO₃ (10 nm)/ NPB (60 nm)/ CBP: Ir(ppy)₃ (5%, 20 nm)/Bphen (50 nm)/

LiF (1 nm)/ Al (100 nm);

Efficiency Optimization of Organic Light-emitting Diodes

S2, ITO/ MoO₃ (10 nm)/ NPB (40 nm)/ TCTA (20 nm)/ CBP: Ir(ppy)₃ (5%, 20 nm)/

Bphen (50 nm)/ LiF (1 nm)/ Al (100 nm);

S3, ITO/ MoO₃ (10 nm)/ TCTA (60 nm)/ CBP: Ir(ppy)₃ (5%, 20 nm)/ Bphen (50 nm)/

LiF (1 nm)/ Al (100 nm).

For all the three devices, MoO₃ is used as the HIL, CBP: Ir(ppy)₃ is the EML, 4,7-diphenyl-1,10-phenanthroline (Bphen) is the ETL and HBL, LiF is the EIL, and Al is the cathode. The only difference among them is the choice of HTL, for the control device S1, NPB is used as HTL, while S2 uses NPB and TCTA as HTL, in device S3, TCTA serves as HTL. Fig. 4-1 shows the structure and band diagram of various devices investigated in this work, the energy levels are extracted from literatures.^{106,115,116}

Fig. 4- 1 Device structure and energy bands for S1, S2 and S3.

The electrical and optical performance of the OLEDs were measured under ambient condition without encapsulation. Details of the OLED characterization were provided in Chapter 3.

Efficiency Optimization of Organic Light-emitting Diodes

4.3. Results and discussions

4.3.1. Electrical and optical performance

Fig. 4-2 shows the current density versus voltage (J-V) and luminance versus current density (L-J) curves for the various devices shown in Figure 1. From Fig. 4-2(a) it can be seen that all devices exhibit similar J-V characteristics, despite of the variation of the hole energy barrier and mobility, e.g., HOMO values of NPB and TCTA are 5.4 eV and 5.6 eV, respectively,¹¹⁷ and NPB has a slight larger hole mobility of $4 \times 10^{-4} \text{ cm}^2/\text{V.s}$ as compared to TCTA ($1 \times 10^{-4} \text{ cm}^2/\text{V.s}$).^{110,111} The L-J curves on the other hand significantly differ for all devices. Fig. 4-2(b) shows that S3 has much larger luminance, which implies improved recombination efficiency as compared to S1 and S2. At a low current density of 0.01 mA/cm^2 , the operating voltage of devices S1, S2 and S3 are 3.0 V, 3.1 V and 3.0 V, at a brightness level of $6.5 \pm 0.2 \text{ cd/m}^2$, $6.4 \pm 0.1 \text{ cd/m}^2$ and $7.9 \pm 0.1 \text{ cd/m}^2$, respectively. The brightness reaches $6578 \pm 74 \text{ cd/m}^2$, $9870 \pm 110 \text{ cd/m}^2$ and $14245 \pm 77 \text{ cd/m}^2$, respectively at the same current density of 22.2 mA/cm^2 .

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 4- 2 (a) Current density versus voltage (J-V) and (b) luminance versus current density (L-J) for devices S1, S2 and S3.

Fig. 4-3 shows the EQE, current and power efficiency versus current density for devices S1, S2 and S3. Compared to the control device S1, which has power efficiency (current efficiency) of $67 \pm 2 \text{ lm/W}$ ($65.6 \pm 0.3 \text{ cd/A}$) at a current density of $0.01 \text{ mA}/\text{cm}^2$, S2 shows a similar performance with power efficiency (current

Efficiency Optimization of Organic Light-emitting Diodes

efficiency) of 66 ± 1 lm/W (63.7 ± 0.6 cd/A), while S3 has improved performance with maximum power efficiency (current efficiency) of 85 ± 2 lm/W (78.6 ± 0.2 cd/A) at the same current level. Furthermore, the control device S1 shows significant efficiency roll-off, for example, the efficiency drops from 61.0 ± 0.1 cd/A (56.0 ± 0.3 lm/W) to 34.1 ± 0.4 cd/A (18.2 ± 0.3 lm/W) when the current density changes from 0.1 mA/cm² to 10 mA/cm². For comparison, much reduced efficiency roll-off happens for device S3 from 77.5 ± 0.2 cd/A (68.7 ± 0.7 lm/W) to 69.5 ± 0.1 cd/A (35.4 ± 0.1 lm/W), for the same current range. Similarly, device S2 also has a better roll-off compared to S1 where it drops from 61 ± 1 cd/A (54 ± 1 lm/W) to 49.0 ± 0.4 cd/A (24.6 ± 0.3 lm/W). The control device S1 has a peak EQE of only $19.1 \pm 0.1\%$, while S2 and S3 reach higher EQE of $19.9 \pm 0.1\%$ and $22.8 \pm 0.1\%$, respectively. The EQE roll-off of S2 and S3 have also improved significantly compared to S1. The measured maximum EQE is smaller than the optimized value of 25% achieved by other researchers using Ir(ppy)₃ doped CBP.^{118,119} Assume a maximum EQE of 25% corresponds to 100% internal quantum efficiency,¹¹⁸ S1, S2 and S3 achieve maximum internal quantum efficiencies of $76.4 \pm 0.1\%$, $79.6 \pm 0.1\%$ and $91.2 \pm 0.1\%$, respectively. While the non-unity internal quantum efficiency was attributed to the combined effect of exciton quenching and un-optimized ETL and ITO thickness.¹¹⁸

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 4- 3 (a) EQE with fitting and current efficiency versus current density and (b) power efficiency versus current density for devices S1, S2 and S3.

Efficiency Optimization of Organic Light-emitting Diodes

4.3.2. Verification of device S1 performance

To ensure that the efficiency of device S1 is optimized, we fabricated devices with different NPB thickness, their structures are shown below:

ITO/ MoO₃ (10 nm)/ NPB (X nm)/ CBP: Ir(ppy)₃ (5%, 20 nm)/ Bphen (50 nm)/ LiF (1 nm)/ Al (100 nm), where X is set to 40, 50, 60 and 70 nm, respectively. Fig. 4-4 shows the EQE, voltage and power efficiency of the devices with different NPB thickness at current density of 0.1 mA/cm², from which we can conclude that the device (S1) with a NPB layer of 60 nm shows the best performance, and hence device S1 is used as the control device.

Fig. 4- 4 EQE, voltage and power efficiency (inset) of devices with NPB thickness of 40nm, 50nm, 60nm and 70 nm, respectively at current density of 0.1 mA/cm²

Efficiency Optimization of Organic Light-emitting Diodes

4.3.3. Exciton distribution analysis

To better understand the factors causing such a significant improvement, we study the triplet exciton distribution for each device. To do so, we fabricated the following structures:

E1, ITO/ MoO₃ (10nm)/ NPB (60 nm)/ CBP (X nm)/ CBP: Ir(ppy)₃ (5%, 5nm)/ CBP (15 – X nm)/ Bphen (50 nm)/ LiF (1 nm)/ Al (100 nm),

E2, ITO/ MoO₃ (10nm)/ NPB (40 nm)/ TCTA (20 nm)/ CBP (X nm)/ CBP: Ir(ppy)₃ (5%, 5nm)/ CBP (15 – X nm)/ Bphen (50 nm)/ LiF (1 nm)/ Al (100 nm),

and

E3, ITO/ MoO₃ (10nm)/ TCTA (60 nm)/ CBP (X nm)/ CBP: Ir(ppy)₃ (5%, 5nm)/ CBP (15 – X nm)/ Bphen (50 nm)/ LiF (1 nm)/ Al (100 nm).

The 5 nm CBP: Ir(ppy)₃ EML acted as a sensing layer. By varying the value of X from 0 to 5 nm, 10 nm and 15 nm, respectively, the average exciton distribution profile within the 20 nm thick CBP host layer can be revealed.

Fig. 4-5 shows the average triplet exciton distribution profile (normalized EQE at current density of 0.22 mA/cm²) within the host layer. It can be seen that triplet exciton distributions are significantly different for device E1, E2 and E3. The normalized EQE is fitted using the following diffusion equation:¹²⁰

$$y = Ae^{-\frac{x}{L_D}} + Be^{\frac{x-d}{L_D}} \quad \text{Eq. 4.1}$$

where A and B represent for the relative peak triplet exciton concentration at the CBP/HTL and CBP/Bphen interfaces, L_D is the diffusion length of triplet in CBP, d is

Efficiency Optimization of Organic Light-emitting Diodes

the thickness of EML. In our case, $d=20$ nm. By fitting the curves, we obtained the diffusion length L_D to be around 14 nm. The value of excion diffusion length obtained here is smaller than 46 nm reported in the literature.¹²⁰ This is perhaps due to the thin EML, where Forster resonance energy transfer (FRET) and Dexter energy transfer between host and guest still dominate the exciton distribution instead of direct exciton diffusion. A and B are 0.8 and 0.4 for E1, 0.3 and 1.1 for E2, 0.4 and 1.2 for E3, respectively. The larger A value in E1 indicates the peak exciton concentration is located at CBP/ NPB interface, while the larger B values for E2 and E3 means the peak exciton concentration shifts to CBP/ Bphen interface.

Fig. 4- 5 Average triplet exciton distribution profile within CBP host for devices E1, E2 and E3.

Fig. 4-6 (a)-(c) depict the emission spectrum with respect to distance (X) between phosphorescent dopants sites to CBP/HTL interface for devices E1, E2 and E3 at a current density of 0.22 mA/cm². From Fig. 4-6 (a), where NPB is used as HTL,

Efficiency Optimization of Organic Light-emitting Diodes

when the Ir(ppy)_3 doping was placed at NPB/CBP interface ($X=0$), we mainly observed the emission spectrum with a peak around 510 nm. When the Ir(ppy)_3 doping was moved towards the cathode side, however, we observed an additional blue emission with a peak around 460 nm, which corresponds to the emission of NPB.¹²¹ Furthermore, an increase in NPB emission is observed as the Ir(ppy)_3 doping was moved away from the NPB/CBP interface. We can conclude that majority of excitons are formed at the NPB/ CBP interface. This is why when the sensing layer was moved away from the interface, the blue emission is increased compared to green emission. EQE of device E1 at $X = 0$ is very small (only around 5%), which indicates that most of Ir(ppy)_3 triplet emission is quenched by the NPB. This is because triplet energy of NPB (2.3 eV)¹¹⁰ is lower compared to the triplet energy of Ir(ppy)_3 (2.4 eV).⁸¹

Fig. 4-6 (b) and (c) show the emission spectrum for device E2 and E3, respectively, where TCTA was placed at HTL/CBP interface. Regardless of the position of the sensing layer, only emission from Ir(ppy)_3 was observed. This means that the structure provides a better exciton confinement within the emission layer. From Fig. 4-5 we can clearly see that the exciton formation zone is located at CBP/Bphen interface for device E2 and E3, which has an EQE of 19% and 20% at a current density of 0.22 mA/cm^2 , respectively. And E3 has a more uniform exciton distribution compared to that of E2. By relating the emission spectrum and triplet exciton distribution of E1, E2 and E3 with the performance of S1, S2 and S3, respectively, we can conclude that the more balanced exciton distribution and better confinement are the reasons why S3 performs the best.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 4- 6 Emission spectrum of (a) E1, (b) E2, and (c) E3 at the current density of 0.22 mA/cm² when the sensing layer was placed at X=0, 5 nm, 10 nm, and 15 nm.

Efficiency Optimization of Organic Light-emitting Diodes

To confirm that the charge trapping effect will not significantly affect the exciton distribution, the J-V characteristics of the devices E1, E2 and E3 with sensing layer at different location within the EML were measured and shown in Fig. 4-8. By comparing the electrical behavior of E1 with E2 and E3. It is found that the device (E1) with NPB adjacent to EML shows the same current conduction level when the sensing layer was placed at different location within EML, while the devices (E2 and E3) with TCTA adjacent to EML shows decreasing voltage as the sensing layer moves away from the TCTA/ EML interface. For device E1, the unchanged current conduction when moving the sensing layer can be attributed to the equal contribution from the large NPB/ CBP energy barrier and trapping effect at low doping level,¹⁰⁹ the holes experienced the same impedance by either surmounting the large energy barrier or by filling the traps at this low doping level. Therefore, at the fixed low dopant concentration of 5% used in this experiment, the exciton density won't be altered by the sensing layer as current conduction is the same when sensing layer is placed at different location. The conclusion of exciton formation zone located at HTL/ EML interface when using NPB adjacent to EML is consistent with previous researches.^{106,109} When TCTA is adjacent to the EML, however, the energy barrier between TCTA/ EML interface becomes smaller as compared to NPB/ EML interface (seen from Fig. 4-1), holes now experience smaller impedance when they surmount the energy barrier between TCTA/ CBP as compared to being trapped by the dopants. It is well understood that the current conduction increases when the sensing layer moves away from the interface. From the discussion in **Chapter 2.2.2**, when traps are present in organic semiconductors, charge conduction are decreased as traps need to be filled first. Therefore, when sensing layer moves away from the TCTA/ CBP interface, more holes can be injected into the EML and transported further towards their electron

Efficiency Optimization of Organic Light-emitting Diodes

counterparts. The main exciton distribution, however, was not determined by the trapping of holes. Since the LUMO of Ir(ppy)₃ is very close to that of the host (Fig. 4-1) and the electron transport is not affected by the Ir(ppy)₃ dopant,¹⁰⁹ if the hole trapping effect dominates the exciton distribution, when the sensing layer is placed adjacent to the TCTA/ EML interface (X=0), it should have similar EQE as the device S3, where the EML was doped uniformly. Because in both case, hole injections at the TCTA/ EML are the same. From Fig. 4-5, E1 with X=0 shows smaller EQE (14% at 0.22 mA/cm²). Furthermore, when the sensing layer is placed close to the EML/ ETL interface (X=15 nm), the EQE reaches 20% at 0.22 mA/cm², which is similar to the EQE of device S3. Therefore, whether the dopants are present at the TCTA/ EML interface or not does not change the exciton formation zone, it is likely that the exciton distribution is determined by the electron transport. Although the current conduction are changed by placing the sensing layer at different location, the exciton formation zone shall not be changed.

Fig. 4- 7 J-V characteristics for devices (a) E1 with NPB as HTL (b) E2 with NPB/ TCTA as HTL and (c) E3 with TCTA as HTL

Efficiency Optimization of Organic Light-emitting Diodes

4.3.4. Hole only devices

To understand why S3 has a better exciton distribution over S2 and S1, we study the electrical behaviour of the hole only devices as follows:

H1, ITO/ MoO₃ (20nm)/ NPB (60 nm)/ CBP (70nm)/ Al (100 nm), **H2**, ITO/ MoO₃ (20nm)/ NPB (40 nm)/ TCTA (20 nm)/ CBP (70nm)/ Al (100 nm), and **H3**, ITO/ MoO₃ (20nm)/ TCTA (60 nm)/ CBP (70nm)/ Al (100 nm).

Fig. 4-8 shows the current density of device H1, H2, and H3.

Fig. 4- 8 J-V characteristics of hole-only devices H1, H2 and H3.

We observed that H1 has the smallest current flow as compared to device H2 and H3. This is because for H1 the holes need to overcome a large energy barrier (0.7 eV) at NPB/CBP interface. For device H2, the addition of 20 nm TCTA layer introduces a step barrier that facilitates better hole transport to the CBP.^{122,123}

Efficiency Optimization of Organic Light-emitting Diodes

Improvement in hole injection and transport towards CBP/Bphen interface shifts the exciton formation zone toward CBP/Bphen interface. The use of TCTA layer only in device H3 eliminates the hole accumulation at the NPB/TCTA interface, which further improves the hole injection into the CBP layer as compared to H2, increasing the recombination efficiency. A recent study in the literature showed that a universal energy alignment trend between transition oxide and organic semiconductors, if the Fermi level of the oxide lies below the HOMO of the organic semiconductors, the HOMO level of the organic material will be pinned at the Fermi level of the oxide,⁵¹ leading to efficient charge injection from oxide into organic semiconductors. Therefore, because of the much deeper lying LUMO (6.7 eV) of MoO₃ as compared to the HOMO values of NPB (5.4 eV) and TCTA (5.6 eV),¹¹⁷ efficient hole injection from MoO₃ into both NPB and TCTA was anticipated.¹²⁴⁻¹²⁶ The elimination of multiple interfaces and a smaller hole energy-barrier at TCTA/CBP for device S3 therefore improves the hole injection significantly.

4.3.5. Exciton quenching analysis via triplet-triplet annihilation

It is known that EQE roll-off is caused mainly by triplet-triplet annihilation (TTA) at high intensity, which is due to the long lifetime of the triplet excitons.^{127, 128} The TTA can be expressed by the following reaction:¹²⁸

where K_{TT} is the TTA rate, and D and A represent donor and acceptor states, while the superscript corresponds to the multiplicity of the exciton and the star means the exciton is in the excited state. This process means two excited state triplet excitons react and result in only one triplet in the excited state and one singlet in the ground

Efficiency Optimization of Organic Light-emitting Diodes

state. Therefore, the expression for triplet exciton density can be shown by the following rate equation:¹

$$\frac{dn}{dt} = -\frac{n}{\tau} - \frac{1}{2}kn^2 + G \quad \text{Eq. 4.3}$$

where n is the triplet exciton density ($1/\text{cm}^3$), τ is the triplet lifetime (s), k is the TTA rate (cm^3/s), $\frac{1}{2}$ is the ratio indicating only one excited triplet state left after each TTA reaction, G is the rate of exciton generation ($1/\text{cm}^3\text{s}^{-1}$), $G = \frac{J}{dq}$, J is the current density (mA/cm^2), and d is the thickness of the organic layer (nm), q is the elementary charge. The Eq. 4.3 leads to EQE fitting equation:¹

$$\eta = \eta_o \frac{J_o}{4J} \left[\sqrt{1 + \frac{8J}{J_o}} - 1 \right], \quad \text{Eq. 4.4}$$

where $J_o = \frac{4dq}{k\tau^2}$. If we let $J=J_o$, Eq. 4.4 results in $\eta = \frac{1}{2}\eta_o$; therefore, J_o is also known as the half current density. The EQEs of all devices shown in Fig. 4-3(a) are fitted using Eq. 4.4. The half current density J_o of S3 is $158.2 \text{ mA}/\text{cm}^2$, more than twice that of S2 ($60.0 \text{ mA}/\text{cm}^2$) and almost 20 times larger compared to that of S1, which is only $8.1 \text{ mA}/\text{cm}^2$. The higher half current density means significantly reduced efficiency roll-off and better device stability. However from Eq. 4.4, it is clear that the half-current density is only influenced by the recombination zone width of the EML (d) and exciton lifetime (τ). Due to the ambipolar nature of the CBP host,¹¹² the exciton recombination zone shall not be confined at the sharp interface, as shown in Fig. 4-5, the recombination zone occupies the 20 nm EML. Therefore it is expected that J_o does not vary much for all devices. The possible explanation why S2 and S3 have much improved roll-off than S1 is because the formers provide better exciton confinement at higher current density. The severe EQE roll-off for S1 is caused by the leakage of

Efficiency Optimization of Organic Light-emitting Diodes

exciton toward NPB at higher current due to lower triplet energy bandgap. Therefore, it is imperative to have TCTA at the interface for a better confinement. For device S3, the excitons are more evenly distributed, and TTA is thus less severe.

Besides exciton quenching by TTA, triplet-polaron annihilation (TPA) also contribute to the efficiency decay.^{1,129} However, based on the study by Baldo *et al.*,¹ the TPA effect was much weaker and insignificant as compared to TTA effect in PHOLEDs with CBP doped by Ir(ppy)₃ as EML.

4.4. Conclusion

We have reported a highly efficient OLED with EQE of $22.8 \pm 0.1\%$ and power efficiency of 85 ± 2 lm/W without external out-coupling, corresponding to 36% increase compared to the control device. This was achieved by employing TCTA as the HTL and CBP as host layer. TCTA serves as a better HTL because of its high hole-mobility and large bandgap, which facilitates better hole transport and prevent exciton leakage toward the anode. CBP with its ambipolar charge transport capability and high bandgap provides as a perfect host layer. With better triplet exciton distribution and confinement, the efficiency roll-off was significantly reduced with much improved half current density of 158.2 mA/cm^2 .

Chapter V

Optimization of the efficiency of red phosphorescent OLED via charge balance by self balanced charge transport

In chapter 4, efficiency and roll-off of OLED was improved by proper choice of hole transport material, which improves hole injection and confines charge and exciton within emission layer. In this chapter, we presented another method to reduce efficiency roll-off by mixing two different materials with electron transport and hole transport ability in a graded manner, respectively.

5.1. Introduction of EML optimization

Since demonstration of nearly unity IQE using phosphorescent materials,⁹ PHOLEDs have been studied extensively. However, efficiency of PHOLED at higher luminance level tends to decrease significantly because of the quenching of excitons (such as TTA) originating from the long triplet excited state lifetime and narrow recombination zone within the EML.¹

There have been many studies on the origins of efficiency roll-off and recombination zone distribution within the emission layer (EML) of an OLED.^{1,130,131} Some researches focus on strategies to broaden the recombination zone and reduce TTA at high luminance.¹³¹⁻¹³⁸ Recently, to reduce quenching effects by adding hole transport layer, Padmaperuma *et al.* shifted the location of exciton formation zone from HTL/ EML interface to EML/ ETL interface within EML by chemical modification of phosphine oxide-based host molecules, such that the transport property of the matrix material was changed.¹³¹ Other than chemical approach, Lee *et al.* improved host transport properties by doping the charge transport material into the

Efficiency Optimization of Organic Light-emitting Diodes

host-dopant matrix.¹³⁶ By using composite emitter approach, Lee *et al.* tuned the charge transport properties of the host matrix and achieved a significantly higher current efficiency (2.5 times larger than conventional devices) at a current density of 20 mA/cm², Lee *et al.* proposed that good charge injection and transport of both charges within the EML were the reasons for better performance. Also, Chu *et al.* reported a high efficiency blue and white PHOLEDs with significant lower roll-off based on a mixed host structure using one electron transport type host and one hole transport type host.^{137,138} By carefully controlling the mixed host concentration, Chu *et al.* achieved a peak EQE of 21.6% and a PE of 44.9 lm/W for the blue device, while a PE of 37 lm/W was realized for the white PHOLED at a luminance level of 1000 cd/m². Here, the significantly improved efficiencies and reduced roll-off were accounted to increased charge injection and reduced TTA because of effective distribution of recombination zone. Despite large performance improvement of the mixed host device as compared to a single host device, a significant charge leakage may occur if a proper charge confinement layer is not used, since charge transport path exists within the EML.¹³⁹

5.2. Experimental: devices fabrication and characterization

In this chapter, we present the utilization of a graded-host (G-host) structure to achieve high efficiency red PHOLEDs with low operating voltage and reduced efficiency roll-off. The EML of G-host was fabricated in such a way that concentration of the hole transport type host decreases uniformly towards the electron transport layer (ETL) side, while concentration of the electron transport type host decreases uniformly towards the hole transport layer (HTL) side. The use of electronic controlled sensing system in our multi-source organic molecular vapour deposition system allows accurate control of deposition rate down to 0.01 nm/s. The improved charge transport

Efficiency Optimization of Organic Light-emitting Diodes

and confinement within the G-host structures allow an effective distribution of recombination zone and efficient charge confinement within EML.

The device configuration used in this study was:

ITO / MoO₃ (5 nm)/ TCTA : MoO₃ (40 nm)/ TCTA (10 nm)/ Host : bis(2-phenylquino-line) (acetylacetonate) iridium(III) (Ir(2-phq)₂(acac)) (5%, 30 nm)/ 1,3,5-tris(N-phenyl-benzimidazole-2-yl)benzene (TPBI) (10 nm)/ TPBI : Cs (40 nm)/ Al (100nm).

Here MoO₃ was used as the HIL, MoO₃ doped TCTA was used as the HTL, the host doped with 5% Ir(2-phq)₂(acac) was the EML, Cs doped TPBI was used as the ETL, intrinsic TCTA and TPBI layers were used as spacer to avoid diffusion of dopants from transport layers into EML. The corresponding device structure, graded host composition and proposed energy diagram are illustrated in Fig. 5-1. The values of the HOMO and LUMO were extracted from literature.^{140,141} Conventional single host devices in this work utilized TCTA for the hole transport type host or TPBI for the electron transport type host, both doped with 5% Ir(2-phq)₂(acac). While the G-host device utilized both TCTA and TPBI hosts, with TCTA concentration decreasing uniformly from 100% at the TCTA spacer / host interface to 0% at the host / TPBI spacer interface, and concentration of TPBI decreasing uniformly from 100% at the host/ TPBI spacer interface to 0% at the TCTA spacer / host interface in a complimentary fashion.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 5- 1 (a) Device structure with layer compositions, (b) layer structure of graded EML with uniformly varying host concentration and fixed dopant concentration, and (c) proposed energy diagram with HOMO-LUMO values available in the literature.

The OLEDs were fabricated on glass substrates with an ITO film thickness of 120 nm and a sheet resistance of 10 Ω /square. All measurements were carried out at room temperature under ambient conditions without encapsulation.

5.3. Results and discussions

To have a better understanding of the G-host device, we first compare it with the single host devices. The normalized EL spectra of devices with TCTA host, TPBI host, and G-host at a current density of 0.07 mA/cm² are plotted in Fig. 5-2 (a). The emission spectra all show a peak emission wavelength at 600 nm, which is characteristic emission peak for Ir(2-phq)₂(acac). From the plot we can see that there is

Efficiency Optimization of Organic Light-emitting Diodes

no difference among the three emission spectra, which implies there is no emission contributed from the host material (i.e., no host emission). The J-V and L-J performances of the G-host and single host devices are demonstrated in Fig. 5-2 (b). Compared to the single host device, the G-host device shows the largest current density. This is understandable since TCTA is a good hole transport material and TPBI is a good electron transport material. The electron and hole injection and transport in the G-host are, therefore, very efficient and, as a result, both electrons and holes contribute to the total current density in the G-host device.¹⁴¹

Furthermore, since the EML/ transport layer interfaces are not abrupt, there is no energy barriers at the transport layer / EML interfaces impeding charges from entering the EML. Thus, elimination of barriers helps to further reduce the applied voltage. The device with TCTA host yields a higher current density compared to TPBI host device, which indicates a better hole transport ability of the TCTA (hole mobility approximately $10^{-4} \text{ cm}^2/\text{Vs}$) than the electron transport ability of the TPBI (electron mobility approximately $10^{-5} \text{ cm}^2/\text{Vs}$).¹⁴² Because of efficient injection of both charges within the EML of the G-host device, the luminance of the G-host device is the largest. To better study the effect charge transport property of host material on the exciton distribution profile, a 0.2 nm sensing layer was insert within the host, the following device structures were tested:

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 5- 2 (a) Electroluminescence spectra for the devices with TCTA host, TPBI host and graded mixed hosts of TCTA and TPBI (G-host) and (b) L-J-V performance of the three devices.

1. ITO /MoO₃ (5 nm)/ TCTA : MoO₃ (40 nm)/ TCTA (10 nm)/ Ir(2-phq)₂(acac) (0.2 nm)/ Host (30 nm)/ TPBI (10 nm)/ TPBI : Cs (40 nm)/ Al (100nm)

Efficiency Optimization of Organic Light-emitting Diodes

2. ITO /MoO₃ (5 nm)/ TCTA : MoO₃ (40 nm)/ TCTA (10 nm)/ Host (**10 nm**)/ Ir(2-phq)₂(acac) (0.2 nm)/ Host (20 nm)/ TPBI (10 nm)/ TPBI : Cs (40 nm)/
Al (100nm)

3. ITO /MoO₃ (5 nm)/ TCTA : MoO₃ (40 nm)/ TCTA (10 nm)/ Host (**20 nm**)/ Ir(2-phq)₂(acac) (0.2 nm)/ Host (10 nm)/ TPBI (10 nm)/ TPBI : Cs (40 nm)/
Al (100nm)

4. ITO /MoO₃ (5 nm)/ TCTA : MoO₃ (40 nm)/ TCTA (10 nm)/ Host (**30 nm**)/ Ir(2-phq)₂(acac) (0.2 nm)/ TPBI (10 nm)/ TPBI : Cs (40 nm)/ Al (100nm)

The choice of host were TCTA only, TPBI only or graded-host, the resultant emission spectrum for different devices were shown in Fig. 5-3 (a)-(c), respectively. The exciton distribution profile was calculated based on the spectrum in Fig. 5-3 (a)-(c) and illustrated in Fig. 5-3 (d).

For TCTA host device, because of the hole transport nature of the host, the exciton formation zone is located at the host / HBL interface, which could be clearly observed in Fig. 5-3 (a). Large drop in red emission intensity indicates that exciton formation zone is well confined within the 10 nm distance from the interface. Due to the electron transport nature, when TPBI was used as host material, exciton generation zone was near the EBL / host interface. However, from the emission spectrum in Fig. 5-3 (b), we could observe that exciton density steady decreases towards the host / HBL interface. Therefore, the exciton distribution zone in TPBI host is broader than that of the TCTA host device (Fig. 5-3 (d)), effectively reduces triplet quenching such as

Efficiency Optimization of Organic Light-emitting Diodes

TTA.^{127,128} That is why the TCTA host device shows a smaller luminance level compared to the TPBI device. When use the graded-host (Fig. 5-3 (c)), although the exciton generation zone is located near the host/ HBL interface, which could be due to the larger hole mobility of TCTA than the electron mobility of TPBI,¹⁴² the exciton distribution is much more uniform as compared to either TCTA or TPBI host. This study agreed well with the finding by Erickson and holmes.^{143,144} They studied the electron and hole mobilities within the mixed TCTA and TPBI film, the hole mobility did not show any decreasing trend despite the increase of TPBI concentration, this would result in slightly hole rich device with exciton peak located near EML/ HBL interface.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 5- 3 Sensing spectrum extracted from device with host of (a) TCTA only, (b) TPBI only and with (c) graded host, respectively, (c) exciton density within the different host materials.

From the luminance efficiency, EQE and power efficiency versus current density shown in Fig. 5-4, we observed a large increase in the device efficiency in the G-host device. The significantly improved performance and reduced efficiency roll-off (which could be observed by the normalized luminance efficiency in the inset of Fig. 5-4 (a)). It indicates charges in the G-host device are more balanced and exciton formation region is more widely distributed (Fig. 5-3 (d)). Because of the unipolar charge transport nature of TCTA and TPBI materials, exciton formation zone of the single host devices was located at EML and transport layer interface. Thus, very high exciton density exists in a narrow zone at the interface, which may induce significant quenching of the triplet excitons, resulting in larger efficiency roll-off.^{145,146} Furthermore, the LUMO and HOMO values of the host matrix material are very important parameters for the charge balance, since electron and hole injections from the neighbouring charge transport layer are determined by the interfacial energy barrier.¹⁴⁷

For the G-host device, however, TCTA concentration at the EML / TCTA interface is 100%, and there is no energy barrier to impede hole injection. After holes are injected into the EML, they face steady decreasing concentration of TCTA and increasing content of TPBI. The intermolecular distance of the TCTA increases and there are fewer hopping sites for holes as they penetrate further towards the ETL side. At the EML/ TPBI interface, there is no TCTA, while TPBI concentration is 100%, this implies that hole transport will be minimized at this interface. When electrons are transported from TPBI into EML, they behave the same manner as holes. Since TPBI

Efficiency Optimization of Organic Light-emitting Diodes

concentration is 100% at the interface, the electron injection is very efficient. As electrons travel further into the EML, TPBI concentration decreases steadily and there are fewer sites for electron to hop. At the TCTA / EML interface, TPBI concentration is 0% and electron transport are minimized. Therefore, both electrons and holes can travel into the EML and the recombination zone will not be confined near a narrow interface. The absence of sharp interfaces and self-confinement nature of the G-host device enable better charge injection and transport, which effectively broadens the recombination zone. This results in an increased quantum efficiency with reduced EQE roll-off.

Fig. 5- 4 Plot of (a) CE-J and (b) PE and EQE-J for OLED with TCTA host, TPBI host and the graded mixed hosts of TCTA and TPBI (G-host). Inset of (a) Normalized CE-J.

Efficiency Optimization of Organic Light-emitting Diodes

Transient photo-luminescence (PL) measurements were performed to give more information on the quenching of single host and graded host devices. Three films consisting of TCTA: Ir(2-phq)₂(acac) (5%, 30nm), TPBI: Ir(2-phq)₂(acac) (5%, 30nm) and graded TCTA: TPBI: Ir(2-phq)₂(acac) (5%, 30nm), respectively were prepared on quartz substrates and excited by a laser source of 355 nm, the signals were detected by a photomultiplier tube (Hamamatsu R928). The normalized transient PL curves are shown in Fig. 5-5, from which we can clearly see that the decay of the graded host is longer than TPBI and TPBI host. Assume the luminescence intensity $L(t)$ is linearly proportional to the concentration of exciton concentration, the PL decay curves are fitted by the following exciton quenching model:¹⁴⁸

$$L(t) = \frac{L(0)}{\left(1 + \frac{1}{2}n_{ex}(0)K_{TT}\tau\right)e^{\frac{t}{\tau}} - \frac{1}{2}n_{ex}(0)K_{TT}\tau} \quad \text{Eq. 5.1}$$

Here $L(0)$ is the initial luminescence intensity, which is normalized to 1, τ is the lifetime and $n_{ex}(0)$ is the initial exciton concentration, while K_{TT} is the rate constant for TTA.

Since all the samples were excited by laser source of the same intensities, the initial exciton concentrations $n_{ex}(0)$ are assumed to be the same. Assuming an initial concentration of $5 \times 10^{17} \text{ cm}^{-3}$ was created.¹⁴⁸ The fitted TTA rate constant and lifetime for the TPBI host, TCTA host and graded host are $1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $1.8 \text{ } \mu\text{s}$, $1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $1.6 \text{ } \mu\text{s}$ and $8.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $2.5 \text{ } \mu\text{s}$, respectively. The results obtained are consistent with the results by Leo *et al.*¹⁴⁸ Compared to TPBI host and TCTA host devices, the graded host device exhibits longer lifetime and smaller TTA rate constant, which indicates that the bimolecular quenching effects are significantly reduced in

Efficiency Optimization of Organic Light-emitting Diodes

graded host device.¹⁴⁴ This further verifies the conclusion that graded host reduces the quenching of excitons.

Fig. 5- 5 Transient PL of EML consisting of TPBI, TCTA and graded TCTA: TPBI as host, respectively.

To confirm the effects of the G-host structure on the device performance, we constructed a double layer heterojunction host (D-host) device with a similar structure:

ITO/MoO₃ (5 nm)/ TCTA:MoO₃ (40 nm)/ TCTA (10 nm)/ TCTA : Ir(2-phq)₂(acac) (5%, 15 nm)/ TPBI: Ir(2-phq)₂(acac) (5%, 15 nm)/ TPBI (10 nm)/ TPBI: Cs (40 nm)/Al (100 nm),

where TCTA and TPBI both doped with Ir(2-phq)₂(acac) are the two host layers and form a sharp interface. The D-host of the device consists of 15 nm TCTA and 15 nm TPBI with uniformly doped Ir(2-phq)₂(acac). A comparison of the PE and EQE of the D-host device with that of the G-host device is illustrated in Fig. 5-6, from which we can observe that the D-host device has smaller power efficiency and larger efficiency

Efficiency Optimization of Organic Light-emitting Diodes

roll-off. The external quantum efficiency of the D-host device decreases from 14.2% at the current density of 0.03 mA/cm² to 8% at 30 mA/cm², corresponding to 40% drops. For the G-host device, however, the efficiency decreased from 14.2% at the current density of 0.03 mA/cm² to 11.8% at 30 mA/cm² corresponding to 16% drops only. The slightly inferior performance of the D-host device is likely due to the narrow recombination zone and poor charge balance. A more uniform exciton distribution allows the G-host device to outperform the D-host device.

Fig. 5- 6 Comparison of PE - J and EQE - J between the D-host and G-host devices.

5.4. Conclusion

In conclusion, we have fabricated a graded-host device with its EML layer constructed in such a way that the concentration of the hole transport type host decreases uniformly from the HTL side (100% in concentration) towards the ETL side (0% in concentration), while the concentration of the electron transport type host

Efficiency Optimization of Organic Light-emitting Diodes

decreases uniformly from the ETL side (100% in concentration) towards the HTL side (0% in concentration). The G-host device showed improved device efficiency as compared to the unipolar host devices and reduced EQE roll-off compared to the double layer heterojunction host device. The superior performance was attributed to better charge injection and balance, and widened recombination zone. However, due to the limitation of materials availability and the concern of the accuracy of the deposition system during non-linear rate control, we could not offer more varieties of EML material and composition gradient. To further improve the device quantum and power efficiencies with better efficiency roll-off, more works on material with different mobility and EML with different gradients shall be done.

Chapter VI

The Study of OLEDs outcoupling using imprinted submicron-size zinc oxide pillar arrays

In previous two chapters, we have experimentally shown both efficiency and its roll-off could be improved significantly by proper use of HTL and G-host layer within the internal structure of OLED, respectively. In this chapter, we will present an external light extraction technique to boost the OLED efficiency.

6.1. Introduction

Although a 100% IQE has been realized by using phosphorescent emitters,⁸⁰ the EQE encounters a bottleneck, which is limited by the low light extraction efficiency. In conventional OLEDs with a planar waveguide-like structure, because of the refractive index difference between organics ($n \approx 1.8$) and ITO (1.8), glass substrate (1.5) and air (1.0),¹⁴⁹ TIR occurs at the glass/ air and organic or ITO/ glass substrate interfaces. This results in about 50% of internally generated light being trapped in the organic/ITO layers (organic/ITO mode), and about 30% are trapped in the glass substrate (substrate mode). Therefore, only around 20% of internally generated photons can be extracted into air.^{9,118,150}

The low light extraction efficiency of OLEDs leaves much room for improvement. Techniques such as substrate roughening¹⁵¹ and microlens array (MLA)^{152,153} were applied to the backside of glass substrate to outcouple the glass mode, while techniques like photonic crystals (PCs)^{99,100}, low index gridding^{101,154,155}, and corrugation structures^{156,157} were commonly introduced inside the OLEDs structure to extract light trapped in the organic/ITO mode. Among the above

Efficiency Optimization of Organic Light-emitting Diodes

mentioned techniques, PCs attracts much attention because of their capability to control photons in various ways by designing different photonic nanostructures.^{99,100,158,159} However, most of these techniques involve several steps necessary for fabricating PCs such as chemical vapour deposition (CVD), electron beam (EB) lithography, and reactive ion etching (RIE), etc.,⁹⁹ which are very time consuming and cost inefficient for industrial production. The pattern replication in non-wetting templates (PRINT) technique,^{158,160,161} in contrast, is a simple, cost-effective method to fabricate the PC gratings with high throughput.

The material used as the PC grating layer, however, has to be carefully chosen. One design principle of the outcoupling layer is that it shall minimize the TIR effect between the glass substrate and the PC grating layer. Therefore, a refractive index equal to or larger than that of the glass ($n=1.5$) should be considered when select the outcoupling material, while material with smaller refractive index will results in a portion of light trapped inside substrate due to TIR the at the glass/ outcoupling interface.^{154,162} Other properties such as high transparency and low light absorption should also be considered. Zinc Oxide (ZnO), which has a has a high refractive index of 1.9 to 2.2 at visible light range¹⁶³ and excellent properties such as high chemical stability, excellent optical transmittance and low material cost,¹⁶⁴ is selected in this experiment.

In this Chapter, we proposed and demonstrated the nano-meter sized zinc oxide pillars prepared by the PRINT technique at the bottom of substrate as the light extraction medium for OLEDs. Significant improvement was achieved compared to the reference device using bare ITO-glass. The best device shows a maximum emission intensity level at 40° viewing angle. At 0° viewing angle, it yields a maximum luminous efficacy of 95.5 ± 1.5 cd/A, which corresponds to 40.4%

Efficiency Optimization of Organic Light-emitting Diodes

improvement compared to that of the reference device (68.0 ± 1.4 cd/A) measured at 0° . When integrated over all viewing angles, we achieved an EQE of $38.5 \pm 0.1\%$ (power efficiency of 127 ± 1 lm/W), corresponding to about 75% enhancement in total light output. Both two-dimensional Lumerical finite difference time domain (FDTD) simulation and numerical fitting using diffraction theory were performed to verify the experimental results. The improvement is attributed to the combined effects of diffraction grating and higher extraction probability due to the light incident on vertical walls of the ZnO nanopillars. Furthermore, the light extraction efficiency is more sensitive to the variation in filling factor at lower fill factor (FF) value as compared to higher values.

6.2. Experimental details

Fig. 6-1(a) briefly illustrates the PRINT technique used to fabricate submicron-size ZnO pillar array. Polydimethylsiloxane (PDMS) mold was first prepared using the patterned silicon master substrate, and then the PDMS mold was pressed on the backside of patterned ITO glass substrate pre-drop-casted with ZnO solgel nanoparticles, holding at constant pressure. The ZnO gel was prepared by stirring the 0.1 M $\text{Zn}(\text{Ac})_2$ solution at 60°C for 10 h and then filtered by a filter paper with a pore size of 400 nm. The filtering process is very critical, if a particle larger than the pillar size (400 nm in diameter in this case) is present after the filtering process, the ZnO periodicity might be disrupted. Following the application of the mold on ZnO solgel, the substrate was then heated for solvent evaporation. Subsequently, the mold was peeled off, leaving behind the periodical pillar arrays. Finally, the as-prepared substrate was annealed at 250°C for 0.5 h to obtain the ZnO pillars array. To ensure high-quality ZnO pillars, filtered ZnO solgel nanoparticles need to be uniformly drop-

Efficiency Optimization of Organic Light-emitting Diodes

casted on the back side of glass substrate and the substrate shall be kept at a fixed position before the the solvent has been evaporated.

Since the ZnO nano-pillars were prepared by solgel technique, it cannot sustain standard ITO cleaning process. Therefore, to ensure good cleaning quality, firstly the ITO substrate needs to be cleaned before the ZnO nano-pillars preparation. Then after ZnO nano-pillars fabrication, the ITO surface shall be cleaned again using cleanroom wiper with Acetone, ethanol and de-ionized water in sequential manner, the wipe shall not touch the ZnO pattern during the cleaning process. After that, the ITO surface was dried using Nitrogen blow. Because the ZnO patterns are on the back side of the substrate, standard plasma treatment can apply.

OLEDs were fabricated with the following device structure:

ITO/ MoO₃ (20 nm)/ TCTA (60 nm)/ CBP: Ir(ppy)₃ (5%, 20 nm)/ TPBI (50 nm)/ LiF (1 nm)/ Al (100 nm),

where Al was used as the cathode, LiF as the EIL, TPBI as the ETL, CBP: Ir(ppy)₃ as the EML, TCTA as the HTL and MoO₃ was used as the HIL. For the reference device, OLEDs stacks were fabricated on plain glass substrate without using any light outcoupling structure, while the test devices were fabricated on the glass substrate with their backsides pre-coated with ZnO pillar arrays with the pitches of 400 nm 500nm, 650 nm and 800nm, respectively. A schematic diagram of the device structure with the ZnO pillar array is demonstrated in Fig. 6-1(b). The radii and heights of the ZnO cylindiral pillars were designed to be fixed around 200 nm. SEM images of the four samples are shown in Fig. 6-2(a) to (d), respectively.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 1 (a) PRINT process used to fabricate ZnO nanopillar array and (b) schematic illustration of the OLED stacks with ZnO nanopillar array at the back side of glass.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 2 Patterns of the ZnO nanopillar array with pitch of (a) 400nm (b) 500 nm (c) 650 nm and (d) 800 nm, respectively measured by SEM.

6.3. Results and discussions

6.3.1. Electrical results and efficiency analysis

Fig. 6-3 shows the luminance versus voltage (L-V) and CE-J for the reference device and the test devices, while the inset of Fig. 6-3 (a) and (b) shows their normalized emission spectra and J-V characteristics, respectively. The performance of various devices was measured at 0° viewing angle (perpendicular to the emitting surface). The J-V characteristics shown in the inset of Fig. 6-3 (b) indicate that devices with different ZnO patterns have similar electrical performance. This is expected since ZnO nano-pillars are in the back side of glass, which shall not affect the charge injection and transport of the OLEDs. From Fig. 6-3(a), it can be seen that different devices have different luminance behavior. Device with 650nm ZnO pillar pitch exhibits the largest luminance, and its luminance reaches $8442 \pm 100 \text{ cd/m}^2$ when the applied voltage (current density) is 6.43 V (10 mA/cm^2). Under the same electrical

Efficiency Optimization of Organic Light-emitting Diodes

conditions, device with the ZnO pillar pitch of 400nm, 500nm and 800nm also exhibits an improved luminance level of 6916 ± 200 cd/m², 7331 ± 128 cd/m² and 6325 ± 75 cd/m², respectively, compared to the reference device that shows a luminance of 6041 ± 16 cd/m². In comparison to the reference device, the enhanced performance of the tested devices implies higher light extraction efficiency. The current efficiency also differs significantly for different devices. For example, as shown in Fig. 6-3(b), at 0° viewing angle, device with 650nm pitch exhibits a maximum efficiency of 95.5 ± 1.5 cd/A. This corresponds to 40.4% improvement as compared to that of the reference device, which shows a maximum current efficiency of 68.0 ± 1.4 cd/A. While devices with 400nm, 500nm and 800nm pitches show maximum current efficiencies of 77.8 ± 0.6 cd/A, 82.6 ± 3.4 cd/A, 73.7 ± 0.1 cd/A, corresponding to an improvement of 14.4%, 21.5% and 8.4%, respectively, in comparison to the reference device shown in Fig. 6-3(b).

The inset of Fig. 6-3 (a) depicts the normalized spectra for the reference device and the tested devices. Corresponding to the efficiency improvement levels, we observed that device with 650nm pitch has the most significantly different spectrum compared to the reference device, while the device with 500nm pitch shows slightly less significant change in spectrum compared with that of the device with 650nm pitch. Furthermore, both devices with 400nm and 800nm pitches show the least deviation from that of the reference device. The significance of change in spectrum follows the trend of efficiency improvement, the difference clearly arises from diffraction of light by the ZnO nanopillars,^{99,100,162} the deeper reason of the efficiency enhancement will be described with simulation in later paragraphs.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 3 (a) L-V and (b) CE-J characteristics of the reference device and devices with grating period of 400nm, 500nm, 650nm and 800nm. Inset: (a) normalized emission spectra for respective device (b) J-V curves.

Efficiency Optimization of Organic Light-emitting Diodes

6.3.2. Angular emission characterization

Assuming when the spectrometer is facing perpendicular to the OLED emitting surface, it is named as 0° viewing angle. Then the angular emission characteristics were measured by rotating the OLED so that its emitting surface normal forms an angle θ with respect to the spectrometer. Here the angle θ was changed from 0° to 90° by step of 10° . Fig. 6-4(a) below shows the normalized angular emission intensity for the reference and tested devices. The reference and devices with 400nm and 800nm pitches have similar angular distribution characteristics, where they both show the maximum emission intensity at the low emission angle (close to normal incidence) in a typical Lambertian emission pattern. This implies that the diffraction effect for devices with the pitch of 400 nm and 800nm is not very significant. The devices with 500nm and 650nm pitches, however, show very different angular emission behaviors. For example, the device with 650nm pitch shows its maximum emission intensity at an observation angle of 40° and its emission intensity decreasing at only higher emission angles. Although the peak intensity of device with 500nm pitch was detected at 0° viewing angle, compared to reference device, it shows a broader emission at higher angles. The different angular emission behaviors could be explained by the grating effect of the ZnO pillar arrays shown below.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 4 (a) Normalized angular distributions of the reference device and device with different pitches. (b) Fitting of the angular distribution.

The presence of the periodic ZnO nanopillars enables the extraction of the trapped light into air. Diffracted light follows^{165,166}

$$\lambda = p(n\sin \theta_{in} + \sin \theta_{dif}) \tag{Eq. 6.1}$$

Efficiency Optimization of Organic Light-emitting Diodes

where λ is the emission wavelength, p is the pitch of ZnO pillar array, n is the refractive index of the glass substrate, θ_{in} is the incident angle, and θ_{dif} is the diffracted angle. From Eq. 6.1, if the incidence angle is 0° (Inset of Fig. 6-5 (b)), the emission intensity of the diffracted light becomes

$$f(\theta) = A \times (\cos(\frac{\pi p}{\lambda} \times \sin(\theta)))^2 \quad Eq. 6.2$$

Here A represents the amplitude of light extracted by the grating, p is the pitch of ZnO pillar array, λ is the wavelength, which is set to the peak wavelength 510 nm in this case, and θ is the emission angle viewed from air.

Fig. 6-4(b) shows the intensity of the diffracted light emitted from the tested devices with different pitches as a function of the viewing angle. These were obtained by subtracting the total angular emission for the corresponding device with that of the control device. The resulted curves were fitted using Eq. 6.2. The fitted lines show good agreement with the experimental results, especially for devices with 500nm and 650nm pitches. The constant A resulted from fitting is 0.05, 0.13, 0.22 and 0.01 for device with 400nm, 500nm, 650 nm and 800nm pitch, respectively. The much smaller fitting coefficient for device with 400nm and 800nm pitches further confirms both devices exhibit weaker diffraction grating effect. The fitting for device with 800 nm pitch was poor, which further indicates diffraction effect plays insignificant role for ZnO nano-pillars with larger pitch.¹⁵⁹ The fitting at low angle is not drawn since Eq. 6.2 is very simple and only describes the diffraction grating effect, while at low angle, significant portion of light are extracted due to the light with incident angle larger than TIR but incident on the vertical walls of the ZnO pillars, this part of light are extracted at low angle, but not because of diffraction effect.

Efficiency Optimization of Organic Light-emitting Diodes

6.3.3. Efficiency over all angles

The total number of photons emitted can be calculated by integrating the angular photon density over all angles. Fig. 6-5(a) and (b) show the overall EQE-J and PE-J, respectively.

Here the best device (650nm pitch) leads to a maximum EQE (power efficiency) of $38.5 \pm 0.1\%$ (127 ± 1 lm/W), significantly larger than that of the reference device, which show a maximum EQE (power efficiency) of $22.0 \pm 0.1\%$ (72 ± 1 lm/W), while device with 400nm, 500nm and 800nm pitch exhibits efficiency level of $24.6 \pm 0.1\%$ (81.1 ± 0.4 lm/W), $29.9 \pm 0.1\%$ (98.5 ± 6.0 lm/W) and $23.3 \pm 0.1\%$ (76.8 ± 1.3 lm/W), respectively. The improvement of EQE and power efficiency shown in Fig. 6-5 is slightly different from that of the current efficiency in Fig. 6-3(b), this is expected since current efficiency was measured at specific 0° angle, while both EQE and power efficiency were integrated for all angles to take into account the non-Lambertian emission angular distribution characteristic of the tested devices.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 5 (a) EQE – J and (b) PE - J. Inset: Diffraction grating with the presence of ZnO nanopillar arrays.

6.3.4. Simulation

To have better understanding of the physics behind the improvement, a two-dimensional Lumerical FDTD simulation was performed to verify the experiment results. A simulation area of $15\ \mu\text{m} \times 15\ \mu\text{m}$ is constructed to include multiple period

Efficiency Optimization of Organic Light-emitting Diodes

of patterning. Dipole light source is placed in emission layer to replicate the light radiation generated due to electron-hole pair. Physically matched layers are used as boundary condition to surround the simulation area in order to absorb any light radiation impinging on it. ZnO nano-pillar array with 200 nm height and 200 nm radius is placed over the glass surface illustrated by Fig. 6-1. The period of ZnO nano-pillar array is varied and light extraction efficiency (LEE) is measured at 510 nm wavelength in the far-field integrating all extracted light radiation in 1° solid angle. Fig. 6-6 (a) and (b) show the intensity field distribution with propagation of the reference device and device with ZnO nanopillars, respectively. We can clearly see that light is escaping out of the glass surface due to the presence of ZnO nano-pillar array in comparison to light undergoing TIR from glass-air interface in conventional OLED structure. Fig. 6-6 (c) shows the light extraction efficiency versus fill factor (FF) for both numerical simulation using Lumerical FDTD and fitting results using Eq. 6.2 together with experimental data.

Our experimental data show similar trend with the simulation results. The simulation deviates slightly from the simplified model using Eq. 6.2, this implies that pure diffraction grating effect may not be the only reason behind the improvement. Compared to the light that initially undergoes TIR in reference OLED, light in the tested devices with incident angle larger than critical angle at ZnO/air interface now has more chance to be extracted if light incident on the ZnO pillars vertical walls. This could be observed clearly from the inset of Fig. 6-6 (b), which shows the zoom-in image of the field distribution, the much higher intensity surrounding the ZnO nanopillars indicates more light were outcoupled through the nanopillars.

Efficiency Optimization of Organic Light-emitting Diodes

Fig. 6- 6 Intensity field distribution with propagation of (a) reference OLED, (b) OLED with ZnO nanopillar array. (c) Experimental results of light extraction enhancement ratio with respect to fill factor in comparison with Lumerical FDTD simulation and fitting result using diffraction theory. Inset of (b): zoom-in image of field distribution.

Efficiency Optimization of Organic Light-emitting Diodes

From the plot, we also observed that light extraction ratio is more sensitive to the variation of FF at lower FF value than that in larger region, the FF for cylindrical pillar shaped photonic crystal is calculated by:

$$FF = \frac{\pi r^2}{p^2} \quad \text{Eq. 6.3}$$

where r is the radius of the nanopillar and p is the pitch. The filling factor for ZnO pillars of 400nm, 500nm, 650 nm and 800nm pitch is 0.8, 0.5, 0.3 and 0.2, respectively. Due to the inverse square proportional relation between the FF and pitch, a small FF change at lower limit equivalent to large variation in pitch. From the experiment results, PC grating resulted in significant drop in efficiency enhancement when the filling factor is too large or too small, which agrees with previous research.¹⁵⁹

6.4. Conclusion

We have fabricated high efficiency OLEDs with ZnO pillar array at the backside of the glass substrate using PRINT technique. The device with the ZnO pillar array pitch of 650 nm (FF of 0.3) achieved a maximum EQE of $38.5 \pm 0.1\%$, which corresponds to 75.0% enhancement in total light output. Furthermore, the best device reached a maximum current efficiency of 95.5 ± 1.5 cd/A measured at 0° viewing angle, improved by 40.4% compared to the reference measured at the normal incidence. The improvement was attributed to the effective diffraction of light trapped in the glass mode by the ZnO nanopillar arrays.

Chapter VII

Conclusion and future challenges

7.1. Conclusion

In this thesis, both internal quantum efficiency and external light outcoupling efficiency of OLED were studied. First, the effects of using TCTA as HTL were tested by comparing its performance with those devices with NPB or NPB/ TCTA as HTL, respectively. By studying the exciton distribution and emission spectrum by placing a sensing layer within the 20nm emission layer, we observed that when NPB is placed adjacent the emissive layer, significant fraction of excitons were quenched and we could not observe NPB emission. While using NPB/ TCTA combination as HTL, although the exciton quenching by the NPB layer was avoided, efficiency roll-off was still significant due to narrower exciton generation region located at EML/ ETL interface, triplet-triplet annihilation was severe at large current density. The use of TCTA as both HTL and EBL can not only eliminate the quenching of exciton by lower-triplet-energy NPB layer, but also broaden the exciton distribution profile due to the more uniform charge dispersion in the EML, which was verified using hole only device. Thus both the peak efficiency and efficiency roll-off were significantly improved.

The key to reduce triplet-triplet annihilation is to broaden the exciton distribution zone, reducing the effective exciton density. To achieve this, the emissive layer needs to possess good charge transport characteristic for both electron and hole. However, most of the time, the host material is either electron transport type or hole transport type. To solve this problem, we mixed the electron transport type host and hole transport host in a graded manner, such that both charges have no barrier injecting

Efficiency Optimization of Organic Light-emitting Diodes

into the EML. Furthermore, the hole will face a reducing mobility when travelling towards the EML/ ETL interface, while electron will also face a decreasing mobility when travelling towards the HTL/ EML interface. In this case, exciton will shift away from the interface to somewhere in the middle of EML. Compared to single electron transport type or hole transport type host, significantly improved efficiency and roll-off were observed for the graded mixed device.

Because of the refractive index difference between organic, ITO, glass substrate and air, total internal reflection occurs at ITO/ glass interface and glass/ air interface, which severely limits the light extraction efficiency to around 20%. To help extract glass mode, we used submicron sized imprinted ZnO nano-pillars at the backside of glass substrate. Due to the diffraction at the glass/ ZnO nanopillar interface, more light were extracted from the device. Besides that, the angular distribution were altered significantly from lambertian emission pattern, the maximum emissive intensity occurred at 40° viewing angle, as compared to 0° in the normal case.

7.2. Future challenges

Compared to a few years back when OLED is only limited to laboratory research, it now starts to enter our daily-life via various commercial products, for example, mobile phones in the market already equipped with OLED display and OLED for mobile TV. Despite the successful commercialization of OLED in display industry, there are still some challenges faced by OLED researchers.

The use of phosphorescent dopant enabled 100% internal quantum efficiency by introducing heavy metal elements into the material, which promotes spin-orbital coupling, the efficient inter-system crossing promotes the harvesting of both excitons (singlets and triplets).²¹ The emitting metal-ligand-charge transfer states however, lies

Efficiency Optimization of Organic Light-emitting Diodes

much lower compared to the singlet state, this places a challenge for blue phosphorescent OLED. To realize blue emission, the triplet state has to be larger than 2.7 eV, which means the optical bandgap needs to be even larger due to the singlet-triplet splitting.¹⁶⁷ To achieve good charge and exciton confinement of the emitter, not only the host material shall have wider bandgap than the emitter, the charge transport layer shall also possess larger bandgap than the host material. From material point of view, materials having large bandgap normally have poor charge transport properties, this is due to higher energy is needed for electrons to be excited from ground states into conduction states, this in turn raises the voltage of the OLED. Therefore, the design of deep blue emitter with low singlet-triplet splitting and suitable host and charge blocking layer with good charge transport and exciton confinement properties at the same time still remains a challenge.¹⁶⁸

As discussed in Section 2.6. in chapter 2, most of internally generated light in OLED are trapped within the organic/ ITO stack or the substrate, only around 20% of light are able to escape from the OLED stack. To solve this problem, extensive research have been done to extract substrate mode or organic/ ITO mode or the combination of both. However, most of the approaches are too complicated and not suitable for commercialization. Furthermore, external light outcoupling technique is not suitable to use in display application, since it might alter the viewing angle and cause emission spectra change.^{169,170} Therefore, more works on light extraction layer that could be evaporated and deposited like normal organic layer should be done, so that the light extraction material can be easily synchronized into OLED fabrication.

Efficiency Optimization of Organic Light-emitting Diodes

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1. **S. W. Liu**, Y. Divayana, A. P. Abiyasa, S. T. Tan, H. V. Demir and X. W. Sun, “The Study of Triplet Distribution and Its Effect on an Improved Phosphorescent

Efficiency Optimization of Organic Light-emitting Diodes

- Organic Light-emitting Diode*", Symposium E: Solid-state devices for light emission and detection, **ICMAT 2013**.
2. A. P. Abiyasa, Y. Divayana, **S. W. Liu**, S. T. Tan, X. W. Sun and H. V. Demir, "*Enhanced Triplet Confinement for Realization of Single Layer Doping of Phosphorescent Organic Light-emitting Diode*", Symposium E: Solid-state devices for light emission and detection, **ICMAT 2013**.
 3. K. S. Leck, Y. Divayana, D. W. Zhao, X. Yang, A. P. Abiyasa, E. Mutlugun, Y. Gao, **S. W. Liu**, S. T. Tan, X. W. Sun and H. V. Demir, "*A Quantum-dot Light-emitting Diode with Quantum Dots Inside the Hole Transporting Layer*", Symposium E: Solid-state devices for light emission and detection, **ICMAT 2013**.
 4. **S. W. Liu**, Y. Divayana, *et al.*, "*High Performance Organic Light-emitting Diodes with Internal Scattering Layer Formed by Nano-particles Deposition*", **ICYRAM 2012**.
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