Novel star-shaped bi-polar blue emitting materials for solution-processed undoped OLEDs

He, Xuehan

2016

He, X. (2016). Novel star-shaped bi-polar blue emitting materials for solution-processed undoped OLEDs. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/69088>

<https://doi.org/10.32657/10356/69088>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**Novel Star-Shaped Bi-Polar Blue Emitting Materials for
Solution-Processed Undoped OLEDs**

He Xuehan

School of Materials Science and Engineering

2016

**Novel Star-Shaped Bi-Polar Blue Emitting Materials for
Solution-Processed Undoped OLEDs**

School of Materials Science and Engineering

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

2016

Abstract

Since the first organic light-emitting diodes (OLEDs) device was fabricated in 1987, great efforts have been put into this research field and produced fruitful achievements. Today, OLEDs have partly entered the commercial marketplace. Full-color displays require highly and equally performance of primary RGB OLEDs. However, blue OLEDs usually show inferior device performance (including color purity, efficiency, stability and longevity) compared with green and red OLED devices. This is because blue emitting materials usually possess intrinsic wide band gaps that cause difficulties in molecular design and injection of charges. Especially, undoped blue emitting materials which could host phosphors with lower energy have attracted much interest for their application in effective white hybrid OLEDs. On the other hand, solution processability of an emitting material enables a low-cost large-area flexible display and is beneficial for the industrialization of OLEDs. Motivated by the above, this project focuses on developing novel undoped blue emitters.

So far, the study of solution processed blue OLEDs based on undoped emitting materials is quite limited. Most reported emitting materials that exhibited good performance are star-shaped oligofluorenes. Inspired by them, a series of star-shaped molecules Sn-Cz-OXD ($n = 1\sim5$) were designed because their highly branched structure could afford high solid quantum efficiency by reducing the molecular aggregation and thus the fluorescence quenching. L1-Cz-OXD, a linear counterpart of S1-Cz-OXD was synthesized for comparison study. Sn-Cz-OXD incorporated an electron-deficient tris(1,3,4-oxadiazole)phenylene (t-OXD) ring as core and three electron-rich 3,6-di-tert-butylcarbazole (t-BCz) as terminal groups bridged by different amount of π -conjugated spacers. Considering the intrinsically unstable emission spectrum of fluorene units, a benzene unit was selected as the conjugated spacer. Owing to the donor- π -acceptor structure, improved balance of hole and electron transport properties was expected. With longer spacers, the quantum efficiency of the emitter was expected to increase due to the better suppressing of intermolecular interactions by longer branches. Besides, the emission spectrum of molecules should be slightly blue shifted because of the reduced

intramolecular charge transfer ability. In addition, to improve the solubility of emitting materials, alkoxy chains were introduced in S4-Cz-OXD and S5-Cz-OXD.

As a result, target star-shaped molecules were successfully synthesized, characterized and applied in undoped OLEDs. They showed high quantum efficiency, excellent spectra thermal stability, good device performance and expected change trend with the extended conjugated length of the branches. Among them (Sn-Cz-OXD, $n = 1\sim5$), solution processed undoped OLED devices based on S4-Cz-OXD with configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al exhibited the best device performance. They achieved a maximum luminance of 7804 cd m^{-2} , a maximum current efficiency (CE) of 4.69 cd A^{-1} , a maximum external quantum efficiency (EQE) of 4.20% and a maximum power efficiency (PE) of 2.08 lm W^{-1} with CIE coordination of (0.157, 0.146).

In addition, it is worth to mention that L1-Cz-OXD emitted deep blue emission at about 430 nm with high solid quantum efficiency and excellent spectrum thermal stability. An optimized undoped device with configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al exhibited good performance. A maximum EQE of 3.09% with CIE coordination of (0.16, 0.07) was achieved. Besides, L1-Cz-OXD exhibited crystallization properties and it could be grown as a single crystal, which endows it the potential to be employed in other applications.

Acknowledgements

Four years of PhD study in NTU have come and gone so quickly. I have experienced a lot of things, happy or sad, elevated or confused, warmed or depressed. I remember all of them as if it was happened yesterday. During the four years, every time I came across difficulties and setbacks, I received much more support and encouragement from many people around me. Here, I would like to express my appreciations to all of them.

First of all, I would like to extend my sincere gratitude to my supervisor, Professor Hu Xiao, who has not only offered me valuable suggestions in the academic studies, but also walked me through all the good and the bad times. Prof Hu strongly supported me and provided a good platform for my study. He also helped me to firm my confidence, and also guided me to have a broad view of the whole life. I learned a lot from his exploring spirit in science and flexible approaches for research. I would respect him in my whole life. In addition, special thanks should go to Dr Liu Ming, who spent a lot of time to help me checking the language of this thesis. She gave me many good suggestions on the expression and layout work which make my thesis more formal.

I am greatly indebted to Professor Ng Siu Choon and Prof Sun Xiaowei. My synthesis experiments were completed in Professor Ng Siu Choon's organic labs in school of chemical and biomedical engineering(SCBE), NTU. The fabrication and characterization of OLED devices were carried out in Prof Sun Xiaowei's lab in school of electrical and electronic engineering(EEE), NTU. They kindly supported me a good condition for my experiments and also gave me many academic advices in specific chemical synthesis and device fabrication.

My sincere thanks should also go to Dr Thelese Foong Ru Bao, Dr Wang Xizu and Dr Sergey Gorelik in the Institute of Materials Research and Engineering (IMRE). Dr Thelese Foong Ru Bao helped me a lot in looking for proper equipment for my experiments. I received very useful knowledge of OPV from her, which is also related to my project. Dr Wang Xizu was my co-supervisor. As an expert in OLEDs field, he

offered me valuable guidance and suggestions in academic research from materials to device, especially the fabrication of device. During my study, he shared me a lot of experience in both doing research and writing thesis. Besides, he also helped me to access other equipment in IMRE for my testing. Dr Sergey Gorelik spent a lot of time together with me to measure and analysis the phosphorescent spectra of my materials. I learned many things from him.

I would like to express my appreciate to Mr Patrick Lai Chee Hoong, Dr Vitali Lipik, Mr Wilson Lim Yan Koon, Ms Sharon Tan Sai Hiang for their patient training in different equipment in the lab of MSE.

I am deeply indebted to Dr Chen Lei, Dr Lu Yong and Dr Zhao Yongbiao for their guidance and help when I came across specific problems in my experiments. They also gave me very useful ideas by inspiring me in daily discussion. I would also thank Dr Hu Peng and Sun Yuanmiao for their co-operation and supporting works. Special thanks should go to all my group members and my friends. Thank you for be together with me, whenever it is sunny, cloudy or rainy. I always feel warm from the heart when I think of them.

I would like to express my gratitude to my beloved parents who have always stayed behind me, supported me in both research and took care of me in life without a word of complaint. Finally, I owe a special debt of gratitude to my husband, Chen Lei. His support was, omnipresent, from the academic research to real life. He was the only one who directly faced my emotion, positive or negative. And he always helped me get to the ground. I never felt lonely and despair because his accompany.

Table of Contents

Abstract.....	i
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions.....	xiii
Abbreviations	xvii
Chapter 1 Introduction.....	1
1.1 Problem Statement	2
1.2 Objectives and Scope	4
1.3 Dissertation Overview.....	7
1.4 Findings and Outcomes.....	9
References.....	10
Chapter 2 Literature Review	11
2.1 OLEDs History	12
2.2 OLEDs Working Mechanism.....	16
2.2.1 General Process of Organic Electroluminescence.....	16
2.2.2 Energy Transfer Mechanism	21
2.2.3 Mechanism of Phosphorescent OLEDs	23
2.2.4 Delayed Fluorescence by Up-Conversion of Excitons.....	25
2.3 OLED Devices Structure	27
2.4 OLED Materials	28
2.4.1 Electrode Materials.....	28
2.4.2 Organic Carriers Transporting Materials.....	29
2.4.3 Organic Electroluminescent Materials	33
2.5 OLED Device Performance Parameters	34
2.5.1 Emitting Color Coordinates	34
2.5.2 Luminous Efficiencies	35

2.5.3 Device Stability and Life Span	38
2.6 General Introduction to Organic Fluorescence Materials	39
2.6.1 Small Molecule Emitting Materials	39
2.6.2 Polymer Emitting Materials	43
2.6.3 Star-Shaped Molecule Emitting Materials	46
2.7 Blue Fluorescent Emitting Materials	47
2.7.1 Motivation	47
2.7.2 Undoped Blue Emitters	49
2.7.3 Undoped Blue Fluorescent Emitters for Solution-Processed OLEDs	52
2.8 Conclusion	55
References	56
Chapter 3 Experimental Methodology	65
3.1 Introduction	66
3.2 Synthesis Methods	66
3.2.1 Suzuki Reaction	66
3.2.2 Ullmann Reaction	68
3.2.3 Huisgen Tetrazole Rearrangement Reaction	70
3.3 Characterization of Materials	71
3.3.1 Chemical Structure and Purity	71
3.3.2 Molecular Weight	72
3.3.3 Photophysical Properties	73
3.3.4 Electrochemical Properties	75
3.3.5 Thermal Properties	76
3.3.6 Surface Morphology of Thin Films	76
3.3.7 Single Crystal Growth	77
3.4 Device Fabrication Technology	77
3.4.1 Thermal Vacuum Evaporation	78
3.4.2 Spin-Coating	79
3.5 Devices Characterization	80
3.5.1 J-V-L Measurements	80
3.5.2 Electroluminescence (EL) Spectra	81

3.5.3 CIE Coordinates	81
3.5.4 Efficiencies	82
References	82
Chapter 4 Deep Blue Linear Emitter L1-Cz-OXD	85
4.1 Introduction	86
4.2 Experimental Methods	86
4.2.1 Synthesis	86
4.2.2 Crystal Growth Method	88
4.2.3 Device Fabrication and Optimization	89
4.3 Materials Characterization and Methods	91
4.3.1 NMR Spectroscopy & EA Characterization	91
4.3.2 MALDI-TOF Spectrometry	92
4.3.3 Absorption and Photoluminescence Spectroscopy	93
4.3.4 Spectrum Thermal Stability	94
4.3.5 Cyclic Voltammetry	94
4.3.6 Differential Scanning Calorimetry	95
4.3.7 Thermogravimetric Analyses	96
4.3.8 Atomic Force Microscopy	96
4.4 Characterization of OLED Devices	96
4.5 Results and Discussion for Synthesized Materials	97
4.5.1 Chemical Structure and Molecular Weight	97
4.5.2 Photophysical Properties	97
4.5.3 Electrochemical Properties	100
4.5.4 Thermal Properties and Spectrum Thermal Stability	101
4.5.5 Surface Morphology	103
4.5.6 Single Crystal Properties	104
4.6 Results and Discussion for Undoped OLED Devices	104
4.7 Conclusions	109
References	110
Chapter 5 Star-Shaped Blue Emitters Sn-Cz-OXD (n = 1 ~ 3)	111
5.1 Introduction	112

5.2	Experimental Methods	112
5.2.1	Synthesis	112
5.2.2	Device Fabrication and Optimization.....	117
5.3	Materials Characterization	118
5.3.1	Chemical Analysis (NMR, EA and MALDI-TOF).....	118
5.3.2	Absorption and Photoluminescence Spectroscopy.....	119
5.4	Characterization of Devices	119
5.5	Results and Discussion for Synthesized Materials	119
5.5.1	Chemical Structure and Molecular Weight	119
5.5.2	Photophysical Properties	120
5.5.3	Electrochemical Properties	125
5.5.4	Thermal Properties	126
5.5.5	Spectrum Thermal Stability.....	127
5.5.6	Surface Morphology	128
5.6	Results and Discussion for OLED Devices	130
5.6.1	Devices C1 and C2: ITO/PEDOT:PSS/EML/3TPYMB/Cs ₂ CO ₃ /Al.....	130
5.6.2	Influence of HTM/EIM on Device Performance.....	134
5.7	Conclusions	138
	References.....	139
	Chapter 6 Star-Shaped Blue Emitters Sn-Cz-OXD (n = 4, 5).....	141
6.1	Introduction	142
6.2	Experimental Methods	142
6.2.1	Synthesis.....	142
6.3	Materials Characterization	148
6.4	Device Characterization.....	148
6.5	Results and Discussion for Synthesized Materials	149
6.5.1	Analysis for Chemical Structure and Molecular Weight.....	149
6.5.2	Photophysical Properties	149
6.5.3	Electrochemical Properties	153
6.5.4	Thermal Properties	154
6.5.5	Spectrum Thermal Stability.....	155

6.5.6	Surface Morphology	156
6.6	Results and Discussion for OLED Devices	158
6.7	Conclusions	160
	References	162
Chapter 7 Conclusions and Future Plans		163
7.1	Outcomes of This Project	164
7.1.1	S1-Cz-OXD VS L1-Cz-OXD	164
7.1.2	Sn-Cz-OXD (n = 1 ~ 3)	166
7.1.3	Sn-Cz-OXD (n = 4, 5)	167
7.2	Conclusions	169
7.3	Future Work	170
7.3.1	Employing Target Emitters as Host Materials in OLEDs	170
7.3.2	Developing Fluorescent Blue Emitters with High Triplet Energy	172
7.3.3	Developing Solution-Processable TADF Emitters	174
	References	175
APPENDIX		179

Table Captions

Table 2.1 Typical efficient RGB materials for SM-OLEDs and their device performance

Table 2.2 Properties of small molecules, linear polymers and star-shaped molecules as emitting materials

Table 4.1 Solubility of L1-Cz-OXD in different organic solvents.

Table 4.2 Optimized condition for deposition of multilayers in device fabrication.

Table 4.3 Summary of photophysical properties for L1-Cz-OXD.

Table 4.4 Electrochemical and thermal properties of L1-Cz-OXD.

Table 4.5 EL performance of devices A1, A2 and B.

Table 5.1 Solubility of target emitters in different organic solvents.

Table 5.2 Optimized condition for deposition of multilayers in device fabrication.

Table 5.3 Photophysical properties of target molecules.

Table 5.4 Electrochemical and thermal properties of target molecules.

Table 5.5 Electroluminescence characteristics of the devices C1, C2, A1 and A2.

Table 5.6 Comparative characteristics of devices C1, C2, D1 and D2.

Table 5.7 EL performance of devices D1 and D2.

Table 6.1 Solubility of target emitters in different organic solvents.

Table 6.2 Optimized condition for deposition of multilayers in device fabrication.

Table 6.3 Photophysical properties of target molecules.

Table 6.4 Electrochemical and thermal properties of target molecules.

Table 6.5 Electroluminescence characteristics of the devices.

Table 7.1 Phosphorescence properties of target molecules.

Figure Captions

- Figure 1.1** Illustration of molecular design concept.
- Figure 1.2** Designed chemical structures of Sn-Cz-OXD ($n = 1\sim5$).
- Figure 2.1** Chemical structures of some mentioned compounds.
- Figure 2.2** left) Simplified energy diagrams for OLED device; right) electrons and holes in the process of generating light near the organic/organic interface in fluorescent OLED device.
- Figure 2.3** Photophysical process of exciton: excitation, radiative decay and lighting.
- Figure 2.4** Several mechanisms for energy transfer.
- Figure 2.5** Energy transfer between host and dopant materials in PHOLED.
- Figure 2.6** Schematic diagrams for triplet-triplet annihilation (TTA).
- Figure 2.7** TADF mechanisms. When ΔE_{ST} is small, up-conversion occurs with a high efficiency, enabling highly efficient EL from the S_1 level.
- Figure 2.8** Typical structures for organic light-emitting diode device.
- Figure 2.9** Examples of hole injection materials.
- Figure 2.10** Examples of organic small molecule hole transport materials.
- Figure 2.11** Examples of polymer hole transport material.
- Figure 2.12** Examples of organic electron transport material
- Figure 2.13** Chromaticity diagram, representing CIE coordinates of different colors.
- Figure 2.14** Spectral response of normal human eye (photopic).
- Figure 2.15** Chemical structures of typical RGB fluorescent materials for SM-OLEDs.
- Figure 2.16** Typical PPV-type emitting materials.
- Figure 2.17** Typical PTh-type emitting materials.
- Figure 2.18** Typical PPP-type emitting materials.
- Figure 2.19** Typical PFO-type emitting materials
- Figure 2.20** Examples for undoped blue fluorescent materials.
- Figure 2.21** Star-shaped oligofluorenes for blue emitters.
- Figure 2.22** Other examples of star-shaped blue emitters.
- Figure 3.1** General equation for the Suzuki Reaction.
- Figure 3.2** Mechanism for the Suzuki reaction: Suzuki Cross-Coupling Catalytic Cycle.

- Figure 3.3** General equation for the Ullmann-type Reaction.
- Figure 3.4** Two possible pathways Cu(I)/Cu(III) mechanism for the Ullmann reaction.
- Figure 3.5** The Ullmann-type reactions used in this study.
- Figure 3.6** General equation for the Huisgen Tetrazole Rearrangement Reaction.
- Figure 3.7** Mechanism for the Huisgen Tetrazole Rearrangement reaction.
- Figure 3.8** MALDI-TOF equipment consists of three parts.
- Figure 3.9** Solvent evaporation for single crystal growth.
- Figure 3.10** Schematic depicted thermal vacuum evaporation.
- Figure 3.11** Schematic depicted spin-coating processes.
- Figure 4.1** Synthesis route for L1-Cz-OXD.
- Figure 4.2** Schematic diagrams for fabrication process of OLED device.
- Figure 4.3** Sample preparation of MALDI-TOF.
- Figure 4.4** Three electrode system for CV measurement in solution.
- Figure 4.5** Schematic diagram for lighting an OLED device; right) Real device images: unlighted (upper) and lighted (lower).
- Figure 4.6** Normalized (left) UV-vis and (right) PL spectra of L1-Cz-OXD in dilute toluene, doped PMMA film and neat film under room-temperature.
- Figure 4.7** Cyclic voltammograms of L1-Cz-OXD.
- Figure 4.8** DSC traces (a) and TGA thermogram (b) of L1-Cz-OXD.
- Figure 4.9** Normalized photoluminescent spectra of L1-Cz-OXD during long period heating treatment.
- Figure 4.10** AFM images of L1-Cz-OXD films spin-casted from chloroform solution (a) before annealing and (b) after annealing.
- Figure 4.11** Molecular packing of orthorhombic structure.
- Figure 4.12** Energy level diagram of the undoped devices based on L1-Cz-OXD.
- Figure 4.13** Normalized EL spectra of device A1, A2 and B at different applied voltages.
- Figure 4.14** EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices A1, A2 and B.
- Figure 5.1** Synthesis route for Sn-Cz-OXD ($n = 1\sim3$).
- Figure 5.2** Chemical structures of Sn-Cz-OXD ($n = 1 \sim 3$).

Figure 5.3 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 1\sim 3$) in dilute solution.

Figure 5.4 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 1\sim 3$) in doped PMMA films.

Figure 5.5 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 1\sim 3$) in neat films.

Figure 5.6 Cyclic voltammograms of Sn-Cz-OXD ($n = 1$ and 2).

Figure 5.7 DSC traces (a) and TGA thermogram (b) of Sn-Cz-OXD ($n = 1\sim 3$)

Figure 5.8 Normalized PL spectrum of Sn-Cz-OXD ($n = 1\sim 3$) during long period heating treatment.

Figure 5.9 AFM images of Sn-Cz-OXD ($n = 1\sim 3$) and L1-Cz-OXD (for comparison) films spin-casted from chloroform solution.

Figure 5.10 Energy level diagram of device C1 and C2.

Figure 5.11 Normalized EL spectra of (a) device C1 and (b) device C2.

Figure 5.12 EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices C1, C2 and control device A1.

Figure 5.13 Energy level diagram of device C1, C2, D1, and D2.

Figure 5.14 EL performances: (a) J-V-L characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices C1, C2, D1 and D2.

Figure 6.1 Synthetic route for S1-Cz-OXD ($n = 4, 5$).

Figure 6.2 Chemical structures of S4-Cz-OXD and S5-Cz-OXD.

Figure 6.3 Normalized absorption (a) and PL spectra (b) of Sn-Cz-OXD ($n = 3\sim 5$) in dilute solution.

Figure 6.4 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 3\sim 5$) in doped PMMA films.

Figure 6.5 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 3\sim 5$) in neat films.

Figure 6.6 Cyclic voltammograms of Sn-Cz-OXD ($n = 4, 5$).

Figure 6.7 DSC traces (a) and TGA thermogram (b) of Sn-Cz-OXD ($n = 4, 5$).

Figure 6.8 Normalized PL spectrum of Sn-Cz-OXD ($n = 4, 5$) during prolonged heating treatment.

Figure 6.9 AFM images of Sn-Cz-OXD ($n = 4, 5$) films spin-casted from chloroform solution.

Figure 6.10 Energy level diagram of the OLED devices E4 and E5.

Figure 6.11 Normalized EL spectra of device E4 (a) and E5 (b) at different applied voltages.

Figure 6.12 EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices E4 and E5.

Figure 7.1 Normalized UV-vis spectra of some commonly used fluorescent dopants and normalized PL spectrum of S4-Cz-OXD.

Figure 7.2 Normalized phosphorescence (Phos.) spectra recorded in toluene solution at 77 K.

Figure 7.3 A Jablonski diagram showing the electronic states of a molecule and the transitions between them.

Abbreviations

AFM	Atomic Force Microscopy
CE	Current Efficiency
CIE	International Commission on Illumination
CV	Cyclic Voltammetry
DSC	Differential Scanning Calorimetry
EA	Elemental Analysis
EIL	Electron Injecting Layer
EL	Electroluminescence
EML	Emitting Layer
EM-OLEDs	Small Molecule based OLEDs
EQE	External Quantum Efficiency
ETL	Electron Transporting Layer
HIL	Hole Injecting Layer
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transporting Layer
ISC	InterSystem Crossing
ITO	Indium Tin Oxide
J-V-L	Current density-Voltage-Luminance
LUMO	Lowest Unoccupied Molecular Orbital
MALDI-TOF	Matrix-Assisted Laser Desorption Ionization Time-of Flight
NMR	Nuclear Magnetic Resonance
OLED	Organic Light Emitting Diodes
PE	Power Efficiency
PHOLED	Phosphorescence OLEDs
PL	Photoluminescence
PLED	Polymer based OLEDs
RGB	Red, Green and Blue
RMS	Root-Mean-Square
TADF	Thermally Activated Delayed Fluorescence

TGA	ThermoGravimetry Analyses
TTA	Triplet–Triplet Annihilation
UV-vis	UltraViolet-Visible

Chapter 1

Introduction

This chapter states current development and existing problems in undoped blue emitting materials for OLEDs application, which is the motivation for this research project. Based on this motivation, a series of novel blue emitters are proposed. Design concepts in molecular structure together with hypotheses or expectations of certain properties are elaborated in detail. Each chapter in this thesis and the final findings and outcomes are also summarized.

1.1 Problem Statement

Electroluminescence in organic materials was discovered in 1963.¹ Then in 1987, an organic electroluminescent material was first applied in organic light emitting diodes (OLEDs).² From then on, OLEDs became a research highlight. People made significant progress in this field and the OLED was supposed to be the next generation of planar display technology. Compared with traditional CRT and LCD technology, OLED has many advantages including low energy consumption, active luminescence, fast response time, wide visual angle, can realize large area and flexible display and so on. Moreover, organic materials are chemically designable and there is much space for material improvement. After more than twenty years development, OLEDs are now partly commercialized and many companies are involved in this developing industry.

To realize white light and full-color display, blue emission is a must as one of the three primary colors and the emission of red, green and blue (RGB) should be equal, (i.e., the performance of RGB OLEDs including EL efficiencies, stability, and color purity should be at a comparable level). However, it is difficult to design highly efficient blue emitting materials because of their intrinsic broad energy bandgaps. Interrupting the conjugation in the molecular structure might be an approach to obtain wide energy bandgap, however, this will negatively influence the charge transportation in the meanwhile. Besides, molecules with wide energy bandgaps have barriers to electron injection from electrodes, leading to a high turn-on voltage and inferior EL performance. As a result, blue OLEDs usually show inferior device performance compared with green and red ones. On the other hand, a blue phosphorescent material is even more difficult to obtain because it should possess both a wide energy bandgap as well as a high triplet energy. Additionally, to build a device based on such blue phosphors, the corresponding host material, holes and electrons transporting materials should also have high enough triplet energy to confine the triplet excitons. However, such materials are quite limited. And, the stability and durability of the blue OLEDs cannot meet the requirement for applications. Therefore the lack of good blue emitters hinders the application of OLED, although green and red emitters have satisfied the requirement for commercialization.

Another important application of fluorescent blue emitters is to be used as host materials in hybrid white OLEDs. They can realize high efficiency white emission by employing a simple device configuration, which is usually composed of a blue fluorescent emitter as host material and green / red phosphorescent emitter as dopant. One good example of hybrid white OLEDs was reported by Leo et al.³ In a hybrid device, the host material provides blue fluorescent light as one of the three-primary color, while also generates light of other colors by transferring energy to phosphorescent dopants. To achieve this, the host blue emitters should possess high solid quantum efficiency (low quenching or so-called undoped property) as well as high triplet energy for phosphorescent dopants of other colors. Many efforts have been put in developing novel undoped blue fluorescent emitting materials and great achievements have been made. To date, most reported solution-processable undoped blue emitters are star-shaped molecules.

Star-shaped molecules possess advantages of well define structure of small molecules and high solubility of polymers. More importantly, the highly branched structure of these molecules can effectively suppress intermolecular interaction in solid state and reduce fluorescence quenching, affording an enhanced solid-state luminescence. Among them, star-shaped oligofluorenes is a group of undoped blue emitters which exhibit the best device performance. Recently, Liu et al reported a series of star-shaped fluorene oligomers using a planar triphenylamine core to achieve a maximum current efficiency (CE) of 3.83 cd A^{-1} and a maximum EQE of 4.19%.⁴ Using phenyl as the core, Zou et al synthesized a group of star-shaped oligofluorenes with a maximum EQE of 6.8% and CE of 5.4 cd A^{-1} .⁵ And later, they reduced the turn-on voltage to 3.6 V by introducing electron donor diphenylamine end-terminals to raise the HOMO level at the expense of reduced spectral stability.⁶ Furthermore, star-shaped branched polyfluorenes also exhibited enhanced device performance than linear polyfluorenes.^{7,8}

However, fluorene unit has an intrinsic short coming of unstable emission spectrum. It is readily oxidized when exposed to oxygen and light, resulting in the generation of ketonic defects which emits green light. As a result, an extra green peak is observed during operation, after long time storage or upon heating, which is harmful for device stability

and life time, hindering the practical application. Being a strong hole conductors, fluorene might lead to unbalanced charge transportation. Most star-shaped oligofluorenes are p type materials and even can serve as hole transporting layers (HTL). Extra electron withdrawing moiety is necessary for better charge transportation and well-matched energy levels in devices.⁶

To sum up, the lack of good blue emitting material is one of the bottle necks for OLEDs application due to its important function in full color display as well as the difficulty in its molecular design. Although many efforts have been put in this field, high efficient undoped star-shaped blue emitters are still quite limited. Therefore, to develop novel undoped blue emitters is necessary and valuable.

1.2 Objectives and Scope

The objective of this project was to develop effective blue emitting materials for OLEDs application. The main idea of molecular design of the target molecules is illustrated in Figure 1.1 and their chemical structure is shown in Figure 1.2. Ideally, the emitters were expected to possess high quantum efficiency, undoped property, good spectrum stability and high electroluminescence efficiencies. Considering the influence of molecular structure on its properties, emitter S1-Cz-OXD was designed while taking the following points into account. (1) Star-shaped backbone was employed to provide high solid quantum efficiency since the branches would prevent intermolecular aggregations and reduce the concentration quenching in solid state. (2) The molecular design was of a well-defined structure, which was beneficial for purification and precise analysis. (3) The molecule featured a D- π -A design to endow the emitter with bipolar properties. An electron-deficient tris(1,3,4-oxadiazole)phenylene (t-OXD) ring was employed to serve as acceptor core, while three electron-rich carbazole units (t-BCz) would function as donors unit at the termini. This was because oxadiazole derivatives have been proven to be very effective in improving the injection / transport of electrons, while carbazole derivatives have been widely used as host materials in OLEDs due to their good hole-transporting ability.⁹ The bipolar property should afford the emitter balanced injection

and transportation of charges and improved recombination efficiency. It was also expected to reduce the turn-on voltage. (4) Since oxadiazole and carbazole derivatives were of high thermal stability, a high spectrum thermal stability could be expected for the fluorene free emitter. (5) *t*-butyl groups were introduced to further suppress the intermolecular interactions and to improve the solubility of the molecule. S1-Cz-OXD was supposed to be a good candidate for blue emitting material. The solution-processed undoped OLEDs based on S1-Cz-OXD were expected to achieve high electroluminescence efficiency. A linear counterpart L1-Cz-OXD was designed for comparative study, the structure of which is shown in Figure 1.1.

Figure 1.1 Illustration of molecular design concept.

The fluorescence quantum yield, especially the value in solid state, is one of the most important parameters for an electroluminescence material. Emitting materials with high solid quantum yield are always desired in order to obtain efficient OLEDs. Increasing the conjugated branches of starburst emitters was found to be a promising approach to high quantum efficiency according to literatures. Therefore based on S1-Cz-OXD, we designed S2-Cz-OXD and S3-Cz-OXD with the expectation that the quantum yield of these emitters increases when the length of branches increases. It was noticed that for

most reported star-shaped oligofluorenes, which were mainly p-type molecules, increasing the branches of the emitters would cause an undesired red-shift in their emission spectrum due to extending of the π conjugation length. However, this undesired red-shift could be avoided by the D- π -A design in Sn-Cz-OXD ($n = 1\sim3$) molecules. In contrast with p-type oligofluorenes, the PL spectra of Sn-Cz-OXD were expected to be blue shifted when the amount of the benzene spacers is increased because (1) the enlarged distance between t-OXD ring and t-BCz terminal groups and (2) the distortion of the biphenyl or terphenyl chain would reduce charge transfer ability between donor and acceptor moieties, leading to larger energy bandgap. As a result, S3-Cz-OXD with the longest branches was expected to possess the highest solid quantum efficiency as well as the deepest blue emission.

Figure 1.2 Designed chemical structures of Sn-Cz-OXD ($n = 1\sim5$).

However, S3-Cz-OXD might have lower solubility than the first two emitters considering its rigid molecular backbone and therefore would have difficulties in solution-processed device fabrication and even in material synthesis and characterization. In order to solve this possible problem, flexible alkoxy chains were introduced in the branches to improve the solubility of the emitters S4-Cz-OXD (see Figure 1.2) and S5-Cz-OXD. Enhanced solid quantum efficiencies were expected to be obtained from S4-Cz-OXD and S5-Cz-OXD because the bulky alkoxy chains would have steric bulk, which could further suppress intermolecular aggregations. Therefore the solution-processed undoped OLED based on S4-Cz-OXD was expected to achieve higher device performance than that based on S1-Cz-OXD. Considering the electron donating ability of the alkoxy chains, they might cause a slight red-shift in the emission spectra of the emitters due to the enhanced

HOMO (the highest occupied molecular orbital) energy level and reduced energy bandgap of the molecules.

To summarize, target molecules Sn-Cz-OXD ($n = 1 \sim 5$) were designed and expected to be good candidates for blue emitting materials. Good performance was anticipated from their undoped OLEDs device. According to the hypothesis, they should possess good undoped properties therefore high solid quantum efficiency are expected. And this value should increase with the length of the conjugated branches. Besides, they should also have excellent spectrum thermal stability due to the fluorene-free design. And the emission spectrum of these emitters should blue shift with the longer branches.

1.3 Dissertation Overview

The thesis addresses the molecular design, synthesis, characterization of a series of novel star-shaped bipolar blue electroluminescence materials and their applications in solution processed undoped OLEDs device.

Chapter 2 gives a general research background for this thesis. It first briefly describes the overall development history of OLEDs during the past 30 years and provides a general introduction of the working mechanism of OLEDs device. Then it reviews literatures concerning blue electroluminescence materials, including the research motivation and current research progress, especially focus on the undoped and star-shaped molecules. Important parameters in basic electroluminescence characterization of an OLED device were also reviewed.

Chapter 3 gives the introduction of all experiments involving in this thesis. Principles underlying the techniques employed in material synthesis and characterization as well as device fabrication and characterization are detailed. It explained why particular experimental methods are appropriate and selected in order to elucidate certain issue or achieve certain measurement purpose. Besides, the methods of data analysis, including errors were also discussed.

Six target materials (L1-Cz-OXD and Sn-Cz-OXD, $n = 1\sim5$) were designed, synthesized, and characterized in this project. According to the design goal, they were divided into three different material systems: (1) L1-Cz-OXD, linear counterpart of S1-Cz-OXD; (2) Sn-Cz-OXD ($n = 1\sim3$), similar star-shaped structure with extending branches; and (3) Sn-Cz-OXD ($n = 4\sim5$), with extra alkoxy chains. The corresponding experimental results of these three material systems were discussed in *Chapters 4, 5 and 6*, respectively.

Chapter 4 elaborates the specific operations for synthesis reactions of linear molecule L1-Cz-OXD, basic characterization experiments, control device fabrications. All the measurement results were carefully discussed. Especially, the deep blue emission and crystallization properties of L1-Cz-OXD are very interesting. An additional characterization of single crystal of it was carried out and additional optimized OLED devices were fabricated.

Chapter 5 elaborates the specific operations for synthesis reactions of Sn-Cz-OXD ($n = 1\sim3$), including basic characterization, device fabrications and optimizations. Results (both material and device) of S1-Cz-OXD were carefully discussed and compared with those of L1-Cz-OXD to study the influence of chemical structures of materials. The difference in results of Sn-Cz-OXD ($n = 1\sim3$) demonstrates the effects of different branches length.

Chapter 6 elaborates the specific operations for synthesis reactions of molecules Sn-Cz-OXD ($n = 4\sim5$), including basic characterization experiments, device fabrications and optimizations. Comparative studies for all obtained results were carried out between S4-Cz-OXD and S3-Cz-OXD, and between S4-Cz-OXD and S5-Cz-OXD to study the influence of introducing alkoxy chains into branches and the influence of extending of branches length, respectively.

Chapter 7 summarizes all the results obtained in this project. It draws together the threads of the whole thesis from the original hypothesis to final outcomes. Whether the results

are consistent with the design purpose, how the design concept works to achieve certain goals, the relationship between chemical structure and its macroscopic properties, etc. all of the above questions are explored in-depth for a deeper understanding. The opportunities and strategies for future work are also provided for subsequent research.

1.4 Findings and Outcomes

This research focuses on undoped blue electroluminescence materials for OLED application and leads to several novel outcomes by:

- (1) Design and synthesis of a series of star-shaped emitting materials Sn-Cz-OXD ($n = 1\sim5$) which emit pure blue emission at around 450 nm with high solid quantum efficiency and excellent spectrum thermal stability. Solution-processed undoped OLEDs with the configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al are fabricated and characterized. Among them the one based on S4-Cz-OXD exhibits the best device performance. It achieves a maximum luminance of 7804 cd m^{-2} , a maximum CE of 4.69 cd A^{-1} , a maximum EQE of 4.20% and a maximum PE of 2.08 lm W^{-1} . This result is believed to be among the most efficient solution-processed undoped blue OLED device employing fluorene-free emitting materials.
- (2) Investigate the relationship between the chemical structure and the properties of emitting materials, the finding of which includes: (a) emitter S1-Cz-OXD are of higher quantum efficiency, higher solubility, better film forming ability than L1-Cz-OXD due to the star-shaped structure; (b) the LUMO energy level of S1-Cz-OXD is lower than that of L1-Cz-OXD because of the improved electron donating ability of the t-OXD core in S1-Cz-OXD compared with the single OXD unit in L1-Cz-OXD, therefore S1-Cz-OXD emits pure blue light ($\sim 457 \text{ nm}$) while L1-Cz-OXD emits deep blue light ($\sim 427 \text{ nm}$); (c) extending the conjugated branches in these novel emitters would enhance the solid quantum efficiency while cause a slight blue-shift, which is a good method to obtain high efficient blue emitting materials; (d) bipolar design could improve the charge transportation and balance, which is benefit for the high recombination efficiency of

charges within the emitting layer in OLED device. These conclusions could facilitate future research since the relationship between structure and properties is the basis of good molecular design.

(3) Designed and synthesized an emitting material L1-Cz-OXD as the linear counterpart for S1-Cz-OXD, which emitted deep blue emission at about 430 nm with high solid quantum efficiency and excellent spectrum thermal stability. An optimized undoped device with configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al exhibited good performance. A maximum EQE of 3.09% with CIE (International Commission on Illumination) coordination of (0.16, 0.07) was achieved. Besides, L1-Cz-OXD exhibited crystallization properties and it could grow into single crystal, which endows with it the potential to be employed in other applications.

References

1. M. Pope, H. P. Kallmann, and P. Magnante, *J. Chem. Phys.*, 1963, **38**, 2042–2043.
2. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913–915.
3. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, and K. Leo, *Nature*, 2009, **459**, 234–238.
4. C. Liu, Y. Li, Y. Zhang, C. Yang, H. Wu, J. Qin, and Y. Cao, *Chem. - A Eur. J.*, 2012, **18**, 6928–6934.
5. Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin, and Y. Cao, *Adv. Funct. Mater.*, 2013, **23**, 1781–1788.
6. C. Liu, Q. Fu, Y. Zou, C. Yang, and J. Qin, *Chem. Mater.*, 2014, **26**, 3074–3083.
7. L. Chen, P. Li, H. Tong, Z. Xie, L. Wang, X. Jing, and F. Wang, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 2854–2862.
8. L. Chen, P. Li, Y. Cheng, Z. Xie, L. Wang, X. Jing, and F. Wang, *Adv. Mater.*, 2011, **23**, 2986–2990.
9. Y. Tao, Q. Wang, C. Yang, C. Zhong, K. Zhang, J. Qin, and D. Ma, *Adv. Funct. Mater.*, 2010, **20**, 304–311.

Chapter 2

Literature Review

This chapter provides a general research background to this thesis by reviewing the literature. Firstly, the development history of OLEDs during the past 30 years and some important milestones are reviewed. Secondly, the working mechanisms for different type of OLEDs are described. Thirdly, OLED materials especially electroluminescence materials are introduced. Among them, undoped blue emitting materials are emphasized for their important function in OLEDs. Finally, some important parameters in basic electroluminescence characterization of an OLED device are also described and discussed.

2.1 OLEDs History

Organic Electroluminescence (EL) is a combination of optical and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field. It was first reported by Pope and co-workers at New York University in 1963. The direct current (DC) electroluminescence (weak blue emission) was observed under vacuum from a single crystal of pure anthracene and on anthracene crystals doped with tetracene, using a small area silver electrode at 400 V.¹ However, their achievement did not stimulate much interest at that time because the operating voltage was too high and the EL efficiency was too low.

The breakthrough in Organic Electroluminescence was achieved by Tang and Van Slyke at Eastman Kodak in 1987.² They used indium tin oxide (ITO) as anode material, 8-hydroxyquinoline aluminum (Alq_3) as the emitting layer, N,N'-diphenyl-N, N'-bis(3-methylphenyl) 1,1'-biphenyl-4,4' diamine (TPD) as hole transporting layer, and Mg/Ag as cathode material. The resultant device afforded an operating voltage of ~ 10 V, a brightness of 1000 cd m^{-2} , aPE of 1.5 lm W^{-1} and an EQE of $\sim 1\%$. The reported device had a two-layer structure with a separate hole transporting layer, which was believed to be of benefit for the transportation of excitons, and caused the recombination and light emission to occur in the middle of the organic emitting layer. This also resulted in a reduction in operating voltage and improvements in exciton injection efficiency and balance. These findings revealed a key rule for developing high efficient OLEDs: the injection and recombination of excitons should be balanced. The exciting achievement showed outstanding advantages and great application prospect of organic light-emitting diodes (OLEDs). From then on, OLED attracted more and more researchers' and industries' attention and the era of OLEDs started. Numerous small molecules suitable for applications in OLEDs (SM-OLEDs) were developed. Device architectures from single layer to multi-layers were adopted in order to achieve a balance transportation of carriers and excitons to enhance the efficiency. The emissive layers are usually prepared by vacuum deposition.

In 1990, Burroughes, Friend et al. reported the first OLED using a polymer electroluminescent material as emitter (PLEDs). The device was fabricated by spin coating a precursor polymer of the luminescent poly-(para-phenylene vinylene) (PPV) ³ onto a ITO coated glass. Later in 1992, Heeger and coworkers at University of California, Santa Barbara fabricated a flexible PLEDs by using a film of poly(2-methoxy,5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene) (MEH-PPV) ⁴ as the emitting layer on a transparent PET substrate. The device realized a high EQE of about 1%. These achievements attracted much enthusiasm for the study of polymer materials for OLEDs. Moreover, in 1992, polymer electroluminescence was rated as one of ten major achievements in the field of chemistry in United States of America (USA). Compared to emissive small molecules, emissive polymers have several potential advantages such as being solution processable with good film-forming ability, low cost, high compatibility with dopant / host to tune emitting color, which could achieve large area and flexible devices, are easy to be designed and modified, and therefore the injection and transportation of carriers can be controlled. In the past three decades, many polymer electroluminescent materials have been developed. Classic polymer emitters such as PPV, polythiophene (PTh), poly(p-phenylene) (PPP), polyfluorene (PF) and their derivatives were fully studied.⁵⁻⁸

In 1989, Tang et al reported a high efficiency OLED by doping Alq₃ with a highly fluorescent dye.⁹ The EQE (2.5%) was greatly improved by a factor of about 2 in comparison with the undoped one. Studies have shown a host-guest doping system could effectively tune emission color, enhance the EL efficiency and improve the device stability.¹⁰ Therefore various host and dopant fluorescent materials were widely developed and today most OLEDs are of this type. Although OLEDs using fluorescent materials have achieved a high reliability, their external quantum efficiencies are intrinsically limited to approximately 5%, due to the limitation of their singlet-exciton production efficiency (25%) under electrical excitation. In more detail, during the energy transfer from the host to the dye via excitons, only the singlet spin states induce fluorescent emission, which means 75% of the energy is lost (triplet states). Considering the limit of 20% light for out-coupling, the upper limit for EQE is thus about 5%, which cannot meet the requirements of commercialization.

Plenty of efforts have been put to solve this problem, and it was finally solved by Baldo et al.¹¹ in 1998, who did pioneering work in showing that phosphorescent dyes (transition metal compounds with organic ligands or organometallic compounds), offered a way of achieving emission from both singlet and triplet states. OLEDs based on phosphorescent dyes are called phosphorescent OLEDs (PHOLEDs). Baldo et al. designed a phosphorescent dye named 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP), which could harvest 90% of the energy transferred from singlet and triplet states of the Alq₃ host material. Later in 2001, Ikai et al fabricated a highly efficient OLED based on a phosphorescent dye, fac tris(2-phenylpyridine)iridium (Ir(ppy)₃), with a maximum EQE of 19.2%.¹² Although these devices usually require elaborate multilayer structures, the fast and efficient intersystem crossing (ISC) from excited singlet to triplet state caused by strong spin-orbit couplings and the ability of triplet harvesting allow theoretical quantum efficiency of 100%.¹³

Figure 2.1 Chemical structures of some mentioned compounds.

So far, phosphorescent dyes with high quantum yields composed of transition metals such as iridium (Ir), platinum (Pt), osmium (Os), ruthenium (Ru), etc. have been greatly developed for phosphorescent OLEDs since they could utilize both singlet and triplet excitons. The emission light of these transition metal complexes has covered the entire visible spectrum. However, a significant roll-off of the EL efficiency has been observed with an increase of the current density, owing to the rather long lifetime of the triplet

excited states, which results in acceleration of various triplet exciton annihilation processes, e.g., triplet–triplet annihilation (TTA).¹⁴ Furthermore, the design of phosphorescent materials is greatly limited because the heavy atom effect (spin–orbital interaction) must be induced by using rare metals such as Ir and Pt, which are high cost due to their limited availability. Since both fluorescent and phosphorescent OLEDs have advantages and disadvantages, the use of a novel light-emitting mechanism has been hoped for to avoid the shortcomings. In order to improve the EL efficiency, several methods including developing phosphorescent materials that are free of rare metals¹⁵ and generating a singlet excited state by TTA¹⁶ have been reported. It is worth to mention that in PHOLEDs, TTA usually leads to the deactivation of triplet excitons and hence decreases the EL quantum efficiency; however, for OLEDs using fluorescent materials, the concentration of singlet excitons can be increased by TTA. Delayed fluorescence attributed to TTA was already confirmed from the EL phenomenon observed in an anthracene single crystal in the 1960s,¹⁷ indicating that triplet excitons actively move around and interact in an organic solid thin film. Hence, scientists have examined the application of the generation of single excitons attributed to TTA for improving the EL efficiency. However, the efficiency of generating singlet excitons by TTA is only 37.5% at maximum, and a novel luminescence mechanism is required.

In 2009, Adachi et al first synthesized a series of porphyrin complexes that exhibited thermally activated delayed fluorescence (TADF) properties. Based on these new materials, they also proposed a novel electroluminescence mechanism.¹⁸ In fact, the theoretical study of TADF could be traced back to 1983.^{19,20} Unlike most traditional electroluminescent materials, TADF materials are a family of molecules that possess a relatively small energy difference (ΔE_{ST}) between the singlet and triplet excited states (< 0.2 eV). The luminous mechanism for TADF materials is therefore completely different that an IQE of 100% is achievable through up-conversion from the triplet excited state, which is generated at a probability of 75% upon electrical excitation, to the singlet excited state.²¹ Besides, compared with traditional phosphorescent material which suffers from high cost and rarity of the noble metal elements (such as Ir or Pt), TADF material is a cheaper substitute. Although the TADF process was considered to show low power-

conversion efficiency because it is generally an endothermic reaction, recent studies have revealed that highly efficient delayed fluorescence can be achieved by optimizing the molecular design. Numerous TADF emitting materials were developed during the past six years. Well-known materials that exhibit TADF are fullerene,²² eosin and porphyrin derivatives.¹⁷

2.2 OLEDs Working Mechanism

OLEDs progress covers a broad research field including materials science, device fabrication and optimization, theoretical studies and so on. Among these, developing of electroluminescent materials is one of the most important issues since they are the key component of an OLED. When looking into the materials chemistry of emitting materials, there are different sorting schemes. Specifically, electroluminescent material can be mainly classified into 1) fluorescent, 2) phosphorescent and 3) TADF materials according to different luminescent mechanisms and they are regarded as the first, second and third generation of electroluminescent materials, respectively. Although there is a small difference between different types of materials, their working principles also have something in common as being reviewed in subsequent pages.

2.2.1 General Process of Organic Electroluminescence

A typical OLED is composed of a layer of organic materials situated between an anode and a cathode, all deposited on a substrate. The general working mechanism is shown in Figure 2.2. The organic materials are generally semi-conductive molecules where the bonding state forms the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO). During operation, a voltage is applied across the OLED and a current of electrons are injected from the cathode (a low work function metal) into the LUMO of the organic layer and withdrawn from the HOMO at the anode (a high work function material). The latter process may also be described as the injection of holes from anode into the HOMO. Electrons and the holes move towards each other under the electrostatic forces and recombine to form an exciton, a bound state of the

electron and hole. The decay of excitons results in a relaxation of the energy levels of the electrons, accompanied by the emission of visible light. The wavelength of the light depends on the energy bandgap between the HOMO and LUMO levels of the organic material.

To sum up, organic electroluminescence process can be further divided into four stages: 1, electrons/holes injection; 2, electrons/holes transportation; 3, electron/hole recombination and the formation of excitons; 4, decay of excitons and emission of light.

Figure 2.2 left) Simplified energy diagrams and basic structure for OLED device; right) electrons and holes in the process of generating light near the organic/organic interface in fluorescent OLED device.

(1) Electron/Hole Injection

Carrier injection is the process of electrons/holes surmounting the potential barrier to enter the electron transporting layer (ETL)/ hole transporting layer (HTL) layer from the cathode/anode when a voltage is applied. The potential barrier between the cathode/anode and ETL/HTL ($\Delta E_{\text{electron}}/\Delta E_{\text{hole}}$) influence the carriers' injection process as well as the device properties. A small barrier facilitates the carrier injection, while a large barrier makes the injection difficult. The values of $\Delta E_{\text{electron}}$ and ΔE_{hole} also determine the working voltage and efficiency of the device.⁹

In order to decrease the working voltage as well as to enhance the efficiency, small potential barriers are needed. Many groups have devoted effort to studying the mechanism of the carrier injection.^{23–25} So far, several strategies have been developed to improve the injection efficiency: (1) control the LUMO/HOMO energy level of the organic emitting materials by chemically modifying the molecular structures; (2) select or modify the appropriate electrode metal to make it match the emitting material; (3) add a carrier injecting layer, i.e., electron injecting layer (EIL)/ hole injecting layer (HIL) to facilitate the process.

(2) Electrons/Holes Transportation

After entering the organic layer, electrons and holes will then be transported to anode and cathode under the effect of electric field, respectively. The carrier mobility of organic materials is much lower (generally within the range of $10^{-4}\sim 10^{-8} \text{ cm}^2 \text{ V s}^{-1}$) than those of metals. However, it is possible to generate a high electrical field ($\sim 10^6 \text{ V cm}^{-1}$) even under a low voltage ($\sim 1 \text{ V}$) because the organic layer is very thin, usually less than 100 nm. To achieve high efficiency, one of the critical factors is the balanced transport of electron and hole in the device.

Generally speaking, the mobility of holes and electrons are different even in the same organic layer. For most organic materials, mobility of holes is higher than that of electrons. As a result, some of the carriers might not combine successfully, while their combination zone might shift from the center of emission layer, even close to interface or electrode. This will seriously decrease the EL efficiency and device lifetime. To improve the balance transportation, multilayer device are designed. Materials with proper carrier transporting ability are selected as hole blocking layer (HBL) or ETL to achieve the balance of holes and electrons.

(3) Electron/hole Combination and Formation of Excitons

During the transportation, holes and electrons move towards each other and form hole-electron-pairs under electrostatic forces. This process is called carrier recombination and the hole-electron-pairs are called excitons. The formation of excitons is the result of a weak interaction (about 0.4 eV) between hole and electron, which holds them together. In organic molecules, two types of excitons of different energy states existed: singlet excitons and triplet excitons. Singlet excitons are states with an antisymmetric spin and a total spin quantum number $S = 0$. They have a short lifetime of about nanoseconds. Triplet excitons are states that have an even symmetry with $S = 1$. As a consequence of the corresponding multiplicities of the angular momentum states (i.e., $m_S = 0$ for $S = 0$ and $m_S = -1, 0, 1$ for $S = 1$) and the random nature of spin production in electroluminescent devices, quantum mechanical calculations predicted that only 25% of the injected charges formed singlet excitons, whereas 75% gave triplet excitons in suitable device architectures.²⁶ The spin asymmetry of triplet exciton leads to less repulsion between the electrons and it has a forbidden transition to singlet ground state due to the Pauli Exclusion Principle. Therefore triplet excitons usually are of lower energy level in comparison with singlet excitons. As a result, triplet excitons are more stable and possess a much longer lifetime of microseconds to seconds. Further studies showed that for small molecules, the ratio of singlet : triplet exciton is about 1 : 3; for polymers, the ratio might be larger.^{27,28}

The recombination region of excitons mainly depends on the balance of carriers' injection and transportation. The ideal situation is both injected amount and transport rate are the same for electrons and holes, so that they can meet each other in the center of emission layer. Otherwise the imbalance injection/transportation will cause the migration of the recombination region to interface or electrodes, where more defects or traps are found. All these may lead to the electrode quenching of excitons and finally decrease the EL efficiency.

(4) Decay of Excitons and Emission of Light

The excitons are known to have a certain lifetime. They would decay and return to ground state when they migrate in the emission layer within their lifetime, and give out energy in the meanwhile. Excitons can return to ground state through two mechanisms: radiative decay and non-radiative decay. In radiative decay, excitons release energy in the form of emission of light. For the latter, the energy is transferred to the surrounding molecules in the form of phonon and then be dissipated as thermal energy through internal conversion (IC), external conversion (EC), intersystem-crossing (ISC), molecular vibration relaxation and so on. Only radiative decay contributes to the lighting, as shown in Figure 2.3. For singlet excitons, their transition to the ground state is quantum mechanically allowed so they could give rise to fluorescence by radiative decay within nanoseconds. Conversely, the transition for triplet excitons to the singlet ground state is quantum mechanically forbidden according to the Pauli Exclusive Principle. Therefore most of them adopt the non-radiative decay to ground state at room temperature, while few of them radiative decay and emit phosphorescence. Considering only 25% of carriers form singlet excitons during the recombination, the theoretical upper limit for fluorescence quantum efficiency is 25%.

Figure 2.3 Photophysical process of exciton: excitation, radiative decay and lighting.

As mentioned above, excitons would transition to the ground state in several different ways. Among them only radiative decay of singlet excitons contributes to the fluorescence. These ways to decay are actually competing with each other and are controlled by their kinetics. Fluorescence quantum yield Φ_f is an important parameter used to describe efficiency in the emission process involved in luminescent materials. It is defined as the ratio of the amount of emitted photons to the amount of absorbed photons per unit time. It could be calculated by formula (2.1):

$$\Phi_f = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} = \frac{K_r}{K_r + K_{isc} + K_{ic} + K_{ec}} \quad (2.1)$$

Where Φ_f is fluorescence quantum yield, K_r is fluorescence rate constant ($S_1 \rightarrow S_0$), K_{isc} , K_{ic} and K_{ec} represent the rate constant for intersystem-crossing, internal conversion and external conversion, respectively.

Φ_f would be very low if the rate constants for non-radiative decay (including ISC, IC and EC) are too large, in this case the corresponding material is not suitable for OLEDs. To achieve high efficiency OLEDs, emitting materials with high Φ_f are desired. Moreover, the wavelength of the emitting light is decided by the energy difference between the excited and base state, or energy bandgap, ($E_p = |E_{HOMO}| - |E_{LUMO}|$). The bandgap could be calculated by expression (2.2), where h is Planck's constant, $h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$, ν is light frequency (s^{-1}), c is the speed of light ($3 \times 10^8 \text{ m/s}$ in vacuum), and λ_{onset} means the onset value of the absorption spectrum.

$$E_p(\text{eV}) = h\nu = hc/\lambda_{onset} \approx 1241/\lambda_{onset}(\text{nm}) \quad (2.2)$$

2.2.2 Energy Transfer Mechanism

Molecules in high-energy excited states can transfer energy to those in low-energy excited states. This process is called energy transfer, usually occurs in doped systems where there is more than one component mixed together. In doped systems, energy transfer occurs from emitters with high energy state (host emitter) to those with lower energy states (guest emitter, also called dopant) and light is then emitted from dopant. This phenomenon was first reported by Tang et al of the Kodak Company in 1989 and

from then on, doped OLEDs attracted many academic and industrial interests all over the world. They used DCM2 (red emitter) as dopant and Alq₃ (green emitter) as host, and observed the emitting color changed from green to red when the concentration of DCM2 increased.⁹ Today, doping is widely used in OLEDs to tune the emitting color by adding different dopant to host materials. Besides, doping could also improve the EL efficiencies and even lifetimes of OLED device because energy can be transferred from a host emitter to a dopant with extremely high fluorescence quantum efficiency.¹⁰

Figure 2.4 Several mechanisms for energy transfer. a) Radiative energy transfer (emitting and re-absorption); b) Förster non-radiative energy transfer (Coulomb interaction); c) Dexter non-radiative energy transfer (exchange of electrons).

According to the mechanism, there are two kinds of energy transfer: radiative energy transfer and non-radiative energy transfer (Figure 2.4). Radiative energy transfer involves emitting of light (host) and re-absorption (dopant) which usually leads to the decrease of Φ_f and therefore needs to be avoided. Non-radiative energy transfer can be further divided into two types: (1) Förster energy transfer, a fast ($\sim 10^{-12}$ s) and long distance energy transfer (in the range of 5 ~ 10 nm), induced by an intermolecular dipole-dipole affect (Coulomb interaction). Here the excited host emitter decays to the ground state,

while transferring the energy to the dopant emitter, and the transition of an electron occurs within the dopant emitter, from ground state of dopant to excited state of dopant. Therefore the direction of electron spin should remain and as a result, a singlet exciton of dopant was formed. (2) Dexter energy transfer. In this mechanism, the transfer of energy involves a direct exchange of electrons between host and dopant molecules, which happens within a short distance (in a range of 1~1.5nm), when molecules are in contact with each other or their electron clouds overlap. The direct exchange of electrons should follow Wigner-Witmer Rules, i.e., electron spin conservation after the exchange. It can be used to explain the energy transfer both from singlet to singlet and from triplet to triplet states.

2.2.3 Mechanism of Phosphorescent OLEDs

During the recombination of holes and electrons, two kinds of excited states can be formed: singlet and triplet excitons. Singlet excitons are states of antisymmetric spin. The transition for singlet excitons to ground state is quantum mechanically allowed, so their excited state staying life time is very short (1~10 ns) and they emit fluorescence. Triplet excitons are states with spin symmetry and emit phosphorescence during the transition to the singlet ground state. Because of spin symmetry, the repulsive force between the electrons in triplet excited states is less than that in singlet excited states, thus triplet excitons are of lower energy compared with singlet excitons. Besides, during the transition of triplet excitons, it will generate a pair of electrons with the same spin direction in the ground state due to the spin symmetry. This violates the Pauli Exclusive Principle and therefore the transition of triplet excitons to ground state is quantum mechanically forbidden. Electrons can remain in triplet excited states for a longer period of time (sometimes even more than 1 ms) and they tend to adopt non-radiative decay, including the rotation and stretch of the molecular bonds, intermolecular collisions and so on. As a result, phosphorescence is seldom observed at room temperature.

In early years of OLEDs, it was believed that only fluorescence contributed to the emission of light. Theoretical study showed that under electrical excitation, the ratio of

generated singlet excitons: triplet exciton is 1 : 3. The internal quantum efficiency of OLED based on fluorescent materials are intrinsically limited to approximately 25%, with the remaining 75% lost in the form of triplet excitons, since they decay in a non-radiative way. So it was very important to utilize the energy of triplet excitons to improve the EL efficiencies of OLEDs.

Electrophosphorescence was first observed in 1998 by Baldo et al.¹¹ Phosphorescent dyes were normally complex compounds involving heavy metals such as Ir and Pt. The mechanism of phosphorescence is to utilize the so-called heavy atom effect (spin-orbital coupling). Under the effect of spin-orbital coupling, the energy levels of singlet and triplet excited states overlap or mix into each other to a certain degree, making it possible for the triplet excitons to transit to ground states while emitting phosphorescence. OLEDs that emit phosphorescence were then called phosphorescent OLEDs (PHOLEDs).

Figure 2.5 Energy transfer between host and dopant materials in PHOLED.

Most PHOLEDs have adopted the host-guest doping system, i.e., the emitting layer is composed of a high energy host and low energy dopant materials. There are two kinds of mechanism for emission of phosphorescence: (1) Energy transfer, occurs when the emission spectrum of host emitter and the absorption spectrum overlap well. Specifically, the energy can be transferred from singlet excited states of host to singlet excited states of dopant, and from triplet excited states of host to triplet excited states of dopant,

respectively. Then the energy at singlet excited states of dopant would be quickly transferred to triplet excited states of dopant through ISC, as shown in Figure 2.5. (2) Carrier trapping. When the energy bandgap of the host is much bigger than that of dopant and the HOMO/LUMO of dopant are covered within the energy level of HOMO/LUMO of the host, for example, deep blue PHOLEDs, carrier trapping might be the primary mechanism. In this case, the recombination of holes and electrons would occur directly at dopant to form Frenkel excitons (Frenkel exciton: a hole-electron pair exists on the same molecule), followed by the emission of phosphorescence from the dopant emitter.

2.2.4 Delayed Fluorescence by Up-Conversion of Excitons

By utilizing both singlet and triplet excitons, a phosphorescent OLED is able to attain 100% internal quantum efficiency. However, it suffers from serious roll-off of the EL efficiency when the current density increases because of triplet–triplet annihilation (TTA).¹⁴ The rather long lifetime of the triplet excitons causes the acceleration of various triplet exciton annihilation processes. Besides, the design of phosphorescent materials is greatly limited because the heavy atom effect (spin–orbital interaction) must be induced by using rare metals such as Ir and Pt, which have limited global resources. Up-conversion from triplet excitons into singlet excitons is proposed as another approach to improve the Φ_f by enhancing the amount of singlet excitons. There are mainly two types of possible mechanisms for effective up-conversion from T_1 to S_1 : 1) triplet–triplet annihilation (TTA)²⁹ and 2) thermally activated delayed fluorescence (TADF).²⁰ Because the materials based on above mechanisms typically exhibit long fluorescent lifetime, they are also called delayed fluorescence materials. According to literatures, the additional singlet exciton production can increase the efficiency by 15% or 37.5% depending on the up-conversion mechanism (i.e., TTA or TADF). Thus, the maximum IQE can be increased by up to 40% or 62.5%.^{16,30,31}

In the TTA mechanism (p-type delayed fluorescence), two triplet excitons (T_1) combine by a fusion process to create one higher-energy singlet state (see Figure 2.6, left). From the energy point of view, the energy gap between S_0 and T_1 is usually bigger than that

between T_1 and S_1 . Thus this process might have enough energy to excite one T_1 to the higher singlet states, and as a result, fluorescence could happen in this system (Figure 2.6, right).³²

Figure 2.6 Schematic diagrams for triplet-triplet annihilation (TTA).³²

Figure 2.7 TADF mechanisms. When ΔE_{ST} is small, up-conversion occurs with a high efficiency, enabling highly efficient EL from the S_1 level.

TADF (also called E-type delayed fluorescence) was first discovered in the eosin system. By contrast to the TTA mechanism, TADF strongly depends on HOMO – LUMO separation in a single molecule. Specifically speaking, TADF materials have a much smaller energy gap between singlet and triplet excited states (ΔE_{ST}), which enables up-conversion of the triplet exciton into singlet excited state through reverse intersystem crossing (RISC), as shown in Figure 2.7. Although the TADF process was considered to show low power-conversion efficiency because the RISC rate ($\sim 10^6 \text{ s}^{-1}$) is usually lower than the radiative rate ($\sim 10^9 \text{ s}^{-1}$), recent studies have revealed that highly efficient delayed

fluorescence can be achieved by optimizing the molecular design. The Adachi group in Kyushu University designed a strong intermolecular charge-transfer system, which greatly reduced the energy gap between T_1 and S_1 , promoted the RISC process and further increased the conversion efficiency. This could lead to a high IQE of nearly 100%.^{33,34}

2.3 OLED Devices Structure

The simplest OLED device has a single layer structure (Figure 2.8, A), where an organic emitting layer is situated between an anode and a cathode. Indium-Tin-Oxide (ITO) is the most commonly used anode material for OLED because of its relatively high work function as well as its high transparency to visible light. Normally the ITO is evaporated onto a glass serving as substrate. For cathode, metal or alloys with high stability and low work function are desired, since they are beneficial for the electron injection. The ideal emitting layer should possess following properties: (1) it should form a smooth interface with both electrodes, which facilitates the carrier injection; (2) it should have high enough mobility for both holes and electrons; (3) it should form a nice film without defects, which would lead to the quenching of excitons; (4) no energy transfer takes place between the emitting molecules and excitons.

Figure 2.8 Typical structures for organic light-emitting diode device.

However, the LUMO and HOMO level of most organic emitting materials does not match well with electrodes, and they usually have different mobilities of holes and electrons, leading to unbalanced injection of carriers as well as the deviation of the recombination region away from the center of emitting layer. Thus single layer device OLED usually suffers from low EL efficiency. In order to enhance the device performance, balanced injection and transportation of holes and electrons is desired and to improve this double-layer and multilayer structures (Figure 2.8, B-D) are adopted. Depending on specific emitting material, proper functional layers could be employed, such as electron/hole injecting layers (EIL/HIL), electron/hole transporting layers (ETL/HTL) and electron/hole blocking layers (EBL/HBL), which are designed to facilitate carriers' injection, transportation and combination efficiency, respectively.

2.4 OLED Materials

Materials applied to OLED device can be divided into three categories according to different functions: electrode materials (including anode and cathode materials), carrier transporting materials (including organic electron and hole transporting materials), blocking materials (including organic electron and hole blocking materials) and organic luminescent materials (for emitting layer).

2.4.1 Electrode Materials

Anode Materials

Generally speaking, transparent high work function materials are used as anode materials. As mentioned above, the most commonly used material is ITO glass which has a light transmission of 80% and a high work function of about 4.7 eV (its sheet resistance is in the range of 20~100 $\Omega \text{ cm}^{-2}$). Some physical/chemical pre-treatments are usually adopted to eliminate the defects on ITO surface, improve the flatness and the work function; these will facilitate the process of holes injection. Physical treatments include ozone plasma treatment, UV Exposure, and ultrasonic processing; chemical treatments usually

introduce a transition layer to facilitate the hole injection by spinning coating of layer of doped polyaniline (PANI)^{4,35} or Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS),³⁶ vacuum depositing a layer of Copper(II) phthalocyanine (CuPc),¹⁰ and so on.

Figure 2.9 Examples of hole injection materials.

Cathode Materials

Generally speaking, electrode materials with high work function have high energy barrier and thus the injection of electrons is difficult. To decrease the barrier and enhance the electron injection efficiency, low work function metals such as Al (4.3 eV), Mg (3.7 eV), Ca (2.9 eV), Ba (2.8 eV), Mg / Ag alloy (3.7 eV), and LiF / Al alloy (2.9 eV) are selected as common cathode materials. However, metals like Ca and Ba whose work function is too low, on the other hand, tend to react with oxygen and water in the air, resulting in rapid aging of the device. Common ways to solve this are (1) using low work function metals as the electron injection layer while being protected by a layer of high work function metal; (2) simultaneously evaporating both low and high work function metals to form a stable alloy with low work function; (3) adopting high work function metal (such as Al) together with proper interface materials (such as LiF, CsF, Ca₂F, Li₂O) to improve device stability as well as efficiency.

2.4.2 Organic Carriers Transporting Materials

The function of carrier transport layers is to improve the balance of injected electron and hole and their transportation in the device, to increase the luminescence efficiency and

device lifetime. An ideal hole transport material should have high HOMO energy level and high hole mobility, while for the electron transport material, a low LUMO energy level and high electron mobility is a must. Besides, they must possess good film-forming ability and high stability.

Hole Transporting Materials (HTM)

Materials having low ionization potential, low electron affinities as well as high hole mobility could serve as hole transporting materials by accepting and transporting hole carriers with a positive charge. According to their molecular weight, organic HTMs can be divided into two groups: small molecules and polymers.

Figure 2.10 Examples of organic small molecule hole transport materials.

Aromatic triamines are candidates for small organic hole transport materials due to their good hole mobility and film-forming ability. N, N'-diphenyl-N, N'-bis(3-methylphenyl) 1,1'-biphenyl-4, 4' diamine (TPD) was the first such molecule to be widely used as hole transport material but it suffered from low glass transition temperature (T_g) and may re-crystallize during repeated operation and storage. Many efforts were taken to improve the thermal and electrochemical stability, mobility of the HTMs and to reduce the energy barrier interface between the anode and ETL. Many good HTMs were developed including 4,4'-Bis(9-carbazolyl)-1,1'-biphenyl (CBP), N, N'-diphenyl-N, N'-bis(1-naphthylphenyl)-1, 1'-biphenyl-4,4'-diamine (NPB), 1,10-Phenanthroline,2,9-dimethyl-4,7-diphenyl (BCP) and so on.

Polymer hole transport material usually are P-type polymers containing arylamine groups. Polyvinyl carbazole (PVK)^{37,38} is the most commonly used polymeric hole transport

material. However, the hole mobility of PVK is low due to its hopping charge transport mechanism, which resulted in a high drive voltage. To solve this, polymers with high hole mobility based on triarylated amine, fluorene and their derivatives were developed (Figure 2.11, TFB³⁹ and poly-TPD^{40,41}). Polysilane is another class of polymer hole transport materials with a hole mobility around $10^{-4} \sim 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.⁴² Besides, since most polymer emitting materials are P-type semiconductors, they can also be used as hole transport material, for example, poly(p-phenylene vinylene) (PPV).⁴³

Figure 2.11 Examples of polymer hole transport material.

In multilayer device, the deposited organic layer could be destroyed during the spin-coating of the next organic layer since it could be re-dissolved. To solve this problem, Cao and co-workers introduced hydrosoluble sodium sulfonate groups into the alternating copolymer of triarylated amine and benzene, in order to obtain polymers that can only dissolved in strong polar solvent such as methanol, while insoluble in normal low polar organic solvents (Figure 2.11, PTPOBS and PTFTS).⁴⁴ This facilitates the fabrication of PLED device as well as greatly enhances the EL efficiency and device lifetime. Later on many groups worked on this and reported polymers with similar functions.^{45,46}

Electron Transporting Materials (ETM)

Materials having good electron transporting and hole/exciton blocking properties, high electron affinities together with high ionization potentials could be used as electron transporting materials. This layer not only provides an electron conductive pathway for

electrons to migrate from the cathode into the emission layer, but also prevents the leakage of holes/excitons at the EL and ETL interface.

Organic electron transport materials normally are compounds containing metal complex, cyan groups, nitrogenous heterocyclic such as oxadiazole, triazole, thiazole, quinoline or perfluorinated molecules (PPOP).^{47,48} Besides, polyfluorenone (PF) as well as the alternating copolymer of fluorene and benzothiadiazole (F8BT) are also good candidates for ETM. The most commonly used ETMs are Aluminum tris-8-hydroxyquinoline (Alq_3), 9, 10-di (2-naphthyl) anthracene (ADN), 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3, 4-oxadiazole (PBD),² and 1,2,4-Triazoles (TAZ),⁴⁹ as shown in Figure 2.12. Some of them can also be used as the luminescent material.

Figure 2.12 Examples of organic electron transport material.

With the same reason, it is necessary to develop water or alcohol soluble polymer electron transport material, in order to produce low cost high efficiency PLED device by solution process. Cao and co-workers have made great contributions in this field. They firstly reported an alcohol soluble ionic polymer electron injection/transport material (**23**),^{50,51} which can be utilized in combination with a high work function metal. The resultant device can achieve a high stability as well as long lifetime without losing the EL efficiency. Many other hydrosoluble polymer electron transport materials were also developed in other groups to improve the EL efficiency of device.^{52–54}

2.4.3 Organic Electroluminescent Materials

The layer in between the HTL and the ETL is called the emitting layer (EML), which as the emitter of the photons, is the critical part of the OLED device. The main requirements for emitting materials are high luminescence quantum yield, especially in the solid state, good carrier mobility, good film-forming properties, good thermal and oxidative stability, as well as good color purity. There are means of classifications for emitting materials. For example, they can be divided into fluorescent, phosphorescent and TADF materials according to the luminescence mechanism; or small molecules, polymers, star-shaped oligomers and dendritic molecules depending on the molecular weight and chemical structures; or host and guest/dopant materials owing to their different functions in OLED device; or red, green and blue emitting materials, which depends on the emission of the light (energy bandgap) of the molecules.

One of the key developments was the host-dopant doping OLEDs,⁹ where a host material with good charge transport and luminescent properties was used together with various dopants materials with high quantum efficiency in order to achieve desired color of emission with high efficiencies. Besides, doping system is able to suppress the concentration quenching of the dopants as well as to improve the operational stability by minimizing non-radiative decay of excitons on the host (the excitons are transferred to dopant site).¹⁰ This doping principle was greatly applied in phosphorescent OLEDs for high EQE (100% IQE could be achieved).⁵⁵

The main work of this thesis was focus on highly efficient star-shaped blue emitters for undoped fluorescence OLEDs. To better illustrate the motivation of developing such kind of emitting material. For a specific review of organic fluorescent materials please refer to Section 2.6 and 2.7.

2.5 OLED Device Performance Parameters

Some important parameters of an organic light emitting diode device are briefly introduced in following paragraphs. They include color coordinate, luminous efficiency, luminous brightness, stability and life span of the device, etc.

2.5.1 Emitting Color Coordinates

The color of emitting light mainly depends on the difference between the HOMO and LUMO energy level of the electroluminescent materials in single layer device. For an organic material, the energy bandgap is determined by the molecular structure. Generally speaking, a long effective conjugated length leads to the red shift of the emitting light while a short conjugated length results in blue shift. Using push-pull designation can somehow adjust the HOMO and LUMO energy level to a desired value. In a multilayer device, the situation is more complex since the carrier transporting layer may also emit light. Besides, there may be interaction between the excitons and molecules of other layer, resulting in the formation of aggregation state, exciplexs, excimers, and the red shift of the emitting light.

Figure 2.13 Chromaticity diagram, representing CIE coordinates of different colors ⁵⁶.

To study the light color in an objective way, in 1931, the International Commission on Illumination (CIE) created a standard colorimetric system (Figure 2.13), where the color spacers were first mathematically defined. CIE also suggested a standard lighting object and standard observer so that any color can be expressed by the chromaticity coordinates x and y on the CIE chromaticity diagram as (x, y) . For further description of CIE coordinates, please refer to Section 3.5.3.

2.5.2 Luminous Efficiencies

There are three parameters to state the performance of OLED device: current efficiency, power efficiency and quantum efficiency.

Figure 2.14 Spectral response of normal human eye (photopic) ⁵⁷.

Current efficiency (CE) η_I (cd A^{-1}) is defined as the luminance divided by the current density, which can be expressed as:

$$\eta_I = \frac{B}{J} \quad (2.3)$$

Where 'B' is the brightness (cd m^{-2}) of the light, and 'J' is the current density (A m^{-2}).

The power efficiency (PE) η_p (lm W^{-1}) is defined as the ratio between the total luminous flux and the total electrical power:

$$\eta_p = \frac{\Phi_{\text{total}}}{W_{\text{total}}} = \frac{\pi B}{VJ} = \frac{\pi \eta_I}{V} \quad (2.4)$$

Where Φ_{total} means the total luminous flux, W_{total} means the total electrical power, V means the drive voltage.

Both current and power efficiency are related to the eye sensitivity (Figure 2.14). Human eyes are particularly sensitive to green-yellow light with a wavelength around 555 nm, while less sensitive to red and blue light under the condition of photopic vision. Therefore the current and power efficiency of green OLEDs are much higher than those of red and blue OLEDs.

Quantum efficiency could be divided into external quantum efficiency (EQE) and internal quantum efficiency (IQE). The former (η_{ext}) is the ratio of the amount of photons emitted by the OLED in the viewing direction (emitted through the device) to the amount of injected electrons, while the latter (η_{int}) is defined as the ratio of total number of generated photons to the total number of injected electrons. Photons are partly absorbed or reflected and cannot finally transfer out of the device. Therefore η_{ext} is mostly used for the EL efficiency of the device. Quantum efficiency is not related to the eye sensitivity. The relationship between them can be expressed by following equation, where η_c is the fraction of light coupled out of the structure into the view direction.

$$\eta_{\text{ext}} = \eta_{\text{int}} \eta_c \quad (2.5)$$

EQE is one of the most important parameters of OLED and the final goal of this work is to design a high EL efficient material for OLED. It is necessary to understand all factors that affect EQE of the device.

Not all injected electrons can contribute to the EQE. During the formation of exciton, only a fraction of the electrons can combine with holes due to the unbalanced injection and transportation of carriers. Among formed excitons, only singlet excitons can release light in organic fluorescent materials. Then, only those singlet excitons decay in a radiative way can generate photons, non-radiative decay of excitons do not release light. Finally, photons are partly trapped inside the device and cannot escape. Therefore the EQE can be expressed by:

$$\eta_{\text{ext}} = \eta_{\text{com}} \eta_{\text{sin}} \eta_{\text{rad}} \eta_{\text{c}} \quad (2.6)$$

Where η_{com} is the ratio of the amount of combined electrons to that of injected electrons, η_{sin} is the ratio of the amount of singlet excitons to that of total excitons (for organic small molecules this value is 25%), η_{rad} is the ratio of the number of radiatively decaying singlet excitons to that of whole singlet excitons, and η_{c} is the fraction of light coupled out, the upper limit of this value is 20%. Therefore the maximum value of EQE in an organic small molecule OLED device is 5%.

According to above discussion, the efficiency of OLED can be improved by various approaches:

- (1) Increase η_{com} , which can be achieved by 1) matched energy level and smooth interface between multi-layers, 2) developing material with improved carriers mobility.
- (2) Increase η_{rad} , this can be achieved by adopting emitting materials with (1) high PL quantum efficiency in order to reduce energy loss in non-radiative decay of excitons; (2) good ability to form amorphous film, to prevent PL quenching caused by concentration and aggregation. Besides, it is also possible to utilize host-dopant system to eliminate the aggregation of dopant, improve the efficiency and lifetime as well as modify the emission color.⁹
- (3) Utilize triplet excitons. By harvesting emission from both singlet excitons (25% ratio) and triplet excitons (75% ratio) which could emit phosphorescence under the existence of organic transition metal complex.¹¹ An IQE of 100% is theoretically achievable in phosphorescent OLED. Using phosphorescent materials led to an increase in the efficiency and selectivity of possible colors. PHOLEDs with host-dopant system have been widely used.^{52,53}
- (4) Increase η_{c} . Poor light extraction is one of the most important factors. According to the ray optics, only 20% of light can be harvested. Part of the emitted light is trapped

inside the substrate or emitted out from the edges of the device.^{60,61} Therefore developing of out coupling methods are believe to greatly improve the efficiencies. In order to extract more generated light, many approaches were reported such as using a shaped substrate,⁶² using micro-lenses on the back side of the substrate surface,⁶³ using substrate with high refractive index, inserting a low refractive index silica aerogel layer in between ITO and glass substrate⁶⁴ and so on. 50% light extraction efficiency from OLEDs was recently reported by insertion of a two dimensional photonic crystal structure.⁶⁵

2.5.3 Device Stability and Life Span

During the storage and usage of OLED device, performance degradation will take place. Life span plays a vital role in dictating the performance of the device and is defined as the time it takes for the brightness to drop to half of its initial value, while maintaining a constant driving voltage or current.

Besides, the life time is also a critical parameter to see if it can be practically used. For full-color solid state lighting, all the primary colors should have good lifetime for the excellent performance. At the present stage, the life time of red and green light emitting materials have already reached to suitable values. However, the life times of blue light emitting materials remains a bottleneck as they are lower than those of the red and green emitters. The materials used for blue emitters have wider band gaps which might affect their life time and also require high energy for effective light emission.^{66,67}

There are many factors that cause the aging of OLED devices ⁶⁸ including: (1) most injected electric powers transformed into heat, which might lead to the deformation or chemical reaction of materials, (2) the presence of oxygen, even in trace amounts, will cause the oxidation and deterioration of electrodes and materials, (3) the existence of water will cause electrochemical reactions and destroy the electrodes and materials, (4) the impurities of different layers can capture the carriers and lead to the non-radiative decay of excitons. They can also partly change the internal electric field and are an

important reason for the aging deterioration of the device. Therefore high purity of materials is a must to extend the life span of OLEDs.

2.6 General Introduction to Organic Fluorescence Materials

The first generation of OLED devices, pioneered by Tang and Van Slyke,² were based on fluorescent materials (first generation of OLED materials). In this case, the emission of light is the result of the recombination of singlet excitons, therefore the EL efficiency is theoretically limited to 25% and 5% for IQE and EQE. Fluorescent materials can be mainly divided into small molecules and polymers. Some commonly used small molecules RGB emitters and polymer emitters will first be introduced. Then focus on blue electroluminescent materials, which are very important but remain a challenge for OLEDs application, including their development situation and existing problems. Especially, undoped blue fluorescent emitters will be comprehensively discussed. Special attention will be placed on the star-shaped oligomer emitting materials, which is the base of the designed molecules in this thesis.

2.6.1 Small Molecule Emitting Materials

The early investigation of OLED emitting materials was mainly focused on small molecules. Their well-defined structures provide them precise chemical and physical properties and good reproduction. And their small sizes make them could be easily purified by crystallization or sublimation. Small molecules are prone to aggregate together, causing concentration quenching; therefore most of them are used as dopants rather than host materials. Typical examples of efficient small molecule RGB materials are shown in Table 2.1 and their chemical structures are shown in Figure 2.15.

Table 2.1 Typical efficient RGB materials for SM-OLEDs and their device performance.

Color	Material	CIE		Efficiencies			Luminance (cd m ²)	Ref.
		x	y	EQE (%)	CE (cd A ⁻¹)	PE (lm W ⁻¹)		

Red	DCJTB-doped Alq ₃	0.64	0.35		3.24	1.19	69
	DCATJP-doped Alq ₃	0.60	0.39		4.2	2.7	70
	DCJMC+Rubrene-doped Alq ₃	0.60	0.40		10.34	5.1	6903 71
	DCJTB+C545T-doped Alq ₃	0.64	0.36		12	10	23000 72
Green	Alq ₃			1.3			>1000 9
	Almq ₃			2.5			26000 73
	C545T-doped Alq ₃			6	23.7	12.4	106800 74
	Coumarin6-doped Almq ₃			7.1	24		140000 49
	C545T-doped TPBA	0.24	0.62	9.9	29.8	26.2	~40000 75
Blue	ADN-doped TBP	0.15	0.23		3.4		76
	41-doped ADN	0.159	0.198		6.7	3.02	11060 77
	BCzVBi-doped Spiro-(3)-F	0.149	0.187	4.92	5.64	2.87	10820 78
	BCzVBi-doped Bepp ₂	0.18	0.31	6.1			~10000 79
	DPSF-doped mCP	0.15	0.08	5.41	3.24	2.54	4745 80

Figure 2.15 Chemical structures of typical RGB fluorescent materials for SM-OLEDs.

The sensitivity of human eyes to visible light is different according the wavelength (Figure 2.14). The most sensitive zone is green-yellow light (around 555 nm) and the sensitivity drops sharply when the wavelength increases (red light) or decreases (blue light). Due to the large value (100 nm) of full width at half maximum (FWHM) for most red emitting materials, their PL spectrum either have a long tail in the yellow region which makes the emission orange, or have a long tail in the infrared region (> 700 nm), leading to a waste of energy. Therefore an effective saturated red emitting material is difficult to design.

Red fluorescent materials are molecules with conjugated structures and narrow bandgaps. These materials are likely to aggregate since there is strong π - π interaction, resulting in concentration quenching so a host material is usually required. For commercialization, a red OLED should achieve an efficiency of 4 cd A^{-1} as well as a saturated red emission with CIE coordinates around (0.65, 0.35). Classic red emitting materials are DCM (4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4Hpyran) and its derivatives, among which the most famous one is DCJTb (4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran).⁶⁹⁻⁷² In most cases, due to the narrow bandgap of the red dopant, the energy compatibility between dopant and host is poor, and the emission from host is difficult to completely suppress. To improve the EL efficiency, rubrene has been added serving as an assistant dopant emitter and this co-guest doping was found to be a good method to enhance the efficiency of energy transfer from host to dopant.^{72,81}

Green fluorescent materials were amongst the first batch of industrialized electroluminescent materials. Today, they are also the most efficient compared with red and blue emitting materials. One famous example of a green emitter is 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one, known as C-545T, which belongs to the class of coumarin and its derivatives.^{49,74,75} C-545MT was designed later by introducing a methyl group at C-4 position of C-545T, which distorted its molecular geometry and prevented molecular

packing, thus effectively suppressing concentration quenching. It could achieve a high EL CE of about 7.8 cd A^{-1} when doped in a concentration range from 2 to 12%.⁶⁸

Many efficient green emitters were covered by patents, for example, quinacridond (QA) proposed by Pioneer Company, N,N-dimethylquinacridond (DMQA) designed by Kodak Company, and 5,12-diphenyltetracene (DPT) reported by Mitsubishi Chemical Company. OLEDs based on these materials possess excellent stability and long lifetime.

As with red light, blue light has low sensitivity to the human eye. Due to the intrinsic wide band gap of the blue emitters, a host material with wider bandgap energy and a well-matched LUMO/HOMO energy level is usually needed in order to effect the sensitization. For full-color OLED displays, blue OLEDs should reach a CE of 5 cd A^{-1} and a pure blue emission with the CIE coordinates of about ($x \approx 0.15$, $y < 0.15$). There are many blue emitters reported to achieve this target, but the device stability, or operational lifetime are still insufficient for practical use. The earliest blue fluorescent materials are anthracene based derivatives.¹ 9,10-di(2-naphthyl)anthracene (ADN) was proposed by Kodak company as a good blue emitter with high fluorescent quantum efficiency in both liquid and solid state. OLEDs based on ADN-doped TBP achieved an efficiency of 3.5 cd A^{-1} and a lifetime of 4000h under brightness of 636 cd m^{-2} with the CIE coordination of (0.15, 0.23).⁷⁶ However, Chen et al found the film of this emitting layer was unstable and tended to re-crystallize over extended periods of operation under electrical power, producing a red-shift of the emission.⁸² By substituting an additional methyl group at the C-2 position of AND, they obtained 1-methyl-9,10-dibromo-anthracene (MADN), with improved film stability.^{83,84} Besides, ADN could also serve as a host material. Lee et al. reported a highly efficient sky-blue OLED based on t-butylated bis(diarylaminoaryl) anthracenes doped ADN.⁷⁷

Distyrylarylene (DSA) and its derivatives, disclosed by Idemitsu Company in Japan,⁸⁵ are other classical blue emitters. In 1995, Hosokawa et al designed DPVBi and BCzVBi based on the DSA structure serving as host and dopant materials, respectively. The doped OLED emitted sky-blue light, where the energy was transferred completely from DPVBi

to BCzVBi.⁸⁶ And especially, when doping DSA-Ph into DPVPA host, the doped OLED achieved a high EL efficiency of 10.2 cd A^{-1} and 4.8 lm W^{-1} with CIE coordination of (0.16, 0.35).⁸⁷ Later in 2013, Yue optimized the intermixed layer and improved the max PE to 8.7 lm W^{-1} for DSA-Ph based blue OLED.⁸⁸ Besides, other commonly used blue emitters include pyrene, spirobifluorene, TBP and their derivatives.

2.6.2 Polymer Emitting Materials

All the above mentioned RGB emitting materials are small molecule. The traditional fabrication technology for SM-OLEDs is vacuum evaporation, which could construct even complicated multilayer device but is relatively expensive and limited to vaporizable low molecular weight materials. Polymer electroluminescent materials, have attracted much interests since 1990 when they were first reported by Burroughes et al. because of their following outstanding advantages: (1) Molecular designability. The light emission color of the polymers strongly depends on the type of the polymer, its chemical composition and the nature of its side groups. So it is possible to obtain any desired emission color in the entire visible spectrum ranging from 400 nm to 800 nm by chemical modification of the polymer structure. (2) Good compatibility. Polymers have high compatibility with small molecules. Small emitters (dopants) can be well dispersed into a polymer matrix by spin casting of their mixed solution, which is extremely good for depositing host-guest doping systems. Concentration quenching of dopant is therefore effectively suppressed; (3) high thermal stability. Polymers usually possess high thermal stability (high T_g); (4) Excellent solution processability. Polymers with long and flexible chains usually possess high solubility in organic solutions, making it possible to use the spin-coating fabrication technology, which is much cheaper and faster than traditional vacuum deposition. And this also facilitates making flexible and large area displays. (5) Good film forming ability. During spin-coating and annealing, polymers tend to form amorphous film rather than stack in order to form crystal structure due to their big size and complex molecular structure, which can reduce the intermolecular forces and is beneficial for device stability and lifetime.

The light emission color of the polymers strongly depends on the type of the polymer, its chemical composition and the nature of side groups. The derivatives of poly-phenylene vinylene (PPV), polythiophene (PTh), poly(p-phenylene) (PPP) and polyfluorene (PFO) are the most commonly used polymer electroluminescent materials.⁵⁻⁸

Poly-phenylene vinylene (PPV) was the first reported polymer electroluminescent material.³ PPV has good EL performance but the pure PPV is an insoluble material so it was synthesized using a solution-processable precursor polymer. Following this, people developed various PPV derivatives by introducing substituents such as alkyl, alkoxy, and phenyl groups (Figure 2.16)⁸⁹ since they offer the advantage of good solubility in organic solvents. The introduced substituents could not only improve the solubility but also prevent the molecular association. The color of the emitting light can be tuned from red to green by introducing electron donating and withdrawing substituents⁹⁰ and sterically bulky substituents which make the backbone distorted.^{91,92} The device efficiency can be improved by using functional groups with high mobility for holes or electrons.⁹⁰

Figure 2.16 Typical PPV-type emitting materials.

Poly(3-alkylthiophene)s (P3AT) have attracted lots of interest because of their red-orange emission.⁹³ In 1991, Ohmori et al. first reported an OLED based on P3AT with orange emission.⁹⁴ By introducing different side chains, the geometric configuration of the molecule as well as the energy bandgap could be controlled, thus the color of the emitted light could be adjusted. For example, PCHMT, PCHT, PTOP and POPT (Figure 2.17) with different substituents at the 3-position can be used as blue, green, orange and red emitters, respectively. However, OLEDs based on polythiophene derivatives suffered from low fluorescent quantum efficiency because of the heavy atom effect introduced by sulphur atoms, which also lead to low EL efficiency. Presently polythiophene materials

are mainly studied for their application in organic photovoltaics (OPVs) and organic field effect transistors (OFET) other than OLEDs due to their good crystallization properties, high carrier mobility as well as wide absorption bands.

Figure 2.17 Typical PTh-type emitting materials.

Poly(p-phenylene) (PPP) with an energy gap of about 3 eV emits blue light.⁹⁵ Blue emitting materials are very important because they are necessary for the full-color display (one of the three-primary colors). And it is more difficult to realize blue emission compared with red and green light. Unsubstituted PPP is an insoluble material. Though the solubility can be improved by introducing substituent groups, the backbone might be twisted at the same time, which changes the energy level of the polymer.

Besides, PPP derivatives are prone to aggregation, leading to the red-shift of their PL spectra. Therefore many OLEDs based on PPP derivatives emit green or even white light rather than pure blue light. One important development was ladder type polyphenylenes (LPPPs, Figure 2.18),⁹⁶ which was reported by Müllen and his co-workers in 1991. LPPPs have good solubility while maintaining a coplanar structure and can show high EL efficiency. Later in 2003, Qiu et al. fabricated a blue OLED based on a LPPP with a maximum CE of 0.66 cd A⁻¹ and a maximum brightness of 5400 cd m⁻².⁹⁷

Figure 2.18 Typical PPP-type emitting materials.

Like PPP, polyfluorene (PF) is a blue emitting material. The fluorene unit is composed of two benzene rings connected via a methylene bridge, forming a coplanar structure. The conjugation degree of PF is between PPP and LPPP. The methylene (9-position) is very reactive and is the normal place for substitution. Side chains attached there can improve the solubility of PF derivatives and modify their carrier transport performance without affecting the electronic energy level of its main chain. PF is easy to modify by introduction of comonomer units to adjust the emitting light to cover the whole visible region. Poly(9,9-dioctylfluorene) (PFO) can be made by short, efficient synthesis with high molecular weight (M_w), and moreover, PFO usually possess high solid fluorescence quantum efficiency ($\Phi_{PL} = 0.55$),⁹⁸ good chemical and thermal stability. Therefore PFO and its derivatives are considered to be the most promising polymer EL materials for commercialization.^{99,100}

Figure 2.19 Typical PFO-type emitting materials.

2.6.3 Star-Shaped Molecule Emitting Materials

Star-shaped molecules can combine the advantages of small molecules and polymers when they serve as the emitting material. The well-defined structure endows star-shaped molecules with precise properties (e.g., emitting color), making them easy to purify and reproduced as small molecules, high solubility^{101–104} allows them to use the low-cost solution processing fabrication technology (like polymers). More importantly, their highly branched structure can more effectively suppress and prevent their intermolecular interaction in film state, resulting in reduced fluorescence quenching and enhanced solid-state luminescence. Also, it allows independent judicious choice of core, branches and the terminal groups, as well as independent chemical modifications on these moieties for further optimization. Functional groups could be attached to provide better solubility,

charge transporting ability, emitting properties, thermal stability and so on. So far most reported star-shaped emitting molecules are based on fluorene backbone. The next section will focus on star-shaped blue emitting materials including important achievements that have been fulfilled by many research groups. Properties of small molecules, linear polymers and star-shaped molecules are summarized in Table 2.2.

Table 2.2 Properties of small molecules, linear polymers and star-shaped molecules as emitting materials.

Properties	Small molecules	Polymers (linear)	Star-shaped molecules
Structure control	High	Low	High
Polydispersity	Monodisperse	Polydisperse	Monodisperse
Film forming ability	Poor	Good	Good
Compatibility	Low	High	High
Potential for chemical modification	Low	High	High
Fabrication technology	Vacuum deposition	Solution process	Solution process
Fabrication cost	High	Low	Low

2.7 Blue Fluorescent Emitting Materials

2.7.1 Motivation

To realize white light and full-color displays, the emission of RGB should be equal, (i.e., the performance of red, green and blue OLEDs including EL efficiencies, stability, and color purity should be of comparable level). In white OLEDs, the blue electroluminescent material plays a very important role. It not only emits blue light as one of the three-primary color, but also transfers energy to dopants and generates light from them (usually of lower energy to emit green or red light). However, it is difficult to design efficient blue emitting materials because of their intrinsic wide energy gaps. Organic electroluminescent materials are generally conjugated molecules. Although the molecular energy gap could be enhanced by interrupting the conjugation, (e.g., introducing of silicon atom or steric substituents to distort the coplanar structure), this will influence the

charge transport and may reduce fluorescence quantum efficiency. Besides, the wide band gap will also cause difficulty in injection of electrons. As a result, blue OLEDs usually show inferior device performance compared with that of green and red OLEDs. Deep-blue emission is even more difficult to obtain, because it should possess even wider energy gap than blue dopant emitters, which usually causes a further decrease in fluorescence quantum yield.

The same problem and challenge also exists for blue phosphorescent materials. Since phosphorescent materials can harvest light from triplet excitons by heavy atom effect and can utilize both singlet and triplet excitons, approaching a 100% IQE theoretically.¹¹ So far, green, yellow and red phosphorescent OLEDs have met requirements for industrialization, but efficient blue phosphors are still limited, as discussed in a recent review.¹⁰⁵ Compared with blue fluorescent emitting materials, it is even harder to design efficient blue phosphorescent emitting materials. A blue phosphor should possess both a wide energy bandgap as well as a high triplet energy ($E_T > 2.6$ eV). Host materials for blue phosphors are even rarer because they should have higher triplet energy than the blue phosphors otherwise the energy will transfer from phosphors to host. Additionally, to build a device based on such blue phosphors, the corresponding functional materials, such as EIM/HIM and ETM/HTM should also possess high enough triplet energy to confine the triplet excitons in order to realize high efficiency. However, such functional and host materials with extremely high triplet energy level are quite limited. Stability and longevity of blue PHOLED are also not good enough to reach the application requirements.

In order to achieve white emission, while taking the lack of efficient blue phosphors into account, hybrid OLED has been promoted. By this method one can obtain blue fluorescence (from host) and complementary phosphorescence (from dopants) at the same time which forms white light when they are mixed together. It is possible to realize an internal quantum efficiency of 100% if a suitable blue emitter with high-lying triplet transition is used. In 2009, Leo et al. fabricated a hybrid device and achieved high efficiency ($EQE_{max} \approx 24.3\%$).¹⁰⁶ Another advantage of a hybrid device is it uses only a

single emitter layer, which could simplify device structure, leading to less energy loss during charge transportation through multilayers in the device. To obtain high efficiency, both balanced charges injection / transportation and effective exciton confinement are desired. Therefore OLED devices normally adopt multilayer configurations involving extra functional organic layers such as EIL/HIL and ETL/HTL to facilitate the balance of charges and improve the device efficiencies. However, the complicated device fabrication processes might introduce many possible problems such as interface defects, impurities as well as thickness errors. Simplification of OLEDs structure is necessary for OLED commercialization since it could not only prevent all the problems mentioned above, but also reduce the overall cost. Considering the above points, developing highly efficient blue (especially deep-blue) fluorescent materials is a pressing concern to realize commercial applications of OLEDs.

2.7.2 Undoped Blue Emitters

Initially, most reported blue fluorescent emitters were small molecules. These are prone to aggregate together and this causes serious fluorescence quenching. In order to prevent the aggregation and enhance the quantum efficiency, a commonly used method is dispersing a small amount of blue emitting molecules into a matrix material. Here the blue emitter is called the dopant (or guest) material; the matrix is called the host material, the corresponding OLEDs were called doped devices. During operation, the host-guest doping system adopts Förster energy transfer. Efficient energy transfer from host to dopant requires a high degree of overlap between the PL spectrum of the host and the absorption spectrum of the dopant. Besides, the HOMO/LUMO energy levels of dopant are desirably located in between the HOMO/LUMO energy levels of the host with optimized energy barriers. A large energy barrier would hinder the charge injection, resulting in an enhanced turn-on voltage, while a small energy barrier would reduce the efficiency of the energy transfer. I.e., for any fluorescent dopant material, a suitable host material is required to obtain highly efficient device. Most doping devices utilized complex multilayer configurations with functional layers such as HIL, HTL, EBL, ETL, EIL, HBL to facilitate charge transport into the EML. However, the complicated device

structure is not that attracting and would cause possible energy loss by defects generated on the interface between multilayers.

Although high efficiency could be achieved by using a host–guest doping emitting layer, it suffers from possible aggregation of dopants and phase separation which might cause deterioration in the device performance. Typical examples of commonly used blue fluorescent dopants involving TBP, DSAPh, DPVBi etc (see Figure 2.15). Moreover, extra suitable host material should be designed to be used together with the blue emitters. Therefore developing of undoped fluorescent emitters would be another approach. As its name implies, undoped fluorescent emitters were used without any host material and they were normally molecules with complex non-planar structures or steric hindrance which could effectively suppress intermolecular interactions and close packing so that they possess high luminescent quantum efficiency in solid state. Utilization of undoped emitters has been proved to be a good method to reduce phase separation and concentration quenching. Blue emitting materials usually suffered from poor charge injection and transportation due to their wide band gaps. This could be partially solved by introducing electron and hole transporting moieties. Most reported undoped blue fluorescent emitters include anthracenes, fluorenes and pyrene derivatives. Examples of these materials are shown in Figure 2.20.

Figure 2.20 Examples for undoped blue fluorescent materials.

Anthracene is a family of deep-blue electroluminescent material. 9,10-diphenylanthracene (DPA) is a classic blue emitter with high quantum efficiency in dilute

solution and it was often the standard reference material for blue PL measurements.¹⁰⁷ However, the fluorescence of DPA in the solid state is poor because of the quenching caused by aggregation. Intrigued by its deep-blue emission and excellent PL properties, much research work has been done in developing undoped deep-blue emitters based on anthracene structure. Introduction of rigid steric substituents was an effective method to distort the coplanar molecular structure of the anthracene, which could reduce molecular aggregation and the luminescence quenching in the solid state.

In 2005, Kwon et al. synthesized a undoped deep-blue fluorescent molecule BTSA, which is composed of two triphenylsilylphenyl at both sides of anthracene. Theoretical simulation showed the skeleton of tetrahedral molecular was twisted at a degree of 80° towards the anthracene backbone, which was expected to suppress the intermolecular interactions. A BTSA based undoped OLED achieved a CE of 1.3 cd A⁻¹ with CIE coordinates of (0.148, 0.09).¹⁰⁸

Replacing tetraphenylsilane with a conjugated tetraphenylethylene structural unit, Shu et al. developed TPVAn with deep-blue emission.¹⁰⁹ The undoped devices showed a maximum CE of 5.3 cd A⁻¹, a maximum PE of 2.8 lm W⁻¹ with CIE coordinates of (0.14, 0.12). In addition, TPVAn was also employed in a white hybrid device as host material and it reached a maximum CE of 13.1 cd A⁻¹. Later in 2009, they reported another emitter BFAn using fluorene as the substituent.¹¹⁰ The bulky fluorene groups afforded BFAn high quantum efficiency (Φ_f) of 0.93 in solution and excellent thermal properties. The undoped device based on BFAn exhibited a high CE of 5.6 cd A⁻¹ and EQE of 5.1% with deep-blue emission and its CIE coordinates were of (0.15, 0.12).

More functional groups such as hole transporting moieties (e.g., triphenylamine, carbazole) and electron transporting moieties (e.g., phosphine oxide, benzimidazole) were also introduced at the 9,10-positions of anthracene in order to tune the charge transport properties of the emitting material as well as to improve the balance of the hole / electron fluxes in simple OLEDs device. For example, Park et al. reported a p-type blue emitter TATa,¹¹¹ the undoped device of TATa exhibited a maximum CE of 6.07 cd A⁻¹

with CIE coordinates of (0.149, 0.177). Shu et al., reported a deep-blue emitting material POAn.¹¹² This n-type emitter could be used as both emitter and electron transporting material in the device and a maximum EQE of 4.3% with CIE coordinates of (0.15, 0.07) was achieved. By introducing both electron donating and withdrawing moieties into anthracene, Tian et al. designed a group of blue emitters Bn ($n = 1 \sim 4$) with bipolar feature.¹¹³ A single layer device of B4 (where it also serves as HTL and ETL) realized a maximum brightness of 8472 cd m^{-2} and a CE of 3.33 cd A^{-1} with CIE coordinates of (0.16, 0.16). Fluorene derivatives have also been widely employed as structural units in molecular design of undoped blue emitters due to their wide bandgaps. Examples include TDAF1,¹¹⁴ a device using which achieved a high EQE of 5.3% with CIE coordinates of (0.158, 0.041); and DCDPF,¹¹⁵ the device of which exhibited maximum CE of 4.4 cd A^{-1} and PE of 3.1 lm W^{-1} with CIE coordinates of (0.15, 0.15).

2.7.3 Undoped Blue Fluorescent Emitters for Solution-Processed OLEDs

Polymer electroluminescent materials have the potential to achieve large-area and flexible displays by a simple technology of spin-coating at low cost since they have been solution-processable and they are extensively investigated and developed.⁵⁻⁸ However, the unsatisfactory purity and reproducibility of polymers hinder their application. Instead, star-shaped molecules, especially monodispersed conjugated star-shaped oligomers, attracted many research interests for their use in OLEDs. These star-shaped molecules possess combined advantages from both small molecules (high purity and well defined structure) and polymers (good solution processibility). Besides, the highly branched structure of these star-shaped emitters could effectively suppress the intermolecular interaction in film state, leading to enhanced solid-state luminescence compared with their linear counterparts.¹¹⁶

In many cases, fluorene is favorably used as the structural unit for the branches due to its easily tuned structure, blue emission, good film forming ability and high quantum yield.¹¹⁷ Therefore many starburst oligofluorenes with different cores have been developed for undoped blue emitters during past decades. In 2008, Wei et al. reported a

group of star-shaped oligofluorenes (**71** ~ **73**) using pyrene as the core.¹¹⁸ The undoped device of **73** achieved a maximum CE of 1.75 cd A^{-1} with sky-blue emission due to the planar structure of the pyrene core. Later, Wang et al. used a propeller-shape (highly twisted) 1,3,5-tri(anthracen-10-yl)benzene as the core and six oligofluorenes branches and designed a series of star-shaped molecules (**74** ~ **76**) with better chromaticity and film-forming capabilities.¹¹⁹ A maximum brightness of 3400 cd m^{-2} and a maximum CE of 1.80 cd A^{-1} with CIE coordinates of (0.149, 0.098) was achieved in an undoped device based on **75**. By replacing the core with a simple phenyl unit, Zou et al synthesized a series of highly twisted star-shaped oligofluorenes (**77** ~ **80**).¹⁰⁴ Double layer device based on **80** realized a maximum EQE of 6.8% and a CE of 5.4 cd A^{-1} with CIE coordinates of (0.16, 0.07). However, it exhibited a high turn-on voltage around 7 V due to the large hole-injection barrier. Subsequently, Zou et al introduced electron donor diphenylamine end-caps and obtained emitters **81**~**84**, with a reduced turn-on voltage of 3.6 V.¹²⁰

Figure 2.21 Star-shaped oligofluorenes for blue emitters.

Figure 2.22 Other examples of star-shaped blue emitters.

More multifunctional blue oligofluorenes were investigated by introducing hole / electron transporting moieties. Ding et al. synthesized a group of deep-blue emitters **85~88** composited TCTA (4,4',4''-tris(carbazol-9-yl)-triphenylamine) core with good device performance (EQE = 1.4%).¹²¹ Besides, they were also better host materials than PVK for red phosphors due to their good hole transporting ability. Huang et al. reported a family of blue emitters (**89~92**) using triazatruxene as the core.¹²² The undoped device of **92** turned on at a low voltage of 3.3 V due to the improved hole injection property endowed by the triazatruxene core, and it exhibited a maximum EQE of 2.16%, with CIE coordinates of (0.16, 0.15). Using triphenylamine as the core, Yang et al obtained highly efficient emitters (**93~95**). The undoped device of **95** achieved a maximum CE of 3.83 cd A⁻¹ and a maximum EQE of 4.9%.¹²³ Fang et al designed a group of star-shaped oligomers (**96~98**) with bipolar feature endowed by 1,3,5-triazine core and triphenylamine terminals.¹²⁴ OLEDs device based on **96** exhibited a maximum luminance of 3093 cd m⁻² at a CE of 1.47 cd A⁻¹.

Although fluorene is favorable structural unit for branches, 9,9-dialkylfluorene has intrinsically unstable EL spectrum. Degradation at 9-position of fluorene could happen during operation, long time storage or thermal treatment, leading to the formation of ketonic defects which emit green light.¹²⁵⁻¹²⁸ In order to prevent this, Pei et al. introduced spirobifluorene moieties instead of fluorene with alkyl chains at 9-position and obtained blue emitters (**99~100**) with greatly improved spectral stability.¹²⁹ Besides, 9,9

diarylfluorenes also show good spectra stability.⁶ For undoped device of **100**, a maximum EQE of 2.9% with CIE coordinates of (0.16, 0.09) was obtained.

Other types of star-shaped blue emitters are also investigated (see examples in Figure 2.22). Chen et al. developed a bipolar emitter p-TPAOXD (**101**). The corresponding device achieved a maximum CE of 0.8 cd A⁻¹ with greenish-blue emission.¹³⁰ By using cores and terminal groups with different electron push/pull properties, Huang et al synthesized a series of star-shaped emitters (**108~110**) with different emission from violet-blue, deep-blue to pure blue.¹³¹ Employing a truxene unit as core and oligo(p-phenylene) as branches, Pei et al synthesized a series of blue emitters (**102~105**) with high quantum yield.¹³² Wang et al reported two triphenylamine centered emitters bridged by diphenyl units to terminal carbazoles with different periphery groups.¹³³ The phosphonate units in TPCA (**106**) are demonstrated to enhance the electron injection to the emission layer from Al cathode. Therefore the device of TPCA exhibited a peak CE of 0.76 cd A⁻¹, much higher than that of p-type TBCA (**107**) with tert-butyl peripheral groups.

2.8 Conclusion

This chapter presented a background for OLEDs. The development history, working mechanism, important parameters and related materials in OLEDs have been introduced. For electroluminescent materials, the evolution of blue fluorescent emitters was thoroughly reviewed, (especially the undoped blue emitters) which are one of the bottle necks for OLEDs application in full-color displays. Specifically, molecular design strategies for undoped blue emitters by reducing the intermolecular interaction as well as reducing fluorescence quenching are demonstrated. Functional blue emitters with hole / electron transporting moieties, especially bipolar blue emitters with both of them are proved to be beneficial for the exciton formation and improve the charge balance in the emitting layer. A undoped bipolar blue emitter has advantages of high quantum yield, high exciton recombination efficiency and less roll-off. Besides, it could also be used as the host material for other low-energy phosphors and consequently simplify the device

structures of hybrid white OLEDs. Star-shaped blue fluorescent materials with independent selection of cores, branches and terminal groups have been comprehensively reviewed as significant candidates for low cost solution-processed OLEDs. So far, solution-processed star-shaped blue emitting materials with bipolar feature and high efficiency are still quite limited. Encouraged by this, it is believed that the research work in this thesis will contribute to this field and paves the way for developing of highly effective, thermally stable and solution-processable blue fluorescent materials.

References

1. M. Pope, H. P. Kallmann, and P. Magnante, *J. Chem. Phys.*, 1963, **38**, 2042–2043.
2. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913–915.
3. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, 1990, **347**, 539–541.
4. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, 1992, **357**, 477–479.
5. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897–1091.
6. A. C. Grimsdale, *Curr. Org. Chem.*, 2010, **14**, 2196–2217.
7. C. Zhong, C. Duan, F. Huang, H. Wu, and Y. Cao, *Chem. Mater.*, 2011, **23**, 326–340.
8. Z. Ma, P. Sonar, and Z. Chen, *Curr. Org. Chem.*, 2010, **14**, 2034–2069.
9. C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610–3616.
10. J. Shi and C. W. Tang, *Appl. Phys. Lett.*, 1997, **70**, 1665–1667.
11. M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature*, 1998, **395**, 151–154.
12. M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.*, 2001, **79**, 156–158.
13. H. Yersin, *Top Curr Chem*, 2004, **241**, 1–26.
14. M. A. Baldo, C. Adachi, and S. R. Forrest., *Phys. Rev. B*, 2000, **62**, 10967–10977.

15. J. C. Deaton, S. C. Switalski, D. Y. Kondakov, R. H. Young, T. D. Pawlik, D. J. Giesen, S. B. Harkins, A. J. M. Miller, S. F. Mickenberg, and J. C. Peters, *J. Am. Chem. Soc.*, 2010, **2**, 9499–9508.
16. D. Y. Kondakov, T. D. Pawlik, T. K. Hatwar, and J. P. Spindler, *J. Appl. Phys.*, 2009, **106**, 124510.
17. C. Adachi, *Jpn. J. Appl. Phys.*, 2014, **53**, 060101.
18. A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato, and C. Adachi, *Adv Mater*, 2009, **21**, 4802–4806.
19. Y. Nichikawa, K. Hiroaki, Y. Onoue, K. Nishikawa, Y. Yoshitake, and T. S. Matsu, *Bunseki Kagaku*, 1983, 32, E115.
20. B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, 2002, vol. 8.
21. H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, *Nature*, 2012, **492**, 234–238.
22. N. Berberan and M. M. Garcia, *J. Am. Chem. Soc.*, 1996, **118**, 9391–9394.
23. R. N. Makers, D. D. C. Bradley, R. W. Jackson, P. L. Burn, and A. B. Holmes, *Synth. Met.*, 1993, **57**, 4128–4133.
24. I. D. Parker, *J. Appl. Phys.*, 1994, **75**, 1656.
25. S. M. Sze and Kwok K. Ng, *Physics of Semiconductor Devices*, John Wiley & Sons Ltd, New York, 1981.
26. S. Kappaun, C. Slugovc, and E. J. List, *Int J Mol Sci*, 2008, **9**, 1527–1547.
27. D. Beljonne, A. Ye, Z. Shuai, and J. Bredas, *Adv. Funct. Mater.*, 2004, **14**, 684–692.
28. Y. Cao, I. D. Parker, G. Yu, C. Zhang, and A. J. Heeger, *Nature*, 1999, **397**, 414–417.
29. J. B. Birks, *Photophysics of Organic Molecules*, John Wiley & Sons Ltd, New York, 1970.
30. H. Fukagawa, T. Shimizu, N. Ohbe, S. Tokito, K. Tokumaru, and H. Fujikake, *Org. Electron.*, 2012, **13**, 1197–1203.
31. D. Y. Kondakov, *J. Appl. Phys.*, 2007, **102**, 114504.
- 32.

http://chemwiki.ucdavis.edu/Core/Theoretical_Chemistry/Fundamentals/Dexter_Energy_Transfer.

33. A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki, and C. Adachi, *Appl. Phys. Lett.*, 2011, **98**, 83302.
34. T. Nakagawa, S. Y. Ku, K. T. Wong, and C. Adachi, *Chem. Commun.*, 2012, **48**, 9580–9582.
35. Y. Cao, G. M. Treacy, P. Smith, and A. J. Heeger, *Appl. Phys. Lett.*, 1992, **60**, 2711.
36. T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, and W. J. Feast, *Appl. Phys. Lett.*, 1999, **75**, 1679.
37. J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.*, 1993, **63**, 2627–2629.
38. I. D. Parker, Q. Pei, and M. Marrocco, *Appl. Phys. Lett.*, 1994, **65**, 1272–1274.
39. M. Redecker, D. D. C. Bradley, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Adv. Mater.*, 1999, **11**, 241–246.
40. C. Schmitz, M. Thelakkat, and H.-W. Schmidt, *Adv. Mater.*, 1999, **11**, 821–826.
41. M. Thelakkat, J. Hagen, D. Haarer, and H.-W. Schmidt, *Synth. Met.*, 1999, **102**, 1125–1128.
42. J. Kido, K. Nagai, Y. Okamoto, and T. Skotheim, *Appl. Phys. Lett.*, 1991, **59**, 2760–2762.
43. J. Morgado, R. H. Friend, and F. Cacialli, *Appl. Phys. Lett.*, 2002, **80**, 2436–2438.
44. W. Shi, S. Fan, F. Huang, W. Yang, R. Liu, and Y. Cao, *J. Mater. Chem.*, 2006, **16**, 2387–2394.
45. X. Gong, S. Wang, D. Moses, G. C. Bazan, and A. J. Heeger, *Adv. Mater.*, 2005, **17**, 2053–2058.
46. T. W. Lee, Y. Chung, O. Kwon, and J. J. Park, *Adv. Funct. Mater.*, 2007, **17**, 390–396.
47. Y. Yang and Q. Pei, *J. Appl. Phys.*, 1995, **77**, 4807–4809.
48. S. C. Moratti, R. Cervini, A. B. Holmes, D. R. Baigent, R. H. Friend, N. C. Greenham, J. Grtiner, and P. J. Hamer, *Synth. Met.*, 1995, **71**, 2117–2120.
49. J. Kido and Y. Iizumi, *Appl. Phys. Lett.*, 1998, **73**, 2721–2723.
50. H. Wu, F. Huang, Y. Mo, W. Yang, D. Wang, J. Peng, and Y. Cao, *Adv. Mater.*, 2004, **16**, 1826–1830.
51. F. Huang, H. Wu, D. Wang, W. Yang, and Y. Cao, *Chem. Mater.*, 2004, **16**, 708–716.
52. F. Huang, Y. H. Niu, Y. Zhang, J. W. Ka, M. S. Liu, and A. K. Y. Jen, *Adv. Mater.*, 2007, **19**, 2010–2014.
53. S.-H. Oh, D. Vak, S.-I. Na, T.-W. Lee, and D.-Y. Kim, *Adv. Mater.*, 2008, **20**, 1624–1629.

54. X. Niu, C. Qin, B. Zhang, J. Yang, Z. Xie, Y. Cheng, and L. Wang, *Appl. Phys. Lett.*, 2007, **90**, 203513.
55. M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Nature*, 2000, **403**, 750–753.
56. <http://hyperphysics.phy-astr.gsu.edu/hbase/vision/cie.html>.
57. http://www.laserpointersafety.com/page52/laser-hazard_diagram/different-lasers-compared.html.
58. R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422–2424.
59. G. Gu, D. Z. Garbuzov, P. E. Burrows, S. Venkatesh, and S. R. Forrest, *Opt. Lett.*, 1997, **22**, 396–398.
60. C. F. Madigan, M.-H. Lu, and J. C. Sturm, *Appl. Phys. Lett.*, 2000, **76**, 1650–1652.
61. S. Möller and S. R. Forrest, *J. Appl. Phys.*, 2002, **91**, 3324–3327.
62. J. Lim, S. S. Oh, D. Y. Kim, S. H. Cho, I. T. Kim, S. H. Han, H. Takezoe, E. H. Choi, G. S. Cho, Y. H. Seo, S. O. Kang, and B. Park, *Opt. Express*, 2006, **14**, 6564–6571.
63. T. Yamasaki, K. Sumioka, and T. Tsutsui, *Appl. Phys. Lett.*, 2000, **76**, 1243–1245.
64. T. Tsutsui, M. Yahiro, H. Yokogawa, K. Kawano, and M. Yokoyama, 2001, 1149–1152.
65. C. Liu, V. Kamaev, and Z. V. Vardeny, *Appl. Phys. Lett.*, 2005, **86**, 143501.
66. N. Thejokalyani and S. J. Dhoble, *Renew. Sustain. Energy Rev.*, 2014, **32**, 448–467.
67. D. H. Huh, G. W. Kim, G. H. Kim, C. Kulshreshtha, and J. H. Kwon, *Synth. Met.*, 2013, **180**, 79–84.
68. L. Hung and C. . Chen, *Mater. Sci. Eng. R Reports*, 2002, **39**, 143–222.
69. T.-H. Liu, C.-Y. Iou, S.-W. Wen, and C. H. Chen, *Thin Solid Films*, 2003, **441**, 223–227.
70. H. S. Jang, K. H. Lee, S. J. Lee, Y. K. Kim, and S. S. Yoon, *Electron. Mater. Lett.*, 2013, **9**, 759–761.
71. K. H. Lee, Y. K. Kim, and S. S. Yoon, *Bull. Korean Chem. Soc.*, 2011, **32**, 4419–4422.
72. J. Chen and D. Ma, *J. Lumin.*, 2007, **122-123**, 636–638.
73. J. Kido and Y. Iizumi, *Chem. Lett.*, 1997, **26**, 963–964.
74. T.-Y. Chu, J.-F. Chen, S.-Y. Chen, C.-J. Chen, and C. H. Chen, *Appl. Phys. Lett.*, 2006, **89**, 53503.
75. K. Okumoto, H. Kanno, Y. Hamaa, H. Takahashi, and K. Shibata, *Appl. Phys. Lett.*, 2006, **89**, 63504.

76. J. Shi and C. W. Tang, *Appl. Phys. Lett.*, 2002, **80**, 3201–3203.
77. K. H. Lee, J. N. You, S. Kang, J. Y. Lee, H. J. Kwon, Y. K. Kim, and S. S. Yoon, *Thin Solid Films*, 2010, **518**, 6253–6258.
78. Z. Li, B. Jiao, Z. Wu, P. Liu, L. Ma, X. Lei, D. Wang, G. Zhou, H. Hu, and X. Hou, *J. Mater. Chem. C*, 2013, **1**, 2183–2192.
79. S. J. He, Z. B. Wang, D. K. Wang, N. Jiang, and Z. H. Lu, *Appl. Phys. Lett.*, 2013, **103**, 83301.
80. X. Xing, L. Xiao, L. Zheng, S. Hu, Z. Chen, B. Qu, and Q. Gong, *J. Mater. Chem.*, 2012, **22**, 15136–15140.
81. Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, and T. Usuki, *Appl. Phys. Lett.*, 1999, **75**, 1682–1684.
82. W. J. Shen, B. Banumathy, H. H. Chen, and C. H. Chen, in *Proceedings of the International Display Manufacturing Conference*, Taipei, Taiwan, 2003, p. 741.
83. K. F. Li, K. W. Cheah, K.-T. Yeung, Y.-K. Cheng, Y.-S. Wu, and C. H. Chen, in *Proceedings of IDMC'05*, Taipei, Taiwan, 2005, p. 136.
84. M.-T. Lee, H.-H. Chen, C.-H. Liao, C.-H. Tsai, and C. H. Chen, *Appl. Phys. Lett.*, 2004, **85**, 3301–3303.
85. C. Hosokawa, S. Sakamoto, and T. Kusumoto, 1995, 389, 444.
86. C. Hosokawa, H. Higashi, H. Nakamura, and T. Kusumoto, *Appl. Phys. Lett.*, 1995, **67**, 3853–3855.
87. S.-W. Wen, M.-T. Lee, and C. H. Chen, *J. Disp. Technol.*, 2005, **1**, 90–99.
88. S. Yue, S. Zhang, Z. Zhang, Y. Wu, P. Wang, R. Guo, Y. Chen, D. Qu, Q. Wu, Y. Zhao, and S. Liu, *J. Lumin.*, 2013, **143**, 619–622.
89. D. Braun and A. J. Heeger, *Thin Solid Films*, 1992, **216**, 96–98.
90. N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature*, 1993, **365**, 628–630.
91. S. Lee, B. Jang, and T. Tsutsui, *Macromolecules*, 2002, **35**, 1356–1364.
92. F. He, H. Zhang, L. He, Y. Zheng, G. Zhang, Y. Ma, and J. Shen, *Synth. Met.*, 2003, **135-136**, 209–210.
93. A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem.Int.Ed.*, 1998, **37**, 402–428.

94. Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Solid State Commun.*, 1991, **80**, 605–608.
95. Y. Yang, Q. Pei, and A. J. Heeger, *J. Appl. Phys.*, 1996, **79**, 934–939.
96. U. Scherf and K. Müllen, *Makromol. Chem., Rapid Commun.*, 1991, **12**, 489–497.
97. S. Qiu, P. Lu, X. Liu, F. Shen, L. Liu, Y. Ma, and J. Shen, *Macromolecules*, 2003, **36**, 9823–9829.
98. C. Chou, S. Hsu, K. Dinakaran, M. Chiu, and K. Wei, *Macromolecules*, 2005, **38**, 745–751.
99. L. Mario, *J. Polym. Sci. Part A Polym. Chem.*, 2001, **39**, 2867–2873.
100. U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, **14**, 477–487.
101. W. Jiang, L. Duan, J. Qiao, D. Zhang, G. Dong, L. Wang, and Y. Qiu, *J. Mater. Chem.*, 2010, **20**, 6131–6137.
102. Z. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita, and M. Kakimoto, *Adv. Funct. Mater.*, 2008, **18**, 584–590.
103. S. Ye, Y. Liu, K. Lu, W. Wu, C. Du, Y. Liu, H. Liu, T. Wu, and G. Yu, *Adv. Funct. Mater.*, 2010, **20**, 3125–3135.
104. Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin, and Y. Cao, *Adv. Funct. Mater.*, 2013, **23**, 1781–1788.
105. Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2010, **39**, 638–655.
106. G. Schwartz, S. Reineke, T. C. Rosenow, K. Walzer, and K. Leo, *Adv. Funct. Mater.*, 2009, **19**, 1319–1333.
107. C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, 1990, **56**, 799–801.
108. Y.-H. Kim, H.-C. Jeong, S.-H. Kim, K. Yang, and S.-K. Kwon, *Adv. Funct. Mater.*, 2005, **15**, 1799–1805.
109. P.-I. Shih, C.-Y. Chuang, C.-H. Chien, E. W.-G. Diau, and C.-F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3141–3146.
110. C.-H. Wu, C.-H. Chien, F.-M. Hsu, P.-I. Shih, and C.-F. Shu, *J. Mater. Chem.*, 2009, **19**, 1464–1470.
111. S.-K. Kim, B. Yang, Y.-I. Park, Y. Ma, J.-Y. Lee, H.-J. Kim, and J. Park, *Org. Electron.*, 2009, **10**, 822–833.

112. C.-H. Chien, C.-K. Chen, F.-M. Hsu, C.-F. Shu, P.-T. Chou, and C.-H. Lai, *Adv. Funct. Mater.*, 2009, **19**, 560–566.
113. J. Huang, J.-H. Su, X. Li, M.-K. Lam, K.-M. Fung, H.-H. Fan, K.-W. Cheah, C. H. Chen, and H. Tian, *J. Mater. Chem.*, 2011, **21**, 2957–2964.
114. C.-C. Wu, Y.-T. Lin, K.-T. Wong, R.-T. Chen, and Y.-Y. Chien, *Adv. Mater.*, 2004, **16**, 61–65.
115. S. Tao, Y. Zhou, C.-S. Lee, X. Zhang, and S.-T. Lee, *Chem. Mater.*, 2010, **22**, 2138–2141.
116. W. Lai, R. Xia, Q. He, P. A. Levermore, W. Huang, and D. D. C. Bradley, *Adv. Mater.*, 2009, **21**, 355–360.
117. M. Zhu and C. Yang, *Chem. Soc. Rev.*, 2013, **42**, 4963–4976.
118. F. Liu, W.-Y. Lai, C. Tang, H.-B. Wu, Q.-Q. Chen, B. Peng, W. Wei, W. Huang, and Y. Cao, *Macromol. Rapid Commun.*, 2008, **29**, 659–664.
119. H. Huang, Q. Fu, S. Zhuang, Y. Liu, L. Wang, J. Chen, D. Ma, and C. Yang, *J. Phys. Chem. C*, 2011, **115**, 4872–4878.
120. C. Liu, Q. Fu, Y. Zou, C. Yang, and J. Qin, *Chem. Mater.*, 2014, **26**, 3074–3083.
121. Q.-D. Liu, J. Lu, J. Ding, M. Day, Y. Tao, P. Barrios, J. Stupak, K. Chan, J. Li, and Y. Chi, *Adv. Funct. Mater.*, 2007, **17**, 1028–1036.
122. W.-Y. Lai, Q.-Y. He, R. Zhu, Q.-Q. Chen, and W. Huang, *Adv. Funct. Mater.*, 2008, **18**, 265–276.
123. C. Liu, Y. Li, Y. Zhang, C. Yang, H. Wu, J. Qin, and Y. Cao, *Chem. - A Eur. J.*, 2012, **18**, 6928–6934.
124. S. Ren, D. Zeng, H. Zhong, Y. Wang, S. Qian, and Q. Fang, *J. Phys. Chem. B*, 2010, **114**, 10374–10383.
125. M. Sims, D. D. C. Bradley, M. Ariu, M. Koeberg, A. Asimakis, M. Grell, and D. G. Lidzey, *Adv. Funct. Mater.*, 2004, **14**, 765–781.
126. S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, and A. B. Holmes, *J. Am. Chem. Soc.*, 2007, **129**, 11910–11911.
127. B. R. Abbel, M. Wolffs, R. A. A. Bovee, J. L. J. Van Dongen, X. Lou, O. Henze, W. J. Feast, E. W. Meijer, and A. P. H. J. Schenning, *Adv. Mater.*, 2009, **21**, 597–602.
128. C. Li and Z. Bo, *Polymer (Guildf.)*, 2010, **51**, 4273–4294.

129. J. Luo, Y. Zhou, Z. Niu, Q. Zhou, Y. Ma, and J. Pei, *J. Am. Chem. Soc.*, 2007, **129**, 11314–11315.
130. H.-C. Yeh, R.-H. Lee, L.-H. Chan, T.-Y. J. Lin, C.-T. Chen, E. Balasubramaniam, and Y.-T. Tao, *Chem. Mater.*, 2001, **13**, 2788–2796.
131. W.-H. Huang, W.-L. Jia, and S. Wang, *Can. J. Chem.*, 2006, **84**, 477–485.
132. W.-B. Zhang, W.-H. Jin, X.-H. Zhou, and J. Pei, *Tetrahedron*, 2007, **63**, 2907–2914.
133. B. Chen, J. Ding, L. Wang, X. Jing, and F. Wang, *Chem. Commun. (Camb.)*, 2012, **48**, 8970–8972.

Chapter 3

Experimental Methodology

In this chapter, experimental techniques involved in this project are described. This project involves a broad range of experiments from material synthesis and characterization to device fabrication, optimization and testing. Understanding the rationale for selection of specific experiments as well as the mechanism of them is very important for doing research in a proper way. Methods and equipment employed in this project are elaborated here including why they were used, what they could achieve, and how they worked.

3.1 Introduction

This project focuses on development of novel emitting materials for OLEDs application. Four types of experiments were carried out. (1) Organic synthesis. Target emitting materials were obtained by a series of organic reactions according to the synthesis routes. (2) Material characterization. The products' purity, chemical identification, and some basic physicochemical properties (such as spectroscopic, electrochemical and thermal properties) are measured by different equipment. (3) OLED devices fabrication and (4) Characterization of device by using target molecules as the emitting materials. The specific reactions, techniques and equipment involved in these experiments are elaborated in sub-Sections from 3.2 to 3.5.

3.2 Synthesis Methods

Chemical structures of target molecules including L1-Cz-OXD and Sn-Cz-OXD ($n = 1\sim5$) are shown in Figure 1.2. The synthesis routes are illustrated in Figure 4.1, Figure 5.1 and Figure 6.1, respectively. Specific synthesis methods are described in the Chapters 4, 5 and 6 respectively. All synthetic methods used in this thesis were traditional reactions. All intermediate compounds were synthesized according to the identical or similar conditions in literature.¹⁻⁷ The mostly used important reactions in this thesis were Suzuki reaction, Ullmann reaction and the Huisgen tetrazole rearrangement reaction. It was necessary to understand the mechanism of these reactions to do the synthesis successfully.

3.2.1 Suzuki Reaction

The Suzuki reaction (also called Suzuki cross-coupling reaction) is the organic reaction of an organohalide with an organoborane to give the coupled product using a palladium(0) catalyst and base. It was first published in 1979 by Suzuki^{8,9} and he shared the 2010 Nobel Prize in Chemistry with Heck and Negishi for their discovery and development of palladium-catalyzed cross couplings in organic synthesis.¹⁰ The Suzuki Reaction could be expressed as the general formula of chemical equation shown in Figure 3.1.

Figure 3.1 General equation for the Suzuki Reaction.

The mechanism of the Suzuki Reaction is shown in Figure 3.2. It begins with the oxidative addition of organohalide **2** to catalyst palladium(0) **1** to form a organopalladium(II) complex **3**. A molecule of the hydroxide or alkoxide base then replaces the halide on compound **3** to give intermediate **4**, while another adds to the organoborane **5** to form a borate complex **6** making its R group more nucleophilic. Next, the transmetalation¹¹ takes place, where the R group of compound **6** replaces the halide group on compound **4**, forming the organopalladium complex **8**. Finally, reductive elimination of **8** gives the desired coupled product **9**, while restoring the original catalyst **1** which completes the catalytic cycle.

Figure 3.2 Mechanism for the Suzuki reaction: Suzuki Cross-Coupling Catalytic Cycle¹².

In this work,^{13–15} the halide was bromine (Br), R₁ and R₂ were aryls, Pd(PPh₃)₄ was used as palladium(0) catalyst (0.01 mole eq), K₂CO₃ was the base, Aliquat 336 was used as the

phase transfer catalyst (PTC, 3d). Since the catalyst $\text{Pd}(\text{PPh}_3)_4$ is sensitive to light, the reaction should be carried out in the dark and the catalyst should be stored in a refrigerator at $-18\text{ }^\circ\text{C}$ to retain activity. An excess of $\text{Pd}(\text{PPh}_3)_4$ could cause catalyst poisoning, leading to low reaction yields.

3.2.2 Ullmann Reaction

The classic Ullmann Reaction is a symmetric biaryl synthesis via copper-catalyzed coupling.¹⁶ The reaction is named after Ullmann, who discovered it in 1901.¹⁷ The traditional version of the Ullmann reaction requires harsh reaction conditions, and the reaction has a reputation for erratic yields. Therefore some improvements and alternative procedures have been introduced.¹⁸ In this thesis, a variations of the Ullmann reaction (so-called the Ullmann-type reaction) is used, which include copper-catalyzed nucleophilic aromatic substitutions between various nucleophiles (e.g., 3,6-di-tert-butyl-9H-carbazole) with aryl halides. These Ullmann-type reactions can be expressed by the general equation shown in Figure 3.3.

Figure 3.3 General equation for the Ullmann-type Reaction.

The mechanisms of the most popular Ullmann-type reactions have been widely studied and a rough picture of the possible catalytic cycle driven by catalyst copper is given in Figure 3.4.^{19,20} Similar to the mechanism of the Suzuki reaction, the catalytic cycle involves the oxidative addition of copper(I)-catalyst to aryl halides which leads to the formation of organocopper(III) intermediates, as well as the reductive elimination of this intermediates, which gives the final coupled products.

In this work, two different synthesis conditions for Ullmann-type reactions were used (see Figure 3.5). Compounds **5** and **7** were synthesized by coupling 3,6-di-tert-butyl-9H-

carbazole (nucleophile) with 4-bromo-4'-iodobiphenyl and 1-bromo-4-iodobenzene respectively in the presence of CuCl (catalyst), KOH (base) and 1,10-phenanthroline.²¹ Compounds **S1-Cz-OXD** and **L1-Cz-OXD** were synthesized by coupling 3,6-di-tert-butyl-9H-carbazole with aryl bromides compounds **11** and **3** in the presence of CuI (catalyst), K₂CO₃ (base), DMPU (solvent) and 18-crown-6.²² This was because 1,10-phenanthroline was only effective with aryl iodides (X = I). For detail of the synthesis experiments, please refer to Chapters 4 and 5 (Sections 4.2.1 and 5.2.1).

Figure 3.4 Two possible pathways Cu(I)/Cu(III) mechanism for the Ullmann reaction^{19,20}.

Figure 3.5 The Ullmann-type reactions used in this study: i) KOH, CuCl, 1,10-phenanthroline, toluene, reflux for 24 hours; ii) CuI, K₂CO₃, 18-crown-6, and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), heat at 170 °C for 48 hours.

3.2.3 Huisgen Tetrazole Rearrangement Reaction

The Huisgen Tetrazole Rearrangement reaction was discovered by Huisgen and Sauer in 1958.²³ This rearrangement reaction of 5-substitued (aryl or alkyl) tetrazoles **1** with carboxylic acid chloride produces the corresponding 2,4-disubstituted 1,3,4-oxadiazole **6** in the presence of a base such as pyridine at elevated temperature.^{23–27} The general formula of Huisgen Tetrazole Rearrangement reaction is shown in Figure 3.6. It had been used as a classic synthesis method for compounds involving 1,3,4-oxadiazoles with aryl or alkyl substituents on the ring, and later on it was expanded for the preparation of 1,2,4-triazoles, 1,3,4-thiadiazoles or 3H-1,3,4-benzotriazepines.^{28,29}

Figure 3.6 General equation for the Huisgen Tetrazole Rearrangement Reaction.

The mechanism of the Huisgen tetrazole rearrangement reaction is illustrated in Figure 3.7. Huisgen proposed that two electrocyclic steps are involved in the reaction. One is the electrocyclic ring opening of acyltetrazole **3**, the other is the electrocyclic ring closure of N-acyl nitrile imines **5**. The aryl- or alkyl-substituted tetrazole **1** has a resonance structure **2**, which is acylated with the acetyl chloride in the presence of base to produce N-acyltetrazole intermediate **3**. Compound **3** is prone to ring opening because the aromaticity in **3** is weakened by a competing carboxamide resonance and this electrocyclic ring opening produces the acylazo diazoalkane intermediate **4**. Followed by this is the loss of nitrogen and the formation of the corresponding N-acyl nitrile imine **5**, which closes to give the disubstituted 1,3,4-oxadiazole ring **6**.

In this thesis, a tris(1,3,4-oxadiazole)phenylene ring was designed as the core of the target molecules. At the beginning toluene was used as solvent according to literature that reported similar compounds to the target molecules in this work.³⁰ However, the reaction

failed, possibly due to the poor solubility of the produced compound **10** in toluene. After several trials, this synthesis was finally successful by using anhydrous pyridine as solvent and heating at 125 °C (reflux).^{4,5} For the detail of this experiment, please see Chapter 5, Section 5.2.1.

Figure 3.7 Mechanism for the Huisgen Tetrazole Rearrangement reaction.

3.3 Characterization of Materials

Basic properties for electroluminescent materials were studied including: (1) chemical structure and molecular weight of the molecules; (2) luminescent properties, which are the most important properties for an emitting material; (3) electrochemical properties, using cyclic Voltammetry (CV) as the traditional method to determine the energy level and bandgap of semiconductors; (4) thermal properties, such as T_g and T_d which provided the thermal stability information of organic materials.

3.3.1 Chemical Structure and Purity

It is important to make sure the synthesized final products are of correct chemical structures as well as high purity because even trace amount of impurities could lead to shift in absorbance and photoluminescent spectra, causing serious fluorescent quenching as well as defects at the interface in the device. The identity and purity of newly reported molecules in the thesis are confirmed by commonly used characterization methods, including nuclear magnetic resonance spectroscopy (NMR spectroscopy) and elemental

analysis (EA). In this work, Both ^1H and ^{13}C NMR spectra of compounds were recorded on a Bruker DRX spectrometer. Elemental analyses of target compounds were carried out on Elementar Vario EL III by using CHN mode.

3.3.2 Molecular Weight

Matrix-assisted laser desorption ionization time-of flight-mass spectrometry (MALDI-TOF-MS) is a soft ionization technique used in mass spectrometry, suitable for the analysis of biomolecules and large organic molecules which tend to be fragile and fragment when ionized by more conventional ionization methods. MALDI utilizes a matrix as a protection from direct laser exposure by forming a co-crystal, which is ablated on laser irradiation, forming predominantly matrix ions in the process. Via a number of different proposed mechanisms, charge can then be transferred to sample molecules, within the ablated plume. In this work, molecular weight of the five target molecules was determined by MALDI-TOF mass spectra (Shimadzu (Kratos) Axima TOF consisting of two time-of-flight mass analyzers in between a sample ion collision cell).

Figure 3.8 MALDI-TOF equipment consists of three parts.

3.3.2.1 Ionization Source

Matrix and sample are spotted on a MALDI plate. The ionization source uses a pulsed nitrogen laser (emitting photons at 337 nm) to irradiate the mixture. The matrix absorbs the laser energy, protects the sample from being destroyed, and assists in the desorption and ionization of the sample molecules.

3.3.2.2 Mass Analyzer

The mass analyzer is a time-of flight (TOF) system. After laser irradiation, ionized molecules can be accelerated under a high voltage (between 15-25 KV) in the flight tube. They move towards the detector, passing through an ion-gate and a collision cell. During this, they are separated according to their molecular weight. Molecules with lighter molecular weights will travel faster up the flight tube than heavier molecules.

3.3.3 Photophysical Properties

The photophysical properties are essential characteristics for emissive materials applied in OLEDs. Traditional characterizations are ultraviolet-visible (UV-vis) spectroscopy and fluorescence spectroscopy. Important information involving emission wavelength (OLED color), fluorescence quantum efficiency (Φ_f) and optical energy bandgap of the analytes could be obtained from these characterizations. For the process of photoluminescence, as a theoretical background of these spectroscopy technologies, please refer to Chapter 2 (Section 2.2.1). These experiments could be performed in solution or in solid state (thin-film). However, the spectrum of solution and film varies with different substrates and solvent polarities. In order to get rid of these influences, quartz cuvette and quartz wafer are usually used as cuvette and substrate and less polar solvents such as hexane and toluene are used to prepare solutions. In this work, the UV-vis absorption spectra of target emitters were collected on UV-Vis Spectrophotometer (Shimadzu UV-2501 PC). Photoluminescence (PL) spectra of target emitters were recorded on Shimadzu RF 5301 Spectrofluorophotometer.

UV-vis spectroscopy is used to calculate optical band gap E_{opt} and also served as a complementary technique for fluorescence spectroscopy to obtain fluorescence quantum efficiency. Absorbance spectra of all target materials as well as the reference compound 9,10-diphenylanthracene were measured in both solution and thin films. In contrast with absorption spectrum which measures transitions from the base state (S_0) to the excited state (S_1), the fluorescence spectrum deals with transitions from S_1 to S_0 . Photoluminescence measurement provides an approximate OLED emitted spectrum in the case that excitons formation and relaxation are confined within a well-defined region in emission layer. Besides, fluorescence quantum yield (Φ_f) could be obtained from the photoluminescence measurement. Photoluminescence quantum yields are among the most important parameters in luminescence analysis. As mentioned, Φ_f is the ratio of photons absorbed to photons emitted through fluorescence (Equation 3.1):

$$\Phi_f = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \quad (3.1)$$

Φ_f can be determined with optical methods either relatively or absolutely.³³ Relative Φ_f can be recorded on common equipment including conventional absorption and fluorescence spectrometers. However, the measurement of the absolute Φ_f requires sophisticated instrumentation of an integrating sphere setup. Therefore the most widely used method for recording Φ_f is the comparative method proposed by Williams et al.,³⁴ which involves the use of well characterized standard samples as reference with known Φ_f values. Assuming that the solutions of the reference and test samples with identical absorbance at the same excitation wavelength absorbs the same number of photons. A simple ratio of the integrated fluorescence intensities of the two solutions recorded under identical conditions should equal to the ratio of their corresponding Φ_f values. Since Φ_f for the reference is known, it is possible to calculate the Φ_f for the test sample by using equation 3.2.

$$\Phi_f = \Phi_{f,\text{ref}} * \frac{\eta^2}{\eta_{\text{ref}}^2} * \frac{I}{A} * \frac{A_{\text{ref}}}{I_{\text{ref}}} \quad (3.2)$$

Where $\Phi_{f,\text{ref}}$ means the quantum yield of the reference compound, η represents the refractive index of solvent, I stands for the integrated fluorescence intensity (peak area of emission spectrum) and A is the value of the absorbance under excitation. The absorbance at the wavelength of excitation is optimally kept in between $A = 0.02 - 0.05$ in order

to avoid inner filter effects and ensure linear response on the intensity. In practice, standards should be selected to ensure maximum overlap of the absorption and emission between sample and reference for valid measurement. A commonly used reference compound for blue emitting materials is 9,10-diphenylanthracene. In this work, the fluorescence quantum efficiency (Φ_f) of target molecules were determined by comparative method in both solution and solid state according to literatures using 9,10-diphenylanthracene as reference.

3.3.4 Electrochemical Properties

Knowledge of charge carrier energy levels in organic thin films is essential for the understanding and design of OLED devices. In a multilayer OLED device, the differences between energies of separate layers act as potential energy barriers to the flow of charge and molecular excited states. In order to achieve good performance, the device should fulfill the energy requirements for each organic layer. Therefore it is important to know the energy levels of HOMO, LUMO and the band gap for a new developed emitting material.

One of the most useful methods for evaluation of the position of HOMO and LUMO energy levels and the energy band diagram is cyclic voltammetry (CV). CV measurements give information of oxidation potential E_{oxd} and reduction potential E_{red} of the analytes. For organic electroluminescent materials, the oxidation potential corresponds to electron extraction from the HOMO level and can be correlated to the ionization potential, whereas the reduction potential is associated with electron affinity and indicates the LUMO level.³⁵ The onset values of redox potentials are determined from intersection of the tangents between the baseline and the signal current. Ferrocene is used as a known reference to calculate the electrochemical energy levels, including the ferrocene value of -4.4 eV. The HOMO and LUMO are calculated using the following empirical equations:³⁶

$$E_{\text{HOMO}} = -e * [E_{\text{onset}}^{\text{oxd}} + 4.4] \quad (3.3)$$

$$E_{\text{LUMO}} = -e * [E_{\text{onset}}^{\text{red}} + 4.4] \quad (3.4)$$

In this thesis of work, due to the difficulty of forming a film of some of the target molecules, CV measurement was carried out in solution by using a CHI660A electrochemical workstation with three electrode system. However, compound S3-Cz-OXD was of poor solubility in methylene chloride, thus no electrochemical data of it was obtained.

3.3.5 Thermal Properties

High durability is an important parameter in the physical performance of OLEDs and is associated with a high glass transition temperature and thermal and morphological stability. These properties can be investigated with thermal analysis techniques that include differential scanning calorimetry (DSC, Q10 TA Instrument, heat/cool/heat mode, heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$, cooling rate: $5\text{ }^{\circ}\text{C min}^{-1}$) and thermogravimetry analyses (TGA, TGA 2950, TA Instrument, Nitrogen gas atmosphere, heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$).

Fluorene based emitting materials usually have an intrinsically unstable EL spectrum due to the oxidation and degradation of fluorene which generates fluorenone moieties.^{37–40} In this thesis, to evaluate the spectrum thermal stability of target molecules, an additional long period heating treatment was applied to the thin films of these materials. The PL spectrum of these thin films were measured from time to time during the heating treatment, which could produce evidence of possible degradation happened in the film.

3.3.6 Surface Morphology of Thin Films

The surface topography of emitting layer deposited by solution-casting is, to some extent, dependent on the molecular structure of the emitting material, and it affects the interface properties between different organic layers in OLEDs and thus influences the final performance. The root-mean-square (RMS) roughness and surface appearance of films of target emitting materials was studied by atomic force microscopy (AFM) for deep understanding of the molecular design. In this work, surface topography of films were studied by AFM Bruker DI 3100 in tapping mode at a rate of 1.0 Hz and size of $3.0\text{ }\mu\text{m}$.

3.3.7 Single Crystal Growth

The solvent evaporation (Figure 3.9) was used to grow a single crystal of L1-Cz-OXD. This is the simplest and the most effective method to grow single crystals and is widely used for most organic crystals. In this method, molecules crystallize due to increased concentration resulting from solvent evaporation. Common organic solvents such as dichloromethane, chloroform, toluene, benzene, and chlorobenzene are used. If a saturated solution is placed in an open system, the solvent can slowly evaporate and form a supersaturated solution. In the meanwhile, the solute will be deposited to form nuclei (seeds), which will grow into larger crystals during the evaporation process.⁴² In this study, mixed solution of chloroform / toluene with different ratios (v/v) from 1:1 to 1:6 were used for crystal growth. The molecular packing of this single crystal was determined by single crystal X-ray diffraction (XRD).

Figure 3.9 Solvent evaporation for single crystal growth.

3.4 Device Fabrication Technology

OLEDs are fabricated by depositing very thin film of organic materials to form multilayer device structures. Deposition techniques involving emitting materials could be divided into dry or wet techniques. Typical examples of dry and wet techniques are vacuum thermal evaporation and spin coating, which are described in detail in the following sections.

3.4.1 Thermal Vacuum Evaporation

Thermal vacuum evaporation is predominantly used for depositing various active layers in fabricating small molecular organic light emitting devices (SM-OLEDs). By using this technique, even complicated multilayer device architecture can be easily achieved. It is usually used with shadow masking, which allows for patterning of a material by preventing deposition in the areas where it is not desired. The high flexibility in multilayer design leads to high efficient devices. However, this technique is limited to vaporizable low molecular weight materials, which can endure thermal stress without decomposition. Besides, it is laborious, relatively expensive and of limited use for large-area devices.

Figure 3.10 Schematic depicted thermal vacuum evaporation.

Equipment for thermal vacuum evaporation is illustrated in Figure 3.10. A boat made out of a resistive metal filled with source materials is placed in a vacuum chamber (typically 10^{-6} torr) and heated by passage of electric current. The source materials, including organic compounds and metals, evaporate or sublime upon heating in the vacuum chamber, followed by the deposition of the evaporated molecules or atoms on the cold

substrate when they contact it, which is located directly above the boat. Because of the even distributions of the initial molecular trajectories, the resulting deposited film is essentially of uniform thickness. In this work, an undoped device based on L1-Cz-OXD was fabricated by using thermal vacuum evaporation fabrication technology.

3.4.2 Spin-Coating

As one of the most widely used wet techniques, spin coating is suitable for polymers and macromolecules with good solubility in organic solutions. The large molecular weight of these big molecules causes their evaporation temperature to be in excess of their decomposition temperature therefore they cannot undergo vacuum thermal evaporation. Compared with vacuum thermal evaporation, spin coating is much cheaper, easier to perform and enables fabrication of large-area and flexible devices with homogeneity throughout the display area.

Figure 3.11 Schematic depicted spin-coating processes.

Spin coating is illustrated in Figure 3.11. The solution of organic emitting material is placed onto an ITO substrate, followed by spinning of the whole system at high speed (typically set at 1000-10,000 rpm). During the spinning, the majority of the solution is expelled from the substrate by centrifugal force, but a fraction of solution stays behind. After undergoing a rapid evaporation caused by the high speed spinning, the residual solution is able to form a thin flat film. This process is controlled by a combination of adhesion forces at the substrate/liquid interface, solution viscosity, and friction at the air/liquid interface. The exact thickness of final film is difficult to predict and is recorded by a surface profilometer. Generally, the thickness of the resultant film is dependent on

the concentration of the solution, the solvent used (if it is volatile or not), the time scales (typically 1~60 seconds), spinning speed and the organic molecule itself (chemical composition, molecular size and morphology). In this work, undoped devices based on all target emitter sexcept S3-Cz-OXD were fabricated by using spin-coating fabrication technology.

3.5 Devices Characterization

The performance of OLED devices are commonly evaluated by current-voltage (V-I) measurements, current density-voltage-luminance (J-V-L) measurements, electroluminescence (EL) spectra, CIE coordinates, luminous efficiencies and so on. In this work, J-V and L-V data were recorded on different equipment simultaneously in the dark when applying a voltage across the OLED device. Electroluminance (EL) spectra of the device driven by an AC voltage are measured with a spectrometer

3.5.1 J-V-L Measurements

J-V-L characterizes the relationships among current density (J), bias voltage (V) and the EL luminance (L). Current density (J) is the ratio of current to the area of the device considered. This characterization allows determining basic parameters of an OLED and to model its behavior in an electrical circuit. Current density and luminance increases exponentially with the driving voltage. Since emission of one photon is the result of the combination of an electron and a hole (an exciton) followed by radiative decay, the luminance is in proportion to the minority carrier current passing through the OLED device. And, the value of L-V curve that intercepts the x-axis is the energy required by a minority carrier to flow from its injecting electrode to the emissive layer. Besides, L-V curve reveals the turn on voltage of the device. The turn on voltage is defined as the voltage that can generate a luminance of 1 cd m^{-2} . Ideally, this value is desired to be as low as possible to achieve a high efficiency. In this work, this was done by separately measuring current-voltage (J-V) and luminance-voltage (L-V) characteristic of the device. J-V characterization revealed the relationship between the direct current through an

OLED and the voltage across it, while L-V plotted the relationship between the luminance emitted by the OLED and the forward voltage. J-V and L-V were recorded using a source meter (Yokogawa GS610) and a luminance meter (Konica Minolta LS-110) with a customized Labview program.

3.5.2 Electroluminescence (EL) Spectra

An electroluminescence (EL) spectrum is a plot of intensity (y-axis) depending on wavelength (x-axis) recorded from the emission of the OLED device. Generally speaking, the EL spectrum can differ from PL spectrum of the same emitting material due to electrical excitation and device optical out coupling. However, the PL spectrum remains to the EL spectrum as it can be regarded as a reference. With further increase in voltage, the intensity of light emission increases and sometimes the EL spectrum also shifts with the voltage, which translates the carrier distribution shift in the OLED stack. In this work, EL spectra were recorded with a spectrometer (Photo Research PR705). The AC voltage used to drive the device for EL spectrum measurement was generated by the same sourcemeter operating in a pulse mode (rectangular shape, 50% duty cycle, 50 Hz).

3.5.3 CIE Coordinates

The color of an emitting light is typically characterized in terms of CIE (International Commission on Illumination) system (see Figure 2.12). Human eye has three types of color sensors that respond to different ranges of wavelengths (short 420~440 nm, middle 530~540 nm and long 560~580 nm). In principle, three parameters, corresponding to levels of stimulus of the three types of sensors, can describe any color sensation. These three values built a tristimulus specification of the objective color of the light spectrum. The CIE 1931 color spaces are the first defined quantitative links between physical pure colors in the electromagnetic visible spectrum and physiological perceived colors in human color vision.

The concept of color can be divided into two parts: brightness and chromaticity. For example, white and grey are of the same chromaticity and different brightness. CIE XYZ color space encompasses all color sensations described by three tristimulus values X, Y, Z. among them, Y is defined as luminance, a measure of brightness; Z is quasi-equal to blue stimulation, and X is a mix of cone response curves chosen to be nonnegative. For any given Y value, the XZ plane will contain all possible chromaticities at that luminance, which could be specified by two derived parameters x and y (derived CIE xyY color space). Any color can be expressed by the chromaticity coordinates x and y on the CIE chromaticity diagram as (x, y) . Using this method the composition of any color in terms of three primaries can be described.⁴³ In this work, CIE coordinates of device were recorded together with the EL spectrum by a spectrometer (Photo Research PR705) at different applied voltages.

3.5.4 Efficiencies

Efficiency refers to various calculated ratios: (1) current efficiency (CE): ratio between the emitted luminance (cd m^{-2}) and the current density (A cm^{-2}); (2) power efficiency (PE): ratio between optical emitted power (lm) and electrical consumed power (W); (3) external quantum efficiency (EQE): ratio between the number of emitted photons and injected carriers, and is expressed in percentage (%). (See Section 2.5.2) In this work, all the efficiencies were calculated by the customized Labview program as a function of voltage.

References

1. S. Maruyama and Y. Kawanishi, *J. Mater. Chem.*, 2002, **12**, 2245–2249.
2. L. Deng, X. Wang, Z. Zhang, and J. Li, *J. Mater. Chem.*, 2012, **22**, 19700–19708.
3. W.-Y. Lai, Q.-Y. He, D.-Y. Chen, and W. Huang, *Chem. Lett.*, 2008, **37**, 986–987.
4. S. Hou and W. K. Chan, *Macromolecules*, 2002, **35**, 850–856.
5. N. Tamoto, C. Adachi, and K. Nagai, *Chem. Mater.*, 1997, **9**, 1077–1085.

6. D. Shin, J. Ahn, Y. Kim, and S. Kwon, *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 3086–3091.
7. R. Fáber, A. Staško, and O. Nuyken, *Macromol. Chem. Phys.*, , 2000, **201**, 2257–2266.
8. N. Miyaura, J. Yamada, and A. Suzuki, *Tetrahedron Lett.*, 1979, **20**, 3437–3440.
9. N. Miyaura and A. Suzuki, *J.C.S. Chem. Comm*, 1979, 866–867.
10. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2010/.
11. K. Matos and J. A. Soderquist, *J Org Chem*, 1998, **63**, 461–470.
12. <http://www.name-reaction.com/suzuki-cross-coupling>.
13. L. Chen, P. Li, H. Tong, Z. Xie, L. Wang, X. Jing, and F. Wang, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 2854–2862.
14. J. Liu and Q. Pei, *Macromolecules*, 2010, **43**, 9608–9612.
15. P.-I. Shih, C.-Y. Chuang, C.-H. Chien, E. W.-G. Diao, and C.-F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3141–3146.
16. P. E. Fanta, *Synthesis (Stuttg.)*, 1974, **1**, 9–21.
17. F. Ullmann and J. Bielecki, *Berichte der Dtsch. Chem. Gesellschaft*, 1901, **34**, 2147–2185.
18. J. Hassan, M. Se, C. Gozzi, E. Schulz, and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359–1469.
19. I. P. Beletskaya and A. V. Cheprakov, *Coord. Chem. Rev.*, 2004, **248**, 2337–2364.
20. E. Sperotto, G. P. M. van Klink, G. van Koten, and J. G. de Vries, *Dalt. Trans.*, 2010, **39**, 10338–10351.
21. B. Liang, S. Hu, Y. Liu, Z. Fan, X. Wang, W. Zhu, H. Wu, and Y. Cao, *Dye. Pigment.*, 2013, **99**, 41–51.
22. S. Ye, Y. Liu, J. Chen, K. Lu, W. Wu, C. Du, Y. Liu, T. Wu, Z. Shuai, and G. Yu, *Adv. Mater.*, 2010, **22**, 4167–4171.
23. R. Huisgen, J. Sauer, and H. J. Sturm, *Angew. Chemie*, 1958, **70**, 272–273.
24. R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, 1960, **93**, 2885–2891.
25. R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Chem. Ber.*, 1960, **93**, 2106–2124.
26. J. Sauer, R. Huisgen, and H. J. Sturm, *Tetrahedron*, 1960, **11**, 241–251.
27. R. Huisgen, C. Axen, and H. Seidl, *Chem. Ber.*, 1965, **98**, 2966–2984.
28. R. Huisgen, H. J. Sturm, and M. Seidel, *Chem. Ber.*, 1961, **94**, 1555–1562.

29. L. El Kaim, L. Grimaud, and S. Wagschal, *Synlett*, 2009, 1315–1317.
30. J. Natera, L. Otero, F. D'Eramo, L. Sereno, F. Fungo, N. Wang, Y. Tsai, and K. Wong, *Macromolecules*, 2009, **42**, 626–635.
31. D. R. T. Zahn, G. N. Gavrilă, and M. Gorgoi, *Chem. Phys.*, 2006, **325**, 99–112.
32. <http://plasticphotovoltaics.org/lc/characterization/lc-advanced-c/lc-uvvis.html>.
33. U. Resch-Genger and K. Rurack, *Pure Appl. Chem.*, 2013, **85**, 2005–2026.
34. A. T. R. Williams, S. A. Winfield, and J. N. Miller, *Analyst*, 1983, **108**, 1067–1071.
35. L. Leonat, G. Sbârcea, and I. V. Brânzoi, *UPB Sci. Bull. Ser. B*, 2013, **75**, 111–118.
36. J. L. Brbdas, R. Silbey, D. S. Boudreaux, and R. R. Chance, *J. Am. Chem. Soc.*, 1983, **105**, 6555–6559.
37. M. Sims, D. D. C. Bradley, M. Ariu, M. Koeberg, A. Asimakis, M. Grell, and D. G. Lidzey, *Adv. Funct. Mater.*, 2004, **14**, 765–781.
38. S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, and A. B. Holmes, *J. Am. Chem. Soc.*, 2007, **129**, 11910–11911.
39. B. R. Abbel, M. Wolffs, R. A. A. Bovee, J. L. J. Van Dongen, X. Lou, O. Henze, W. J. Feast, E. W. Meijer, and A. P. H. J. Schenning, *Adv. Mater.*, 2009, **21**, 597–602.
40. C. Li and Z. Bo, *Polymer (Guildf.)*, 2010, **51**, 4273–4294.
41. https://en.wikipedia.org/wiki/Atomic_force_microscopy.
42. H. Jiang and C. Kloc, *MRS Bull.*, 2013, **38**, 28–33.
43. https://en.wikipedia.org/wiki/CIE_1931_color_space.

Chapter 4

Deep Blue Linear Emitter L1-Cz-OXD

This chapter describes the experimental works related to THE deep blue emitter, including the motivation for its molecular design, synthesis methods, basic characterizations, fabrication of the control device (solution-processed) and other optimized devices. As a deep-blue emitting material, it showed a high quantum efficiency of 41% in neat film with excellent spectra thermal stability. An optimized vacuum-deposited undoped OLED based on L1-Cz-OXD achieved a maximum EQE of 3.09% with a CIE coordination of (0.16, 0.07). It exhibited crystallization and could grow into needle-shaped single crystals, the further study on which could be a subject for future work.

4.1 Introduction

L1-Cz-OXD was designed and synthesized as the linear counterpart of the star-shaped molecule S1-Cz-OXD for the sake of comparative study. L1-Cz-OXD contains an oxadiazole (OXD) unit in the center and two 3,6-di-tert-butylcarbazole (t-BCz) units at both sides linked by a phenyl spacer. Electron deficient oxadiazole and electron rich carbazole derivatives are commonly used acceptor and donor moieties in organic semiconductors due to their good charge transport properties. They also possess excellent thermal stability. Therefore the D- π -A design should endow L1-Cz-OXD with bipolar properties and high thermal stability. Four bulky tert-butyl peripheral groups were introduced to improve the solubility of the molecule in organic solvents and to suppress the molecular aggregation. As a result, L1-Cz-OXD was expected to have high solid quantum efficiency and good undoped properties. In this work, L1-Cz-OXD was successfully synthesized and characterized. A control device was fabricated and optimized. The specific operations of these experiments are detailed in the following sections. The optimized undoped vacuum-deposited devices of L1-Cz-OXD were also fabricated and exhibit much better device performance. The characterization results of both material and devices were fully investigated.

4.2 Experimental Methods

4.2.1 Synthesis

The synthesis route for emitter L1-Cz-OXD and specific reaction conditions for each step are shown in Figure 4.1.

Figure 4.1 Synthetic route for L1-Cz-OXD. Specific reaction conditions: i) $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$, Et_3N , CH_2Cl_2 ; 40 °C for 2 hours; ii) SOCl_2 , toluene; reflux for 12 hours; iii) 3,6-Di-tert-butyl-9H-carbazole, CuI , K_2CO_3 , 18-crown-6, and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), heat at 170 °C for 48 hours.

Synthesis of Compound 2:

Compound **2** was synthesized according to a literature procedure.¹ 2.0 g of hydrazine monohydrate (40 mmol) and 18 mL of triethylamine (compound **1**) were dissolved in 180 mL water in a 500 mL round-bottom flask. 17.6 g of 4-bromobenzoyl chloride (80 mmol) and 180 mL methylene chloride was added to the mixture, which was then heated at 40 °C for 2 hours. After the reaction was finished, the solvents were distilled off to give the crude product. The product was washed with water, and then recrystallized from methyl alcohol to give compound **2** as a white solid (yield 78%).

Synthesis of Compound 3:

Compound **3** was synthesized according to a literature procedure.¹ 8.0 g of compound **2** (20 mmol), 37.5 mL thionyl chloride and 37.5 mL toluene was mixed in a 150 mL flask and refluxed for 12 hours. After the reaction, excess thionyl chloride was distilled off from the reaction mixture and the residue was slowly poured into water. The product was then extracted with methylene chloride and the solvent was evaporated to give crude product. The product was further purified by recrystallization to produce a white solid (yield 83%).

Synthesis of L1-Cz-OXD

L1-Cz-OXD was prepared using an Ullmann Reaction. 5.6 g of 3,6-di-tert-butyl-9H-carbazole (20 mmol), 1.9 g of compound **3** (5 mmol), 2.76 g of K₂CO₃ (20 mmol), 0.19 g of CuI (2 mmol), 1 ml of DMPU, and 0.09 g of 18-crown-6 (0.3 mmol) were mixed in a 150 mL round bottom flask filled with N₂ and stirred at 170 °C for 48 hours. After cooling to room temperature, the mixture was dissolved with dichloromethane and washed with brine several times. Then the solution was dried over anhydrous sodium. After filtration and removal of the solvent, the residue was purified by silica column chromatography followed by precipitation to give the final product **L1-Cz-OXD** as a white solid (yield: 60%). ¹H NMR (CDCl₃, 400 MHz, δ): 1.48 (s, 36H), 7.46-7.53 (m, 8H), 7.81 (d, J = 8.5 Hz, 4H), 8.16 (d, J = 1.3 Hz, 4H), 8.40 (d, J = 8.5 Hz, 4H). ¹³C NMR (CDCl₃, 400 MHz, δ): 29.9, 32.1, 35.0, 109.4, 116.6, 122.0, 124.1, 126.9, 128.7, 138.8, 141.8, 143.9, 164.4. MS (MALDI-TOF, m/z): [M]⁺ Calcd. For C₅₄H₅₆N₄O: 776.5. Found: 774.4. Anal. Calcd. for C₅₄H₅₆N₄O: C, 83.47; H, 7.26; N, 7.21. Found: C, 83.44; H, 7.29; N, 7.15.

4.2.2 Crystal Growth Method

The crystal growth of **L1-Cz-OXD** was carried out by a solution evaporation method. The solubility of **L1-Cz-OXD** in different solvents is listed in Table 4.1. Chloroform and toluene were selected as the good and poor solvent for **L1-Cz-OXD**, respectively. Six tubes were cleaned and dried before being filled with a mixed solution of chloroform / toluene with different ratios (v/v) from 1:1 to 1:6. 5 mg of **L1-Cz-OXD** was added into the mixed solvent in each tube. After this, the six tubes were placed in a fume hood for natural evaporation without disturbance in order to get crystals of **L1-Cz-OXD**.

Table 4.1 Solubility of L1-Cz-OXD in different organic solvents.

Compound	Solubility (mg mL ⁻¹)						
	CHCl ₃	THF	Toluene	CB	Hexane	Toluene : CB (1:1)	CHCl ₃ : CB (1:1)
L1-Cz-OXD	15	8	< 2	6	< 0.1	< 4	12

4.2.3 Device Fabrication and Optimization

L1-Cz-OXD was found to be suitable for spin-coating and vacuum deposition. Its four tert-butyl groups afforded it solution processability and its small molecular size and relatively regular chemical structure enabled its vacuum deposition. Therefore both fabrication technologies were employed for **L1-Cz-OXD**-based OLED devices. Since **L1-Cz-OXD** was the linear counterpart of star-shaped emitter **S1-Cz-OXD**, **L1-Cz-OXD** based OLED device fabricated by spin-coating served as the control device for that based on **S1-Cz-OXD**, with an identical configuration of ITO/PEDOT:PSS/EML/3TPYMB/Cs₂CO₃/Al.

For the sake of comparison, a device with the same device structure of ITO/PEDOT:PSS/L1-Cz-OXD/3TPYMB/Cs₂CO₃/Al was also fabricated. Besides, a **L1-Cz-OXD** based device with an optimized configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al was fabricated by vacuum deposition to achieve better EL performance.

4.2.3.1 Spin-Coating Fabrication

The patterned ITO-coated glass substrates (sheet resistance 10 Ω per square) were cleaned by sequentially immersing them into detergent solution, DI water, acetone and isopropanol in an ultrasonic bath, each for 20 min followed by being blow-dried with nitrogen gas and exposed to O₂ plasma treatment for 10 min. The aim of this step was to remove any organic residue from the substrate, while also enhancing the work function of the ITO and the surface wettability, which facilitates the formation of a film from solutions. Then, filtered PEDOT:PSS (4083) was spin-coated onto the ITO surface to form a thin solid layer (hole transporting layer), followed by annealing treatment for 10 min on hot plate at 150 °C. The annealing was to improve the surface evenness of the deposited layer. Then emitting layer was spin-coated on top of the PEDOT:PSS layer from a solution of **L1-Cz-OXD** (in mixed solvent of CHCl₃: CB, 1: 1 in volume, 12 mg mL⁻¹) followed by annealing. Specifically, the thickness of spin-coated layers could be

tuned by changing the solution concentration and spin parameter; their surface morphology was affected by annealing conditions. After this, the ITO substrate was placed into the vacuum chamber. Electron transporting material (ETM) and electron injecting material (EIM) were successively evaporated on top of the emitting layer in a multi-source vacuum evaporator at a base pressure of 4×10^{-4} Pa. Finally, aluminum was deposited onto all these organic layers through a mask to form the cathode of the OLED. Several active areas (size: $2\text{mm} \times 2\text{mm}$) between patterned ITO and Al were formed on the device for electroluminescence characterization. The specific conditions for spin-coated layers and the parameters for source materials involving 3TPYMB, Cs_2CO_3 and Al in vacuum deposition are summarized in Table 4.2. Except for the deposition of PEDOT:PSS, all other operations were carried out in a glove box (less than 1 ppm oxygen and moisture). Figure 4.2 shows a schematic fabrication process of the OLED device.

Figure 4.2 Schematic of the fabrication process for the OLED device.

4.2.3.2 Vacuum Deposition Fabrication

The fabrication procedure was similar to that of the spin-coating technology. The only difference was the emitting layer which was formed by vacuum evaporation of the emitting materials. The pressure of the chamber for stable evaporation of **L1-Cz-OXD** was around 4×10^{-4} Pa and the deposition rate was about 0.1 nm s^{-1} . The parameters for all used source materials (MoO_3 , TCTA, TPBI and LiF) in vacuum deposition are summarized in Table 4.2.

Simple optimizations of device fabrication included adjusting the thickness of each organic layer, improving the film quality and reducing the interface defects between each layer for better EL performance. For vacuum deposited layers, the rates of evaporation and thickness of deposited layers were monitored with quartz crystals close to the sample holders. A fast evaporation rate might lead to the formation of interface defect. It should also be noted that the vacuum deposition could only be started when the evaporation rate was stable. Calibration of the thickness for each layer was performed using a surface profilometer. The best values for thickness of each organic layer were confirmed by optimizations and they are summarized in Table 4.2.

Table 4.2 Optimized condition for deposition of multilayers in device fabrication.

Spin coated	Spin rate (rpm) / t (s)	Anneal T (°C) / t (min)	Thickness (nm)	Vacuum deposited	T (°C) / I (A)	Thickness (nm)
PEDOT:PSS	4000 / 60	120 / 15	30	MoO ₃	440 / 2.5	2
L1-Cz-OXD	2500 / 60	120 / 30	70	TCTA	250 / 1	35
				L1-Cz-OXD	190 / 1	60
				3TPYMB	127 / 0.5	40
				Cs ₂ CO ₃	630 / 3.4	1
				TPBI	200 / 1	40
				LiF	630 / 3.6	0.5
				Al	>70 / 60	> 120

4.3 Materials Characterization and Methods

4.3.1 NMR Spectroscopy & EA Characterization

Both ¹H and ¹³C NMR spectra of **L1-Cz-OXD** were recorded on a Bruker DRX spectrometer. **L1-Cz-OXD** was dissolved in deuterated chloroform (CDCl₃) to form solutions with a concentration of 2 mg mL⁻¹ (for ¹H) and 5 mg mL⁻¹ (for ¹³C). Each solution was put into a NMR tube covered with a cap. Then the NMR sample tube was installed with a spinner and then was inserted into the magnet. The calibration, setting of parameters, adjusting of acquired signals and data analysis were all completed on a

controlling computer using the Bruker software.

Elemental analyses of **L1-Cz-OXD** were carried out on an Elementar Vario EL III by using CHN mode. 5 mg of **L1-Cz-OXD** was weighed and wrapped in a tinfoil as the real samples. Acetanilide (also about 5 mg in tinfoil) was used as the standard sample, while blank sample was also used for reference. All the samples were put into the sample disk. After calibration, the measurement was run in the following order: blank sample with oxygen → blank sample without oxygen → five standard samples → real sample. The setting of parameters and collection of data were completed using software of Elementar Vario EL III.

4.3.2 MALDI-TOF Spectrometry

Molecular weight of **L1-Cz-OXD** was determined using the MALDI-TOF technique. The instrument used was a Shimadzu (Kratos) Axima TOF² consisting of two time-of-flight mass analyzers in between a sample ion collision cell. The sample plate was cleaned sequentially with acetone, methanol and fresh DI water, each for 10 min in an ultrasonic bath and then dried before use. **L1-Cz-OXD** was dissolved in dry THF solvent at a concentration of 2 mg mL⁻¹. 1 μL of this solution was taken by pipettor and was transferred onto the sample plate. After evaporation of solvent, a deposited thin film of **L1-Cz-OXD** was formed (see Figure 4.3). No sacrificial matrix was used because **L1-Cz-OXD** is a small molecule (its molecular weight is not very high). The plate was then inserted into the instrument. The operations of calibration, measurement and analysis of data were completed on a controlling computer using the corresponding software.

Figure 4.3 Sample preparation of MALDI-TOF.

4.3.3 Absorption and Photoluminescence Spectroscopy

UV-visible absorption spectrum of **L1-Cz-OXD** was collected on UV-Vis Spectrophotometer (Shimadzu UV-2501 PC). Photoluminescence (PL) spectrum of **L1-Cz-OXD** was recorded on Shimadzu RF 5301 Spectrofluorophotometer. Both measurements were performed in dilute solution, doped PMMA film and neat film.

4.3.3.1 Sample Preparation

Three types of samples were prepared as described below:

1) Dilute Solution:

Quartz cuvettes were cleaned with dichloromethane and acetone. Then they were blow-dried with nitrogen gas and filled with a dilute toluene solution of **L1-Cz-OXD** (10^{-6} M) as the sample solution. 9,10-diphenylanthracene in toluene at the same concentration was used as a reference.

2) L1-Cz-OXD Doped PMMA Film:

Quartz wafers were cleaned and blow-dried with nitrogen gas. 0.7 mg of **L1-Cz-OXD** and 10 mg of PMMA ($M_w \sim 20,000$ mg mol⁻¹) were well dissolved in 1 mL chloroform to form a mixed solution (concentration $< 10^{-3}$ M). The PMMA solution containing **L1-Cz-OXD** was spin-coated (3000 rpm, 60 sec) onto the quartz wafers followed by annealing (120 °C, 30 min) treatment to form a thin film of **L1-Cz-OXD** doped PMMA layer on quartz substrate using as sample. 9,10-diphenylanthracene doped PMMA film (concentration $< 10^{-3}$ M) was used as a reference.

3) L1-Cz-OXD Neat Film:

Quartz wafers were cleaned and dried before use. 6 mg of **L1-Cz-OXD** was dissolved in 1 mL of chloroform and a thin film of it was deposited on quartz substrates by spin-coating (3000 rpm, 60 sec) and annealing (120 °C, 30 min). 9,10-diphenylanthracene doped PMMA film (concentration $< 10^{-3}$ M) was used as reference.

4.3.3.2 Absorption Spectroscopy

Before the measurement of absorption spectra, the optical path alignment should be ready and the calibration of the baseline was carried out using blank samples of toluene solution, pure PMMA films on quartz substrates and clean quartz wafers, corresponding to the three types of samples. Then the sample / reference cuvettes or wafers were placed into the spectrophotometer for measurement. The scanning range of the absorption spectrum from samples was from 280 nm to 700 nm. The peak value (λ_{max}) in absorption spectrum was usually the excitation wavelength in fluorescence spectroscopy.

4.3.3.3 Fluorescence Spectroscopy

The excitation wavelength for **L1-Cz-OXD** was determined by the maximum absorption in UV-vis spectrum. This value was 360 nm. After setting of parameters, the sample / reference cuvettes or wafers were placed into the spectrophotometer for measurement. The scanning range of the PL spectrum was from 380 nm to 700 nm.

4.3.4 Spectrum Thermal Stability

Solid neat film of **L1-Cz-OXD** was spin-cast (3000 rpm, 60 sec) onto a clean quartz wafer from a 6 mg mL⁻¹ chloroform solution. Then it was annealed at 120 °C for 30 min. PL spectrum of this film was recorded on Shimadzu RF 5301 Spectrofluorophotometer. The film was heated at 150 °C on a hot plate in ambient air. The heating process was interrupted by PL spectrum measurement from time to time. This heating treatment lasted for more than 9 days (about 220 hours)

4.3.5 Cyclic Voltammetry

Cyclic voltammetry characterization of **L1-Cz-OXD** was performed in solution by using CHI660A electrochemical workstation with a three-electrode-system (see Figure 4.4). A solution of 0.1 M Tetrabutylammonium perchlorate ((C₄H₉)₄NClO₄) in anhydrous

methylene chloride (CH_2Cl_2) was prepared in advance as the supporting electrolyte. Before measurement, the glassy carbon working electrode was carefully grinded and cleaned to ensure a smooth surface and a good electron transporting ability. A Pt wire (counter electrode) and an Ag/AgCl reference electrode were also rinsed thoroughly. 10 mL of supporting electrolyte and 0.1 mg of **L1-Cz-OXD** were added into the electrolytic bath. Three electrodes were then immersed in this solution without touching each other. Then, the circuits was connected and the solution was bubbled with nitrogen gas for more than 10 minutes (nitrogen-saturated solution). The studying of redox behavior of **L1-Cz-OXD** was achieved by running a voltammogram at a scan rate of 100 mV s^{-1} between -1.8V and 1.8V (the value can be further modified depending on the resultant curve), which provided a CV curve.

Figure 4.4 Three electrode system for CV measurement in solution.

4.3.6 Differential Scanning Calorimetry

Glass transition temperature of **L1-Cz-OXD** was recorded using differential scanning calorimetry (DSC, Q10 TA Instrument). 5 mg of **L1-Cz-OXD** was weighed and sealed using standard aluminium sample pan, a blank standard pan/lid pair was used as the reference. The measure mode was heat/cool/heat process with a constant heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and a constant cooling rate of $5 \text{ }^\circ\text{C min}^{-1}$ in the range from room temperature to $300 \text{ }^\circ\text{C}$ under nitrogen purge.

4.3.7 Thermogravimetric Analyses

Thermal decomposition temperature of **L1-Cz-OXD** was determined by thermogravimetric analyses (TGA 2950, TA Instrument). Dynamic heating was performed from room temperature to 800 °C with a constant heating rate of 10 °C min⁻¹ under a constant nitrogen purge. Sample size was kept at 10~15 mg.

4.3.8 Atomic Force Microscopy

Surface topography of films (both non-annealed and annealed) of **L1-Cz-OXD** was obtained by atomic-force microscopy (AFM Bruker DI 3100) in tapping mode at a rate of 1.0 Hz and size of 3.0 µm. Sample films of L1-Cz-OXD were spin-cast (3000 rpm, 60 sec) onto flat glass substrate from a 6 mg mL⁻¹ chloroform solution. The annealing treatment was done at 120 °C for 30 min. The operations of calibration, scanning and analysis of images were completed on a controlling computer using the corresponding software.

4.4 Characterization of OLED Devices

After the deposition of different functional materials, the resultant OLED device was obtained, with multi-layers of organic compounds covering the ITO glass. For the device characterization, it was necessary to connect the circuit and apply a voltage between anode (ITO) and cathode (Al). Therefore the organic layers in the non-active area above ITO patterns should be removed in order to expose the ITO layer, as shown in Figure 4.5. Generally, organic layers were erased by cotton bud with CHCl₃ solvent or scratched by a flat glass sheet. After the active area was lighted, J-V and L-V data of it were collected using a source meter (Yokogawa GS610) and a luminance meter (Konica Minolta LS-110) with a customized Labview program. Electroluminescence (EL) spectra were recorded with a spectrometer (Photo Research PR705). The AC voltage used to drive the device for EL spectrum measurement was generated by the same sourcemeter operating in a pulse mode (rectangular shape, 50% duty cycle, 50 Hz).

Figure 4.5 left) Schematic diagram for lighting an OLED device; right) Real device images: unlighted (upper) and lighted (lower).

4.5 Results and Discussion for Synthesized Materials

4.5.1 Chemical Structure and Molecular Weight

^1H NMR, ^{13}C NMR, EA and MALDI-TOF data of **L1-Cz-OXD** are summarized in Section 4.2.1. The spectrum for NMR and MALDI-TOF result are attached in the Appendix. The chemical structure and purity of **L1-Cz-OXD** are well proved by the combined results of NMR, EA and MALDI-TOF measurements. It is worth mentioning that in the MALDI-TOF spectrum, the main peak was located at 774.40, which was in accordance with the theoretical molecular weight of **L1-Cz-OXD**, which was 776.5 g mol $^{-1}$. Besides, two small peaks at 759.42 and 718.51 were observed, which could be attributed to the fragmentation of the molecule losing a methyl and a tert-butyl group, respectively.

4.5.2 Photophysical Properties

Optical energy bandgap (E_{opt}), triplet energy (E_{T}) and relative fluorescence quantum yields (Φ_{f}) of the analytes were obtained from the characterization of their absorbance and photoluminescence spectra. Usually, E_{opt} (eV) of emitting material depends on the incident photon wavelength by means of a Planck relation (equation 4.1):

$$E_{\text{opt}} = h * \nu = h * \frac{c}{\lambda} \approx \frac{1240 \text{ nm}}{\lambda_{\text{onset}}} \quad (4.1)$$

Where h is Planck's constant, ν is the wave frequency; c is lightspeed in vacuum and λ_{onset} is the longest incident photon wavelength. Experimentally, the optical band gap E_{opt} of the analytes is estimated by linear extrapolation from the absorption feature edge to $A=0$ and subsequent conversion of the wavelength (nm) into energy value versus vacuum (eV).

Φ_f of emitting material both in dilute solution and in solid film was calculated according to Equation 4.3, using 9,10-diphenylanthracene ($\Phi_f = 0.92$ in dilute toluene at a concentration of about 10^{-6} M and $\Phi_f = 0.83$ in doped PMMA films^{2,3} with a concentration less than 1×10^{-3} M) as standard reference.

$$\phi_n = \frac{\phi_s I_n A_s \eta_n^2}{A_n I_s \eta_s^2} \quad (4.3)$$

Where Φ_n is the fluorescence quantum efficiency of sample material, Φ_s is the known fluorescence quantum efficiency of the standard reference material (9,10-diphenylanthracene). I_n and I_s are the integrated intensities (peak area of PL spectrum) of sample and reference materials, respectively. η_n and η_s stand for the refractive indexes of the corresponding solutions ($\eta_{\text{toluene}} = 1.4961$, $\eta_{\text{PMMA}} = 1.492$). In this thesis, sample and reference materials were dissolved or dispersed in the same solution or matrix, therefore the value of η_n^2 / η_s^2 is 1). A_n and A_s are the absorbance of the sample and the standard at the excitation wavelength. Notice that the absorbance at the wavelength of excitation is optimally kept in the range $A = 0.02 \sim 0.05$ in order to avoid inner filter effects (defined as the decrease in the fluorescence intensity because of the chromophore optical absorption in the excitation or emission region when the solution is of high concentration)⁴⁻⁶ and ensure a linear response to the intensity.

Figure 4.6 shows the UV-vis absorption and photoluminescence (PL) spectra of L1-Cz-OXD in a dilute toluene solution, in a dispersed PMMA film and in a neat film on quartz substrates, respectively. The corresponding photophysical properties are summarized in Table 4.3. In dilute toluene, the maximum absorption peak of L1-Cz-OXD located at 354 nm and it exhibited an intensive deep-blue emission centered at 397 nm. The onset value of absorption was 390 nm, from which the value of E_{opt} could be calculated to be 3.18 eV. The photoluminescence quantum yield Φ_f of L1-Cz-OXD was calculated to be 95% by

using 9,10-diphenylanthracene as reference.

Figure 4.6 Normalized (left) UV-vis and (right) PL spectra of L1-Cz-OXD in dilute toluene, doped PMMA film and neat film under room-temperature.

Table 4.3 Summary of photophysical properties for L1-Cz-OXD.

$\lambda_{\max}^{\text{Abs}}^{[a]}$ (nm)	$\lambda_{\max}^{\text{PL}}^{[a]}$ (nm)	$\Phi_f^{[a],[b]}$ (%)	$\lambda_{\text{onset}}^{[c]}$ (nm)	$E_{\text{opt}}^{[c]}$ (eV)
354 / 356 / 364	397 / 421 / 427	95 / 64 / 41	390	3.18

^[a]: The three values are corresponding to UV-vis and PL measurements performed in dilution toluene solution (10^{-6} M) / doped PMMA film / neat film; ^[b]: the relative values of Φ_f is calculated by using 9,10-diphenylanthracene as reference ($\Phi_f = 0.92$ in dilute toluene at a concentration of about 10^{-6} M and $\Phi_f = 0.83$ in doped PMMA films^{2,3} with a concentration less than 1×10^{-3} M); ^[c]: The value are estimated from UV-vis measurements performed in dilution toluene solution (10^{-6} M).

When dispersed in a PMMA film, the PL of L1-Cz-OXD showed a broader emission spectrum with a small red-shift (PL peak locates at 421 nm). The absorption spectrum became wider with higher onset value and the peak was slightly red-shifted to 356 nm. The value of Φ_f was greatly reduced to 64%. This was caused by the weak aggregation since molecules tend to be closely packed together in solid state. In a spin-casted neat film, both absorption and PL spectrum of L1-Cz-OXD exhibited further red-shift to 364 nm and 427 nm, respectively. Compared with the doped-PMMA film where L1-Cz-OXD was still in isolated state, in the neat film L1-Cz-OXD molecules touched each other. The

increased intermolecular interactions led to red-shifted spectrum and serious concentration quenching. As a result, the quantum yield Φ_f of this film was further reduced to 41%. However, this was still a high value for a solid neat film, indicating the high potential of L1-Cz-OXD to be used as an undoped emitter.

4.5.3 Electrochemical Properties

In order to determine the HOMO energy level, the LUMO energy level and the HOMO / LUMO energy bandgap of L1-Cz-OXD, CV measurements were carried out by using three-electrode system in solution and the resultant cyclic voltammograms, shown in Figure 4.7. The curve exhibited reversible oxidation and reduction behavior under positive and negative drive bias, which is attributed to carbazole (*t*-BCz) donor units and oxadiazole (OXD) acceptor unit respectively, indicating its distinct bipolar properties. The onset oxidation and reduction potentials of L1-Cz-OXD were determined to be 1.27 V and -1.58 V from the curve. Their HOMO / LUMO energy levels were then calculated by equations 4.4 and 4.5 to be -5.67 eV and -2.28 eV, respectively.

$$E_{\text{HOMO}} = -e * [E_{\text{onset}}^{\text{oxd}} + 4.4] \quad (4.4)$$

$$E_{\text{LUMO}} = -e * [E_{\text{onset}}^{\text{red}} + 4.4] \quad (4.5)$$

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4.6)$$

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt}} \quad (4.7)$$

The energy bandgap between HOMO and LUMO energy levels was 2.85 eV. This is a major deviation for the optical energy bandgap calculated from UV-vis spectroscopy ($E_{\text{opt}} = 3.18$ eV). This is caused by different characterization methods being used since CV measurement was a redox process while UV-vis spectroscopy is an optical process. The LUMO energy from CV is usually believed to be unreliable in donor-acceptor molecules because it only reveals the reduction of the acceptor moiety of the emitting material on the electrode in solution and cannot accurately represent the process of obtaining an electron by injection. A more reliable LUMO energy level was determined with Equation 4.7, which combined the UV-vis spectroscopy and CV measurements together. The value

was calculated to be -2.53 eV. All these data are summarized in Table 4.4.

Figure 4.7 Cyclic voltammograms of L1-Cz-OXD.

Table 4.4 Electrochemical and thermal properties of L1-Cz-OXD.

$E_{\text{onset}}^{\text{oxd}}$ ^[a]	$E_{\text{onset}}^{\text{red}}$ ^[a]	HOMO ^[b]	LUMO ^[b]	LUMO ^[c]	E_g ^[d]	T_g	T_d	RMS ^{[e] / [f]}
(V)	(V)	(eV)	(eV)	(eV)	(eV)	(°C)	(°C)	(nm)
1.27	-1.58	-5.67	-2.82	-2.53	2.85 / 3.14	141	423	0.52 / 0.48

^[a]: Performed in 0.1M (C₄H₉)₄NClO₄ in CH₂Cl₂; ^[b]: Estimated from $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ obtained from CV curve with ferrocene calibration; ^[c]: Calculated from equation 4.7; ^[d]: Energy bandgap calculated from CV measurement / estimated from UV-vis spectroscopy; ^[e]: RMS value of non-annealed films and ^[f]: RMS value of annealed films.

4.5.4 Thermal Properties and Spectrum Thermal Stability

The thermal properties of L1-Cz-OXD were explored by TGA and DSC measurements. The thermographs are shown in Figure 4.8 and the corresponding data are summarized in Table 4.4. The glass transition temperature (T_g) determined to be 141 °C for L1-Cz-OXD. The decomposition temperature (T_d) of analyte is generally defined as the temperature at

which the analyte lose 5% of its weight. T_d of L1-Cz-OXD was found to be 423 °C. The high T_d and T_g temperatures indicate a good thermal stability.

Figure 4.8 DSC traces (a) and TGA thermogram (b) of L1-Cz-OXD.

To further study the spectra stability of **L1-Cz-OXD**, prolonged heating was applied to the solid film. As shown in Figure 4.9, there was almost no significant change in the PL spectrum after 220 hours of annealing at 150 °C in ambient air, indicating **L1-Cz-OXD** has excellent spectral thermal stability compared with fluorene-based materials. This is favorable for the overall stability of the electroluminescent devices.

Figure 4.9 Normalized photoluminescent spectra of L1-Cz-OXD during long period heating treatment.

4.5.5 Surface Morphology

The surface morphology of the emitting layer is very important for OLED devices. A stable amorphous film not only provides good interface properties (fewer defects) between organic layers, but also prolongs the device operational lifetime. The excellent heat tolerance of L1-Cz-OXD indicated that it could form a thermally stable film. Besides, four bulky t-butyl groups at both sides of L1-Cz-OXD endowed good morphology for its film. In order to verify this, the surface morphology of spin-casted thin films of L1-Cz-OXD was recorded with AFM (Figure 4.10).

The solution-processed film of L1-Cz-OXD showed smooth surface morphology with the root-mean-square (RMS) roughness of 0.52 nm and 0.48 nm for films before and after annealing treatment (heating at 120 °C for 30 min), respectively. The slight decrease in RMS roughness indicated annealing treatment could improve the surface quality of the film. This could also be proved by the AFM images. The color contrast between the raised and depressed areas on the surface of the non-annealed film implied the large particles present. While in the annealed film, the color was much more evenly distributed, implying a much more homogeneous film.

Figure 4.10 AFM images of L1-Cz-OXD films spin-casted from chloroform solution (a) before annealing and (b) after annealing.

4.5.6 Single Crystal Properties

A needle shaped single crystals of L1-Cz-OXD were obtained by solution evaporation (three months' slow evaporation) in a mixture of chloroform : CB (volume 1:6). The molecular packing of this single crystal was determined by single crystal X-ray diffraction (XRD). The results are shown in Figure 4.11. The orthorhombic single crystals belonged to the $Pbcn$ (60) space group with $a = 5.6766(11)$ Å, $b = 20.846(5)$ Å, $c = 37.522(8)$ Å.

Figure 4.11 Molecular packing of orthorhombic structure: (a) along (100) direction, (b) along (010) direction, (c) along (001) direction, (d) along (111) direction.

4.6 Results and Discussion for Undoped OLED Devices

The initial reason for designing L1-Cz-OXD was to use it as a linear counterpart for the star-shaped molecule S1-Cz-OXD. It was used as the emitting layer (EML) for the control device. However, different from those star-shaped molecules which emit pure blue light (PL peaking at around 450 nm, solid film), L1-Cz-OXD was a deep-blue emitter with a λ_{max} of 427 nm in solid neat films. It was worthwhile to further study its

electroluminescence performance since the deep-blue emission enables it to be used not only an emitting material but also a host material for blue OLEDs. In this project, three undoped devices (A1, A2 and B) based on L1-Cz-OXD were fabricated and optimized. Their configurations are shown in Figure 4.12.

Figure 4.12 Energy level diagram of the undoped devices for L1-Cz-OXD: Device **A1** was fabricated by spin-coating, employing the configuration of ITO/PEDOT:PSS/L1-Cz-OXD/3TPYMB/Cs₂CO₃/Al; Device **A2** was fabricated by vacuum-deposition with the same configuration of device **A1**; Device **B** was fabricated by vacuum-deposition, employing an optimized configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al.

Device **A1** was the control device based on the star-shaped emitter S1-Cz-OXD (Device **C1**, for detail please refer to Section 5.6.1). For the sake of constructive analysis, device **C1** and **A1** were of the same device structure and were both fabricated by spin-coating. Considering the small molecular size, high thermal decomposition temperature and the crystallization ability, L1-Cz-OXD was supposed to also be suitable for vacuum-deposition. It would be interesting to study the influence of different fabrication technology on device performance, so device **A2** was fabricated. Here PEDOT:PSS (poly(3,4-ethylenedioxythiophene)polystyrene sulfonate) was employed as hole transporting layer; 3TPYMB (tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane) served as both electron transporting and hole blocking layer and Cs₂CO₃ was used as an electron injecting layer.

Figure 4.13 Normalized EL spectra of device A1, A2 and B at different applied voltages.

The HOMO level of emitting layer L1-Cz-OXD was -5.67 eV, much lower than the work function of ITO glass (5.0 eV) and the hole injection layer PEDOT:PSS (-5.2 eV). This is a big energy barrier for hole injection into the emitting layer. In order to solve this problem, MoO₃ buffer layer and Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) hole transporting layer were introduced to fabricate an optimized device **B**. MoO₃ is a good hole injection material for optoelectronic devices.⁷ It was first employed in OPV field to achieve high efficiency and it also worked well in OLEDs.⁸ The mid-gap states of MoO₃ evaporated thin films aligned well with the HOMO level of organic HTL layer and reduced the hole injection barrier at the interface.⁹ TCTA was selected because the HOMO level (-5.6 eV) of it was close to that of L1-Cz-OXD, which could facilitate the injection of hole from into the emitting layer. The energy level diagram of these devices is shown in Figure 4.12.

The EL spectra of devices A1, A2 and B are shown in Figure 4.13. All of them are quite stable under different driving voltages, indicating an excellent stability in emission. They all exhibited deep-blue emission purely from L1-Cz-OXD peaking at about 429 nm. The corresponding CIE coordinates are (0.16, 0.07), which almost matches the standard blue point recommended by the National Television Standards Committee (NTSC) (0.15, 0.07).¹⁰

Figure 4.14 illustrates the J-V-L characteristic of the three undoped devices and the performances of these devices are summarized in Table 4.5. Device A1 turned on at 4.3 V and the maximum EQE, CE, and PE were 1.30%, 1.03 cd A⁻¹, and 0.63 lm W⁻¹, respectively. The maximum luminance was only 686 cd m⁻². However, with identical device configuration, device A2 exhibited much better performance. The turn-on voltage slightly increased to 4.6 V while EL efficiencies were greatly improved, and achieved a maximum EQE of 2.42%, CE of 1.27 cd A⁻¹, and PE of 0.67 lm W⁻¹. The maximum brightness of device A2 achieved 1731 cd m⁻². A possible reason for this result was that the thin film of L1-Cz-OXD deposited from vacuum-evaporation was of higher quality compared with that deposited from spin-coating. L1-Cz-OXD was of poor solubility in toluene and chlorobenzene (CB), therefore a mixed solvent of chloroform and CB (1:1 in volume) was used to facilitate the spin-coating process because chloroform was a better solvent for L1-Cz-OXD. However, chloroform is not a good solvent for spin-coating technology because it is extremely volatile. The rapid evaporation of solvent might lead to the formation of defects inside or on the surface of the deposited films. Besides, it also brought difficulties in precisely controlling the thickness of the deposited layer. From this point of view, vacuum-deposition was more suitable for L1-Cz-OXD since it could undergo the vaporization process without being broken down. In vacuum-evaporation, L1-Cz-OXD could form an even homogeneous film with a certain thickness.

Figure 4.14 (a) shows that the value of current density of device A1 was higher than that of device A2 under the same driving voltage, and the brightness of device A1 increased very fast from 4 to 5 V exceeding that of device B, but then became very slow and was much lower than that of device A2. This indicated the poor recombination efficiency of

holes and electrons in device A1, which is likely caused by the defects in the emitting layer.

Figure 4.14 EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices A1, A2 and B.

Table 4.5 EL performance of devices A1, A2 and B.

Device	$V_{on}^{[a]}$ (V)	at 100 / 1000 cd m ⁻² ^[b] (V/%)	Max L (cd m ⁻² , V)	EQE (%)	CE (cd A ⁻¹)	PE (lm W ⁻¹)	λ_{max} (nm)	CIE (x, y)
A1	4.3	6.5, 0.3 / ----, ----	686, 10.4	1.30	1.03	0.63	429	(0.16, 0.07)
A2	4.6	6.1, 2.3 / 8.5, 1.3	1731, 11.6	2.42	1.27	0.67	429	(0.16, 0.07)
B	3.7	5.3, 3.0 / 7.2, 2.9	3547, 10.6	3.09	1.46	1.06	429	(0.16, 0.07)

^[a]: Turn-on voltage at which brightness exceeds 1 cd m⁻²; ^[b]: The values of driving voltage and EQE of device at 100 and 1000 cd m⁻².

Device B (fabricated by vacuum-deposition with a configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al) displayed a low turn-on voltage at 3.7 V. It exhibited a maximum brightness of 3547 cd m⁻² at 10.6 V, a maximum EQE of 3.09%, CE of 1.46 cd A⁻¹, and PE of 1.06 lm W⁻¹, with a CIE coordination of (0.16, 0.17).

4.7 Conclusions

In summary, L1-Cz-OXD as the linear counterpart was successfully synthesized, characterized and employed as the emitting material in an undoped solution processed OLED device for the sake of comparison to the star-shaped molecule S1-Cz-OXD. L1-Cz-OXD was a D- π -A type molecule. Electron withdrawing oxadiazole (OXD) and electron donating carbazole (t-BCz) functioned as acceptor and donor unit, providing L1-Cz-OXD with bipolar properties. Besides, these moieties were of high thermal stability. Bulky tert-butyl groups were introduced to suppress the molecular aggregation and improve the solubility. With such molecular design, L1-Cz-OXD possessed solution-processability, high solid quantum efficiency (43%) as well as excellent spectrum thermal stability. It emitted saturated deep-blue emission peaking at 427 nm in neat film and had potential as undoped blue emitter and host material in hybrid white OLEDs. However, the solution-processed undoped blue OLED based on L1-Cz-OXD exhibited poorer performance compared with that fabricated by vacuum-deposition technology due to the low solubility of L1-Cz-OXD and the low quality of the resultant film from spin-coating. This indicated the solubility and the film forming ability of an emitting material was very important for the low-cost solution-processed fabrication (that is why the star-shaped molecules were developed). Considering L1-Cz-OXD was more suitable for vacuum-deposition fabrication, a undoped device with configurations of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al was fabricated. After optimization, the device achieved a maximum EQE of 3.09% and a deep blue EL emission with CIE = (0.16, 0.07), which was close to the blue coordinate (0.14, 0.08) in the NTSC color gamut.

References

1. D. Shin, J. Ahn, Y. Kim, and S. Kwon, *J. Polym. Sci. Part A Polym. Chem.*, 2000, **38**, 3086–3091.
2. W. Lai, R. Xia, Q. He, P. A. Levermore, W. Huang, and D. D. C. Bradley, *Adv. Mater.*, 2009, **21**, 355–360.
3. W.-Y. Lai, Q.-Y. He, R. Zhu, Q.-Q. Chen, and W. Huang, *Adv. Funct. Mater.*, 2008, **18**, 265–276.
4. U. Resch-Genger and K. Rurack, *Pure Appl. Chem.*, 2013, **85**, 2005–2026.
5. B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, 2002, vol. 8.
6. <http://www.fluorotools.com/software/ae/documentation/qy>.
7. H. You, Y. Dai, Z. Zhang, and D. Ma, *J. Appl. Phys.*, 2007, **101**, 026105.
8. S. Höfle, H. Do, E. Mankel, M. Pfaff, Z. Zhang, D. Bahro, T. Mayer, W. Jaegermann, D. Gerthsen, C. Feldmann, U. Lemmer, and A. Colmann, *Org. Electron.*, 2013, **14**, 1820–1824.
9. K. Kanai, K. Koizumi, S. Ouchi, Y. Tsukamoto, K. Sakanoue, Y. Ouchi, and K. Seki, *Org. Electron.*, 2010, **11**, 188–194.
10. Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin, and Y. Cao, *Adv. Funct. Mater.*, 2013, **23**, 1781–1788.

Chapter 5

Star-Shaped Blue Emitters Sn-Cz-OXD (n = 1 ~ 3)

This chapter describes all the experimental works related to star-shaped blue emitters Sn-Cz-OXD (n = 1 ~ 3), including the molecular design, synthesis methods, basic characterizations, and fabrication for solution-processed undoped devices. They showed pure blue emission at around 455 nm and good spectra stability upon long period of heating. With more extended conjugation length in the branches, they exhibited simultaneously enhanced quantum efficiency in neat films and greater color purity of their blue emission. An optimized solution processed undoped OLEDs based on S2-Cz-OXD achieved a maximum brightness of 6538 cd m⁻², maximum efficiencies of 3.42%, 3.86 cd A⁻¹ and 1.65 lm W⁻¹ with CIE coordinates of (0.159, 0.157).

5.1 Introduction

Target star-shaped molecules Sn-Cz-OXD ($n = 1\sim3$) with different arm lengths were designed for solution-processed blue OLED applications. These molecules are composed of a tris(1,3,4-oxadiazole)phenylene (t-OXD) ring as core and three 3,6-di-tert-butylcarbazole (t-BCz) as terminal groups bridged by different numbers of rigid benzene units. The highly branched star-shaped structure should effectively suppress and prevent the intermolecular interactions compared with linear molecules. Therefore star-shaped molecules were expected to have higher solid quantum efficiency (Φ_f) than linear L1-Cz-OXD. And the value of Φ_f was expected to increase from S1-Cz-OXD to S3-Cz-OXD due to the extended conjugated branches, which could further prevent the molecular aggregation. Due to the D- π -A structure and the high thermal stability of the oxadiazole and carbazole derivatives, these emitters were expected to possess bipolar properties with optimized charge transport properties and high spectral stability. The synthesis and characterization of these three emitters were successfully carried out. The undoped devices based on Sn-Cz-OXD ($n = 1, 2$) were fabricated and optimized, and exhibited good performance. The characterization of material and devices were fully investigated.^{1,2}

5.2 Experimental Methods

5.2.1 Synthesis

The synthesis route of Sn-Cz-OXD ($n = 1 \sim 3$) and specific reaction conditions for each step are shown in Figure 5.1. The specific chemical structures of these target emitters are shown in Figure 5.2.

Figure 5.1 Synthetic route for Sn-Cz-OXD ($n = 1\sim3$). Specific reaction conditions: i) KOH, CuCl, 1,10-phenanthroline, toluene, reflux for 24 hours; ii) THF, n-BuLi, $-78\text{ }^{\circ}\text{C}$ to room temperature (RT); iii) 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $-78\text{ }^{\circ}\text{C}$ to RT, stir for 24 hours; iv) anhydrous pyridine, reflux for 24 hours; v) 3,6-Di-tert-butyl-9H-carbazole, CuI, K_2CO_3 , 18-crown-6, and DMPU, heat at $170\text{ }^{\circ}\text{C}$ for 48 hours; vi) K_2CO_3 , toluene, Aliquat 336, $\text{Pd}(\text{PPh}_3)_4$, stir in dark, heat at $100\text{ }^{\circ}\text{C}$ for 20 hours.

Figure 5.2 Chemical structures of Sn-Cz-OXD ($n = 1 \sim 3$).

Synthesis of Compound 5:

Compound **5** was synthesized by an Ullmann reaction.³ 26.14 g of 1-bromo-4-iodobenzene (92.4 mmol), 15.65 g of 3,6-di-tert-butyl-9H-carbazole (56 mmol), 15.68 g of KOH (280 mmol), 0.56 g of CuCl (5.6 mmol), 1.1 g of 1,10-phenanthroline (5.6 mmol) and 200 mL toluene were added into a 500 mL round bottom flask in N₂ atmosphere. This mixture was heated and stirred under reflux for 24 hours. After cooling to room temperature, the product was washed with water, dilute ammonia, dilute HCl solution and finally DI-water successively. Then the organic layer was separated and the water phase was extracted with CH₂Cl₂. The combined organic phases were collected and dried over MgSO₄. After filtration and evaporation, the residue was purified by silica gel column chromatography followed by recrystallization to give white crystals (yield: 61%).

Synthesis of Compound 6:⁴

4.34 g of compound **5** (10 mmol) and 55 mL anhydrous THF were mixed in an oven-dried 150 mL round bottom flask filled with N₂ atmosphere. The reaction system was cooled to -78 °C by immersing the whole flask into an EA (ethyl acetate) – liquid nitrogen bath. 6 mL n-BuLi (2.0 M, 12 mmol) was added dropwise via syringe under vigorous stirring. The mixture was continuously stirred for about 30 minutes after the addition of n-BuLi. Then 5.3 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13 mmol) was added dropwise. The reaction was warmed to room temperature and stirred for 24 hours. After the reaction was completed, the mixture was again cooled to 0 °C, and plenty of DI-water was added. Then the aqueous mixture was stirred for another 20 min. The organic phase was separated and the water phase was extracted with ether. The combined organic phases were washed with brine, and then dried over anhydrous MgSO₄. The crude product of compound **6** was collected after filtration and evaporation without further purification and was used directly in the next step.

Synthesis of Compound 7:

Compound **7** was prepared by a similar reaction to that used for the synthesis of compound **5**, while replacing 1-bromo-4-iodobenzene with 4-bromo-4'-iodobiphenyl.⁵

The specific amounts of each reagents were: 33.17 g of 4-bromo-4'-iodobiphenyl (92.4 mmol), 15.65 g of 3,6-di-tert-butyl-9H-carbazole (56 mmol), 15.68 g of KOH (280 mmol), 0.56 g of CuCl (5.6 mmol), and 1.1 g of 1,10-phenanthroline (5.6 mmol). The reaction yield of this step was 64%.

Synthesis of Compound 8:

Compound **8** was prepared using a similar reaction to that used for the synthesis of compound **6**. The specific amounts of each reagent were: 5.10 g of compound **7** (10 mmol), 55 mL of anhydrous THF, 6 mL n-BuLi (2.0 M, 12 mmol), 5.3 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13 mmol). The crude product of compound **8** was collected without further purification and was directly used in the next step. ^1H NMR (CDCl_3 , 500 MHz, δ): 1.25-1.58 (m, 66H), 7.43, 7.47 (dd, $J = 8.4$ Hz, 10H), 7.64-7.72 (m, 10H), 7.82, 7.88 (dd, $J = 8.4$ Hz, 8H), 8.16 (d, $J = 1.3$ Hz, 4H). ^{13}C NMR (CDCl_3 , 400 MHz, δ): 25.1, 32.2, 34.9, 84.0, 109.4, 116.4, 123.6, 126.5, 127.0, 127.6, 127.7, 128.5, 128.6, 128.8, 129.1, 135.6, 137.8, 139.3, 139.6, 143.1. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd. For $\text{C}_{38}\text{H}_{44}\text{BNO}_2$: 557.35. Found: 556.21. Anal. Calcd. for $\text{C}_{38}\text{H}_{44}\text{BNO}_2$: C, 81.86; H, 7.95; N, 2.51. Found: C, 81.83; H, 7.97; N, 2.47.

Synthesis of Compound 11 (core):

13.5 g of 1,3,5-benzenetricarboxylic acid chloride (compound **9**, 60 mmol) and 3.98 g of 5-(4-bromophenyl)-1H-tetrazole (compound **10**, 15 mmol) were mixed with 250 mL anhydrous pyridine in a 500 mL round bottom flask filled with nitrogen. The mixture was refluxed under stirring for 24 hours. After cooling the reaction to room temperature, the solid product, collected by filtration, was washed repeatedly with methanol and water each three times to afford a gray powder with a yield of 75%. After drying, the product was used directly in the next step. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{30}\text{H}_{15}\text{Br}_3\text{N}_6\text{O}_3$: 747.19. Found: 749.2. No NMR data was recorded for this compound because it is almost insoluble in organic solvents such as CHCl_3 , THF, and DMSO.

Synthesis of S1-Cz-OXD:

S1-Cz-OXD was prepared using a similar Ullmann reaction to that used for the synthesis of **L1-Cz-OXD** (for details please refer to Section 4.2.1). The specific amounts of each reagent were: 5.0 g of compound **4** (18 mmol), 2.3 g of compound **11** (3 mmol), 2.76 g of K_2CO_3 (20 mmol), 0.19 g of CuI (1 mmol), 1 ml of DMPU, and 0.09 g of 18-crown-6 (0.3 mmol). The reaction yield of this step was 37%. 1H NMR ($CDCl_3$, 500 MHz, δ): 1.49 (s, 54H), 7.49-7.53 (m, 12H), 7.86 (d, $J = 8.5$ Hz, 6H), 8.17 (d, $J = 0.9$ Hz, 6H), 8.48 (d, $J = 8.5$ Hz, 6H), 9.15 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 32.0, 34.8, 109.2, 116.5, 121.1, 123.9, 124.0, 126.3, 126.7, 127.3, 128.9, 138.5, 142.1, 143.8, 162.8, 165.1. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. for $C_{90}H_{87}N_9O_3$: 1341.7. Found: 1339.19. Anal. Calcd. for $C_{90}H_{87}N_9O_3$: C, 80.51; H, 6.53; N, 9.39. Found: C, 80.47; H, 6.56; N, 9.41.

Synthesis of S2-Cz-OXD:

S2-Cz-OXD was synthesized by the classic Suzuki Reaction. 3.37 g of crude product of compound **6** (7 mmol), 1.50 g of compound **11** (2 mmol), 20 mL of 2M solution of K_2CO_3 , 60 mL toluene, three drops of Aliquid 336, and 0.12 g of $Pd(PPh_3)_4$ (0.10 mmol) were added to a 150 mL round bottom flask charged with a nitrogen atmosphere. The mixture was heated in the dark at 100 °C for 20 hours under vigorous stirring. After cooling to the room temperature, the organic phase was separated and the aqueous phase was extracted with toluene. The combined organic phases were washed with water and dried over $MgSO_4$. After filtration and evaporation, the pure product of **S2-Cz-OXD** was obtained by silica-gel column chromatography followed by several precipitation steps (white solid, yield: 42%). 1H NMR ($CDCl_3$, 400 MHz, δ): 1.49 (s, 54H), 7.42-7.51 (m, 12H), 7.70 (d, $J = 8.3$ Hz, 6H), 7.88, 7.91 (dd, $J = 8.4$ Hz, 12H), 8.16 (s, 6H), 8.35 (d, $J = 8.2$ Hz, 6H), 9.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 32.0, 34.7, 109.2, 116.3, 122.2, 123.6, 123.7, 126.2, 127.0, 127.2, 127.7, 127.8, 128.5, 137.8, 138.5, 139.0, 143.1, 144.1, 162.8, 165.3. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. For $C_{108}H_{99}N_9O_3$: 1569.79. Found: 1569.16. Anal. Calcd. for $C_{108}H_{99}N_9O_3$: C, 82.57; H, 6.35; N, 8.02. Found: C, 82.60; H, 6.33; N, 8.04.

Synthesis of S3-Cz-OXD:

S3-Cz-OXD was prepared using a similar Suzuki reaction for the synthesis of **S2-Cz-OXD**. The specific amounts of each reagent were: 2.23 g of compound **8** (4 mmol), 0.75 g of compound **11** (1 mmol), 20 mL of 2M solution of K₂CO₃, 60 mL toluene, three drops of Aliquat 336, and 0.12 g of Pd(PPh₃)₄ (0.10 mmol). The reaction yield of this step was 37%. ¹H NMR (CDCl₃, 400 MHz, δ): 1.48 (s, 54H), 7.42-7.50 (m, 12H), 7.68 (d, J = 8.4 Hz, 12H), 7.84 (s, 12H), 7.86, 7.92 (dd, J = 8.4 Hz, 12H), 8.16 (d, J = 1.7 Hz, 6H), 8.35 (d, J = 8.4 Hz, 6H), 9.11 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ): 29.7, 32.0, 34.8, 109.3, 116.3, 122.2, 123.5, 123.6, 126.3, 127.0, 127.6, 127.7, 127.8, 128.3, 137.8, 138.7, 138.8, 139.1, 140.3, 143.0, 144.4, 162.8, 165.4. MS (MALDI-TOF, m/z): [M]⁺Calcd. For C₁₂₆H₁₁₁N₉O₃: 1797.88. Found: 1797.51. Anal. Calcd. for C₁₂₆H₁₁₁N₉O₃: C, 84.11; H, 6.22; N, 7.01. Found: C, 84.06; H, 6.25; N, 6.97.

5.2.2 Device Fabrication and Optimization

The thermal vacuum evaporation is limited to vaporizable low molecular weight materials and can only be applied to compounds which can undergo certain thermal stress without decomposition. A trial experiment showed that S1-Cz-OXD turned into black solid after the vacuum-deposition, indicating S1-Cz-OXD with high molecular weight is not suitable for vacuum evaporation technique. However, the good solubility of S1-Cz-OXD makes it possible to be deposited by spin-coating technique. The solubility of Sn-Cz-OXD (n = 1~3) in different organic solvents is summarized in Table 5.1. Solubility decreases when the length of the rigid conjugated branches increases. Chloroform was the best solvent, but it was extremely volatile, therefore unsuitable for spin-coating. A mixed solvent of toluene : chlorobenzene (1 : 1 in volume) was used to facilitate the solution-processed device fabrication. However, the poor solubility of S3-Cz-OXD made it difficult to be spin-coat into a nice film, so only S1-Cz-OXD and S2-Cz-OXD were selected as the emitting materials for OLED devices. For specific fabrication details, please refer to Section 4.2.2. The conditions for all spin-coating layers, the parameters for vacuum deposition for all used source materials and the optimized thickness for each layer are summarized in Table 5.2.

Table 5.1 Solubility of target emitters in different organic solvents.

Compound	Solubility (mg mL ⁻¹)				EML for OLEDs
	CHCl ₃	Toluene	Hexane	Toluene : CB (1:1)	
S1-Cz-OXD	>20	15	5	18	Selected
S2-Cz-OXD	15	10	2	12	Selected
S3-Cz-OXD	<3	<0.01	insoluble	< 1	No

Table 5.2 Optimized condition for deposition of multilayers in device fabrication.

Spin coated	Spin rate	Anneal T (°C)	Thickness	Vacuum deposited	T (°C) / I (A)	Thickness
	(rpm) / t (s)	/ t (min)	(nm)			(nm)
PEDOT:PSS	4000 / 60	120 / 15	30	3TPYMB	127 / 0.5	40
S1-Cz-OXD	3000 / 60	120 / 30	70	CsCO ₃	630 / 3.4	1
S2-Cz-OXD	3000 / 60	120 / 30	70	TPBI	200 / 1	40
				LiF	630 / 3.6	0.5
				Al	>70 / 60	120

5.3 Materials Characterization

The characterization of Sn-Cz-OXD (n = 1~3) was similar to L1-Cz-OXD. For details of the chemical analysis, absorption and photoluminescence spectroscopy, electrochemical and thermal properties, surface morphology, please refer to Section 4.3. Several small differences in operations are listed below.

5.3.1 Chemical Analysis (NMR, EA and MALDI-TOF)

NMR, EA and MALDI-TOF were applied to all newly reported molecules (including compounds **11**, **12**, **14**, **15**, **18** and **Sn-Cz-OXD**, n=1~3). In MALDI-TOF characterization, a matrix material sinapic acid was used for **Sn-Cz-OXD** (n = 1~3) to protect the sample molecules under high accelerate voltage. **Sn-Cz-OXD** (n = 1~3) and sinapic acid were dissolved in dry THF solvent at a concentration of 2 mg mL⁻¹ and 20 mg mL⁻¹, and they were mixed at a ratio of 1 : 10 (v/v) for sample preparation.

5.3.2 Absorption and Photoluminescence Spectroscopy

The preparation method of a neat film of **S3-Cz-OXD** is difference from other molecules due to its poor solubility. First an oversaturated solution of **S3-Cz-OXD** in chloroform was formed by heating, after cooling it was filtered and the filtrate is used for deposition of thin films.

5.4 Characterization of Devices

Characterization of OLED devices based on S1-Cz-OXD and S2-Cz-OXD was completely the same as those applied to L1-Cz-OXD based ones. The only difference was the solution applied for Sn-Cz-OXD was mixed toluene : chlorobenzene (1:1 in volume). For more experimental details please refer to Section 4.4.

5.5 Results and Discussion for Synthesized Materials

5.5.1 Chemical Structure and Molecular Weight

^1H NMR, ^{13}C NMR, EA and MALDI-TOF data of all newly reported compounds including compounds **8,11**, and **Sn-Cz-OXD** (n = 1~3), were summarized in Section 5.2.1. The spectra for NMR and MALDI-TOF are in the Appendix. The chemical structure and purity of these compounds were confirmed by the combined results of NMR, EA and MALDI-TOF measurements.

It is worth mentioning that in the MALDI-TOF spectra of **Sn-Cz-OXD** (n=1~3), (Figure A.23~A.25 in Appendix), there are many small noise peaks in the low molecular weight region (from 200 to 1200). The location of these noise peaks in the spectra of **Sn-Cz-OXD** (n = 1~3) were in accordance with peaks in that of the pure matrix material (Figure A.29 in Appendix. E.g., peaks 211.01, 224.87, 241.91, 450.29, 476.40, 673.39, 896.22, and 1119.24.), implying they were from the sinapic acid matrix and there was almost no impurities in the synthesized products. Besides, all star-shaped molecules exhibited two

small peaks close to the main peak of the target compound, which could be assigned to the product fragments losing a methyl group and a tert-butyl group, respectively.

5.5.2 Photophysical Properties

UV-visible absorption spectrum and photoluminescence spectrum of **Sn-Cz-OXD** (n = 1~3) were characterized in dilute toluene solution, doped PMMA films and solid neat films. The resultant spectra are shown in Figures 5.3, 5.4 and 5.5, respectively. The photophysical properties of these three emitters are summarized in Table 5.3.

Figure 5.3 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD (n = 1~3) in dilute solution.

Figure 5.3 depicts the UV-vis absorption and PL spectra of Sn-Cz-OXD (n = 1~3) in dilute toluene solution. The maximum absorption peaks were located at 369 nm, 356 nm and 348 nm, and the PL emission peaks were centered at 422 nm, 420 nm and 418 nm for S1-Cz-OXD, S2-Cz-OXD and S3-Cz-OXD, respectively. Blue-shift could be observed in both absorption and emission spectra from S1-Cz-OXD to S3-Cz-OXD as the amount of benzene units increased (i.e., when the conjugated branches are more extended). The onset wavelengths ($\lambda_{\text{onset}}^{\text{Abs}}$) of the absorption for these three emitters were 413 nm, 410 nm and 403 nm. The optical energy bandgaps were estimated from $\lambda_{\text{onset}}^{\text{Abs}}$ to be 3.00 eV, 3.03 eV and 3.08 eV, which was increasing with the length of the conjugated branches. To explain the results, it is necessary to understand the photoluminescence mechanism for D- π -A type molecules.

During photoluminescence, the outermost electrons of the electroluminescent material first absorb a certain amount of energy from the excitation light source and jump from the HOMO (ground state) to LUMO level, which is the excited state of the molecule. Then, they release energy in the form of light when they return from the excited state to the ground state. Therefore the absorption and emission wavelength depend on the HOMO/LUMO energy bandgap of the molecules. Generally speaking, extending of conjugation length of a common (unipolar) molecule would lead to the greater delocalization of electrons in the molecule, resulting in a narrower energy difference between the ground and excited states of the molecule. This normally causes an undesired red-shift in the PL spectrum for blue emitters, which has been reported in many studies. However, the phenomenon is different for D- π -A type molecules. The HOMO and LUMO energy levels of D- π -A molecules are respectively determined by the electron donating and withdrawing abilities of the donor and acceptor units. Therefore during photoluminescence, electrons are transferred from the donor to the acceptor unit. The absorption / emission peak for D- π -A is also called the charge transfer peak. Extending of the π conjugation between donor and acceptor unit would enlarge the distance between these units, specifically in the case of increasing the number of benzene units, it would also cause a slight distortion to the conjugation bridge because the coplanarity of polyphenyls is not great. Both of these weaken the charge transfer process, leading to a wider HOMO/LUMO energy bandgap of the molecule. As a result, both absorption and emission spectra show blue-shift.

Excellent quantum efficiencies (Φ_f) of 93%, 91% and 87% are obtained for Sn-Cz-OXD (n = 1~3) in dilute solution by using 9,10-diphenylanthracene as a reference. The value of Φ_f decreases from S1-Cz-OXD to S3-Cz-OXD. It could be that the bulky 3,6-di-tert-butyl-carbazole substituents are more crowded around the OXD core in S1-Cz-OXD and the whole molecule is quite rigid. By contrast, there is more space for molecular vibration and single bond rotation in larger molecules such as S2-Cz-OXD and S3-Cz-OXD. The vibrations and rotations of molecular bonds would result in energy loss by non-radiative decay, leading to a lower Φ_f .

Photophysical properties, especially the fluorescence quantum efficiency (Φ_f) in solid thin films are very important for undoped emitting materials. Two types of thin films including doped PMMA films, and neat films of Sn-Cz-OXD (1~3), are fully investigated since they represent two different states of the target molecules. Molecules are in isolated states when dispersed in PMMA matrix whereas they are packed together in the neat films.

Figure 5.4 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 1\sim3$) in doped PMMA films.

Figure 5.4 depicts the UV-vis absorption and PL spectra of Sn-Cz-OXD (1~3) in doped PMMA films. Both absorption and PL spectra of doped PMMA films exhibit an obvious red shift compared with the dilute solution. The absorption peaks are located at 372 nm, 358 nm and 349 nm, while the emission peaks (at excitation of 355 nm) are centered at 455 nm, 450 nm and 446 nm for Sn-Cz-OXD ($n = 1\sim3$), respectively. The red-shift in both spectra in films could be explained by the increased intermolecular interaction, implying the weak aggregation in solid state. From S1-Cz-OXD to S3-Cz-OXD, both absorption and PL spectra exhibited blue-shift. This changing trend in spectrum with molecular structure is similar to that in dilute solution due to the same reasoning discussed above.

The corresponding Φ_f in doped PMMA films of Sn-Cz-OXD ($n = 1\sim3$) are calculated to be 72%, 76% and 79% using 9,10-diphenylanthracene as reference. These values are

much lower than those in solution due to the greatly increased intermolecular interactions between different molecules in solid state, although Sn-Cz-OXD molecules are supposed to be in isolated state in the doped PMMA films. This is because that PMMA itself is also a polar material. Different from dilute solution, the doped PMMA films exhibit ascending value of Φ_f from S1-Cz-OXD to S3-Cz-OXD. This is because in solid state, non-radiative decay caused by molecular vibration and single bond rotation is almost suppressed. In this case, quantum efficiency usually increases with the conjugation length because longer branches would suppress the intermolecular interactions more effectively.

Figure 5.5 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD ($n = 1\sim3$) in neat films.

Figure 5.5 illustrates the UV-vis absorption and PL spectra of Sn-Cz-OXD in solid neat films. Both absorption and PL spectra of the neat films were similar to the doped PMMA films. The maximum absorption are 373 nm, 359 nm and 349 nm, while the maximum emission at excitation of 355 nm are located at 457 nm, 452 nm and 448 nm for Sn-Cz-OXD ($n = 1\sim3$). The changing trend of spectra from S1-Cz-OXD to S3-Cz-OXD is identical in the solution and doped PMMA films due to the same reason. High Φ_f of 54%, 58% and 61% are obtained for Sn-Cz-OXD ($n = 1\sim3$) in neat films by using 9,10-diphenylanthracene as a reference, indicating their high potential as undoped emitters. Generally speaking, the aggregation of emitting molecules in the neat films might lead to serious fluorescence quenching and obvious red shift in emission spectrum due to the enhanced intermolecular interactions compared with the doped PMMA films, where the emitting molecules are isolated. However, their Φ_f are still of high values and they only

red shift very slightly (only 2 ~ 3 nm) compared with the corresponding doped PMMA films, implying the bulky branches and tert-butyl groups suppressed the intermolecular aggregation effectively.

Table 5.3 Photophysical properties of target molecules.

Emitter	Dilute solution ^[a]				Solid film ^{[c]/[d]}		
	$\lambda_{\max}^{\text{Abs}} / \lambda_{\max}^{\text{PL}}$	$\lambda_{\text{onset}}^{\text{Abs}}$	E_{opt}	$\Phi_{\text{f}}^{\text{[b]}}$	$\lambda_{\max}^{\text{Abs}}(\text{nm})$	$\lambda_{\max}^{\text{PL}}(\text{nm})$	$\Phi_{\text{f}}^{\text{[e]}}$
	(nm)	(nm)	(eV)	(%)			(%)
S1-Cz-OXD	369 / 422	413	3.00	93	372 / 373	455 / 457	72 / 54
S2-Cz-OXD	356 / 420	410	3.03	91	358 / 359	450 / 452	76 / 58
S3-Cz-OXD	348 / 418	403	3.08	87	349 / 349	446 / 448	79 / 61

^[a]: Analyzed in dilute toluene solution (10^{-6} M); ^[b]: 9,10-diphenylanthracene is reference material, $\Phi_{\text{f}} = 0.92$ in dilute toluene; ^[c]: Analyzed in doped PMMA films ($<10^{-3}$ M); ^[d]: Analyzed in solid neat films; ^[e]: 9,10-diphenylanthracene is reference material, $\Phi_{\text{f}} = 0.83$ dispersed in PMMA films ($<10^{-3}$ M).

When compared with its linear counterpart L1-Cz-OXD, S1-Cz-OXD exhibits obviously red-shifted absorption and PL spectra in both solution and film state (smaller energy bandgap). This could be explained by their molecular structures. L1-Cz-OXD and S1-Cz-OXD are both D- π -A type molecules composed of 3,6-di-tert-butyl-carbazole (*t*-BCz, as donor unit) and oxadiazole (OXD, as acceptor unit). S1-Cz-OXD is star-shaped, with three *t*-BCz groups at the end of each branch and three OXD units combined in a conjugated core. In linear L1-Cz-OXD, there is only a single OXD unit in the center and *t*-BCz groups on both sides. The electron withdrawing ability of the tris(1,3,4-oxadiazole)phenylene core in S1-Cz-OXD is much higher than that of the individual oxadiazole unit in L1-Cz-OXD due to the synergistic effect. The electron donating ability of three *t*-BCz units in S1-Cz-OXD should also be higher than that of only two *t*-BCz units in L1-Cz-OXD. Considering the HOMO / LUMO level is dependent on the electron donating / withdrawing ability of the acceptor unit in the D- π -A type molecules, the HOMO / LUMO energy bandgap of S1-Cz-OXD should be narrower than that of L1-Cz-

OXD. S1-Cz-OXD exhibits higher solid quantum efficiency ($\Phi_f = 54\%$) than that of L1-Cz-OXD ($\Phi_f = 41\%$), which is in accordance with this hypothesis. This result implies that the star-shaped structure could reduce the fluorescence quenching by effectively suppressing the intermolecular interactions in the solid state and is beneficial for undoped emitters with high quantum efficiencies.

5.5.3 Electrochemical Properties

CV curves of S1-Cz-OXD and S2-Cz-OXD are shown in Figure 5.6. S3-Cz-OXD is almost insoluble in CH_2Cl_2 solvent and therefore no good result is obtained. Both S1-Cz-OXD and S2-Cz-OXD exhibit reversible oxidation and reduction behavior under positive and negative drive voltages, which could be ascribed to the electron donating *t*-BCz terminals and the electron withdrawing core, indicating their distinct bipolar features.

Figure 5.6 Cyclic voltammograms of Sn-Cz-OXD (n = 1 and 2).

The onset oxidation potentials ($E_{\text{onset}}^{\text{oxd}}$) were 1.26 V and 1.27 V, while the reduction potentials ($E_{\text{onset}}^{\text{red}}$) were -1.51 V and -1.53 V for S1-Cz-OXD and S2-Cz-OXD, respectively. Their HOMO levels estimated from $E_{\text{onset}}^{\text{oxd}}$ were -5.66 eV and -5.67 eV, while the LUMO levels estimated from $E_{\text{onset}}^{\text{red}}$ were -2.89 eV and -2.87 eV. The HOMO / LUMO values were very similar for S1-Cz-OXD and S2-Cz-OXD since they had the same donor units and

acceptor core, which determined the HOMO / LUMO level of the molecules. The corresponding HOMO / LUMO energy bandgaps for these two emitters were then calculated to be 2.77 eV and 2.80 eV, which were consistent with the PL measurement results. The slight increase in the energy bandgap was caused by the additional benzene spacer. Similarly to L1-Cz-OXD, there was a big difference between the energy bandgap calculated from CV results and the optical energy bandgap calculated from UV-vis spectroscopy for Sn-Cz-OXD. For specific explanation on this, please refer to Section 4.5.3. A more reliable LUMO energy level was calculated to be -2.66 eV and -2.64 eV by equation $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{opt}}$ for S1-Cz-OXD and S2-Cz-OXD. All these results are summarized in Table 5.4.

Table 5.4 Electrochemical and thermal properties of target molecules.

Compounds	$E_{\text{onset}}^{\text{oxd}} / E_{\text{onset}}^{\text{red}}$ ^[a] (V)	E_{HOMO} ^[b] (eV)	E_{LUMO} ^{[b]/[c]} (eV)	E_{gap} ^{[d]/[f]} (eV)	T_g (°C)	T_d (°C)	RMS ^{[g]/[h]} (nm)
S1-Cz-OXD	1.26 / -1.51	-5.66	-2.89 / -2.66	2.77 / 3.00	137	447	0.48 / 0.41
S2-Cz-OXD	1.27 / -1.53	-5.67	-2.87 / -2.64	2.80 / 3.03	141	453	0.70 / 0.66
S3-Cz-OXD	-	-	-	-	145	470	0.82 / 0.80

^[a]: Performed in 0.1M (C₄H₉)₄NClO₄ in CH₂Cl₂; ^[b]: Estimated from $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ obtained from CV curve with ferrocene calibration; ^[c]: Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt}}$; ^[d]: Determined from CV; ^[f]: Estimated from UV-vis absorption spectrum (E_{opt}); ^[g]: RMS value of non-annealed films and ^[h]: RMS value of annealed films.

5.5.4 Thermal Properties

The thermal properties of Sn-Cz-OXD (n = 1~3) were explored by TGA and DSC. The resultant DSC traces and TGA thermogram are shown in Figure 5.7 and the results are summarized in Table 5.4. The glass transition temperature (T_g) is determined to be 137 °C, 141 °C and 145 °C respectively for S1-Cz-OXD, S2-Cz-OXD and S3-Cz-OXD, i.e., slightly increasing with molecular size. The thermal decomposition temperatures (T_d , 5% weight loss) for Sn-Cz-OXD (n = 1 ~ 3) are 447 °C, 453 °C and 470 °C, respectively. The

trend is similar to that of T_g . T_d increased with molecular size from S1-Cz-OXD to S3-Cz-OXD. Sn-Cz-OXD are composed of rigid aromatic rings. The three benzene rings attached to the core might be twisted to some degree (not coplanar with the core) due to the steric terminal groups and rigid benzene spacers, which make it difficult for crystallization.⁶⁻⁸ The increase of the length of branches would enhance the molecular rigidity in the same time. And as a result, the T_g and T_d also increase. To sum up, all emitters possess high T_g (> 135 °C) and T_d (> 410 °C) temperatures, which could provide the needed thermal stability during practical application.

Figure 5.7 DSC traces (a) and TGA thermogram (b) of Sn-Cz-OXD ($n = 1\sim3$).

5.5.5 Spectrum Thermal Stability

Long period annealing experiments were employed to test the spectrum thermal stability of the neat films of Sn-Cz-OXD ($n = 1\sim3$). The resultant spectra are shown in Figure 5.8. There is no significant change in their fluorescent spectra after 220 hours of thermal annealing at 150 °C on a hot plate in ambient air. The spectrum stability of all these emitters is much better than those fluorene-based materials. This is favorable for the overall stability of the electroluminescent devices.

Figure 5.8 Normalized PL spectrum of Sn-Cz-OXD ($n = 1\sim3$) during long period heating treatment.

5.5.6 Surface Morphology

The excellent heat tolerance of Sn-Cz-OXD ($n = 1\sim3$) emitters show that they have the potential to form thermally stable films. However, when the amount of benzene increases, the molecule is supposed to become more rigid and less soluble, which has been proven (Section 5.2.2, Table 5.1). Therefore the quality of solution-cast films of these emitters is expected to become reduced with molecular size. As a result, the surface morphology of the film of S1-Cz-OXD is expected to be the best. In addition, the star-shaped structure of S1-Cz-OXD is supposed to endow better morphology properties for their films compared with the linear molecule L1-Cz-OXD. In order to verify these assumptions, the surface morphology of spin-cast thin films of Sn-Cz-OXD ($n = 1\sim3$) are recorded with AFM and the resultant images of both non-annealed and annealed films are shown in Figure 5.9.

Figure 5.9 AFM images of Sn-Cz-OXD ($n = 1\sim3$) and L1-Cz-OXD (for comparison) films spin-casted from chloroform solution.

The RMS roughness is 0.48 nm, 0.70 nm and 0.82 nm for films of Sn-Cz-OXD ($n = 1\sim3$) without annealing treatment and is 0.41 nm, 0.66 nm and 0.80 nm for films after annealing. For both non-annealed and annealed films, the roughness is obviously increasing with the molecular size, indicating the extension of the conjugated branch would increase the rigidity of the molecules and lead to less amorphous films by spin-coating. This could also be observed in AFM images, where the range in fluctuation height is becoming greater from S1-Cz-OXD to S3-Cz-OXD. Moreover, the slight decrease in RMS roughness for the annealed films compared with those non-annealed ones indicates annealing could improve the surface quality of these films. Large particles could be observed on the surface of the non-annealed films, while in the annealed films, the color is much more evenly distributed, implying much more homogeneous films. Finally, compared with the film of L1-Cz-OXD (RMS = 0.48 nm), S1-Cz-OXD exhibits less roughness (RMS = 0.41 nm). Besides, small particles with high contrast could be observed in the AFM image of the annealed film of L1-Cz-OXD. For comparison, the height fluctuation in that of S1-Cz-OXD is of low relief, indicating better surface topography. These results are in accordance with expectations.

5.6 Results and Discussion for OLED Devices

5.6.1 Devices C1 and C2: ITO/PEDOT:PSS/EML/3TPYMB/Cs₂CO₃/Al

Undoped devices with configurations of **ITO/PEDOT:PSS/EML/3TPYMB/Cs₂CO₃/Al** were fabricated by spin-coating based on S1-Cz-OXD and S2-Cz-OXD (**Device C1**: EML = S1-Cz-OXD; **Device C2**: EML = S2-Cz-OXD). L1-Cz-OXD as the linear counterpart of S1-Cz-OXD was used for the EML in a control device with the identical configuration (for detail of **device A1**, please refer to Section 4.6).

Figure 5.10 Energy level diagram of device C1 and C2.

In device C1 and C2, PEDOT:PSS served as hole transporting material; 3TPYMB served as electron transporter; and Cs₂CO₃ served as the electron injecting layer. The energy diagrams of the two devices are shown in Figure 5.10.

Both devices emitted pure blue light at 459 nm and 455 nm, which were almost identical with the PL spectra of S1-Cz-OXD (457 nm) and S2-Cz-OXD (452 nm) in solid films (with only a slight red-shift). This implied the emissions were coming from pure emitting materials. Figure 5.11 depicts the electroluminescent spectra of devices C1 and C2. No significant difference in the EL spectra were detected at different applied voltages,

implying the emission was quite stable. The CIE coordinates were (0.167, 0.168) for device C1 and (0.159, 0.156) for device C2. Electroluminescence characterization data of these two devices, the control device A1 and A2 (an optimized device based on A1), are summarized in Table 5.5. The much better device performance of device C1 and C2 than A1 and A2 shows that these star-shaped emitters are better (regardless of deposition method) than the linear emitter **L1-Cz-OXD**.

Figure 5.11 Normalized EL spectra of (a) device C1 and (b) device C2.

Figure 5.12 shows the J-V-L characteristics and plots of luminous efficiencies-current density characteristics for devices C1, C2 and A1 (control device based on L1-Cz-OXD). C1 exhibited much higher EL efficiencies than its control device A1. Device C1 achieved a maximum luminance of 3648 cd m^{-2} at 11.4 V, a maximum CE of 4.21 cd A^{-1} , an EQE of 3.37%, and a PE of 2.55 lm W^{-1} . High efficiencies of 3.1% and 2.3% are obtained at the brightness of 100 cd m^{-2} and 1000 cd m^{-2} . In comparison, the maximum brightness of control device A1 was only 686 cd m^{-2} at 10.4 V, while the maximum efficiencies of it were 1.03 cd A^{-1} , 1.30%, and 0.63 lm W^{-1} , respectively.

The inferior EL performance of device A1 is likely due to: (1) the solid quantum efficiency of S1-Cz-OXD (50%) was higher than that of L1-Cz-OXD (41%) in neat films; and (2) the film quality of L1-Cz-OXD deposited from spin-coating was not as good as that of S1-Cz-OXD. Compared with device A1, which turned on at 4.3 V, device C1 exhibited a much lower turn-on voltage at 3.7 V. A possible reason for this difference

was the LUMO energy level of S1-Cz-OXD was lower than that of L1-Cz-OXD. As discussed earlier, the enhanced electron withdrawing ability of the tris(1,3,4-oxadiazole)phenylene core in S1-Cz-OXD was higher than that of the individual oxadiazole unit in L1-Cz-OXD. This led to a lower LUMO energy level and a narrower energy barrier between ETL (3TPYMB) and EML for S1-Cz-OXD, which facilitated the electron injection process. Another reason for the reduced turn-on voltage in device C1 was again due to the improved film quality of emitting layer of S1-Cz-OXD. This is elaborated in following paragraphs.

Figure 5.12 EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices C1, C2 and control device A1.

As mentioned earlier, the solubility of L1-Cz-OXD in organic solvents was much lower than that of S1-Cz-OXD. The best solvent for it was mixed CHCl_3 : CB (1: 1 in volume), which was used for its spin-coating. However, the volatile CHCl_3 would cause fast

evaporation lead to the generation of defects in the deposited film. On the other hand, the film forming ability of linear L1-Cz-OXD was also inferior to that of S1-Cz-OXD with a star-shaped structure. During the process of evaporation of solvent, star-shaped molecules tended to form an amorphous film since the highly branched arms prevented the aggregation. By contrast, it is much easier for linear molecules to form ordered stacks and microcrystalline domains. As a result, the film quality of L1-Cz-OXD obtained from spin-coating was poor. The defects on the surface of L1-Cz-OXD might trap charges and hinder the injection of holes and electrons, leading to a high turn-on voltage at 4.3 V. This could be further proven by the reduced turn-on voltage of device A2 (4.6 V) fabricated by vacuum-deposition with the same configuration as device A1 (please refer to Section 4.6). Moreover, the defects inside L1-Cz-OXD emitting layer made it vulnerable to be broken down by the applied voltage, leading to the leakage of current, while also affecting the recombination of excitons. An evidence of this is shown in Figure 5.12, where device A1 exhibited a higher current density but a lower luminance compared with device C1 under the same driving voltage, implying the poor quality of L1-Cz-OXD film in device A1.

Table 5.5 Electroluminescence characteristics of the devices C1, C2, A1 and A2.

Device	$V_{on}^{[a]}$ (V)	at 100 / 1000 $cd\ m^{-2[b]}(V/\%)$	$Max\ L$ ($cd\ m^{-2}$, V)	EQE (%)	CE ($cd\ A^{-1}$)	PE ($lm\ W^{-1}$)	λ_{max} (nm)	CIE (x, y)
C1	3.7	4.7, 3.1 / 6.7, 2.3	3648, 11.4	3.37	4.21	2.55	459	(0.167, 0.168)
C2	3.7	4.7, 3.1 / 6.0, 3.7	4352, 11.1	3.84	4.41	2.62	455	(0.159, 0.156)
A1	4.3	6.5, 0.3 / ----, ----	686, 10.4	1.30	1.03	0.63	429	(0.16, 0.07)
A2	4.6	6.1, 2.3 / 8.5, 1.3	1731, 11.6	2.42	1.27	0.67	429	(0.16, 0.07)

^[a]: Turn-on voltage at which brightness exceeds $1\ cd\ m^{-2}$; ^[b]: The estimated values of driving voltage and EQE of device at brightness of 100 and $1000\ cd\ m^{-2}$

Device C2 turned on at 3.7 V and achieved a maximum brightness of $4352\ cd\ m^{-2}$, a maximum CE of $4.41\ cd\ A^{-1}$, a maximum EQE of 3.84% and a maximum PE of $2.62\ lm\ W^{-1}$. High efficiencies of 3.1% and 3.7% were obtained at the brightness of $100\ cd\ m^{-2}$ and $1000\ cd\ m^{-2}$. Its EL efficiencies were superior to device C1, which could be

attributed to the enhanced solid quantum efficiency of S2-Cz-OXD (compared with S1-Cz-OXD) with extended conjugated branches. Although large charge injection barriers existed between HTL / ETL and the HOMO / LUMO energy level of EML, devices C1 and C2 exhibited low turn-on voltage. This could be explained by emitters' D-A structure with both good hole and electron transporting properties.

5.6.2 Influence of HTM/EIM on Device Performance

In a previous study, 3TPYMB was selected as the material for the electron transporting layer due to its high electron affinity, which led to a reduced energy barrier and facilitated the electron injection from cathode. Besides, it possessed high electron drifting mobility and good hole-blocking properties (low-lying LUMO energy level at -6.77 eV), which confined the recombination domain inside emitting layer.⁹ A thin layer of Cs₂CO₃ was served as the electron injecting layer, but the EL efficiencies (EQE, CE and PE) decreased rapidly with the current density for all these devices. Similar roll-off phenomenon for devices employing 3TPYMB as ETL was also reported by others.^{10,11} For further investigation of this issue, traditional electron transporting material TPBI was used to replace 3TPYMB to serve as ETL in devices, while lithium fluoride (LiF) served as EIL. As a result, devices **D1** and **D2** with configurations of ITO/PEDOT:PSS/EML/TPBI/LiF/Al (**D1**: EML = S1-Cz-OXD and **D2**: EML = S2-Cz-OXD) were fabricated for comparative study. Figure 5.13 shows the energy band diagrams for devices based on these two configurations.

Figure 5.14 (a) illustrates the J-V-L characteristics and plots of EL efficiencies (including EQE, CE and PE) – current density characteristics for devices C1, C2, D1 and D2. The turn-on voltage of D1 (4.1 V) was higher than C1 (3.7 V) due to the high electron affinity of 3TPYMB.⁹ The current density of device D1 was 51.06 mA cm⁻² at 7.0 V, higher than that of device C1 (43.77 mA cm⁻², at 7.0 V). It exhibited similar characteristics under other voltages. Although 3TPYMB was supposed to have higher electron mobility, the higher value of current density in device D1 suggests that the electron transportation was better when TPBI was employed as ETL compared with 3TPYMB. This is because the

energy barrier between the LUMO energy level of 3TPYMB (-3.32 eV) and EML (-2.65 eV) is much larger than that between TPBI ($E_{\text{LUMO}} = -2.70$ eV) and EML. It is therefore more difficult for electron transporting from 3TPYMB, leading to a lower current density.

Figure 5.13 Energy level diagram of device C1, C2, D1, and D2.

The electroluminescence in OLEDs mainly depends on the current density passing through the device. However, the luminance of devices D1 and C1 were 981 cd m^{-2} and 1146 cd m^{-2} at lower driving voltage of 7.0 V, whereas they were 5714 cd m^{-2} and 3262 cd m^{-2} at higher driving voltage of 10.0 V. The maximum luminance of device D1 (5436 cd m^{-2}) was also higher than that of C1 (2960 cd m^{-2}). In device C1, The combination of the high electron mobility and large energy barrier of 3TPYMB promoted the recombination zone of charges to be close to the interface between emitting layer and ETL (3TPYMB) at low voltages. The recombination zone might be shifted to the interface of EML and HTL when driving voltage was increased because more electrons could be transported to EML through the energy barrier under high voltages. The luminance would be reduced due to the lack of electron blocking layer between HTL (PEDOT:PSS) and EML. To sum up, current density and luminance in the device C1 is more dependent on hole confinement at the low voltages; while D1 is more dependent on electron transport and electron confinement at high voltages.¹² Similar characteristics in J-V-L curves could be observed in device C2 and D2 as summarized in Table 5.6, which had the same cause.

Figure 5.14 EL performances: (a) J-V-L characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices C1, C2, D1 and D2.

Table 5.6 Comparative characteristics of devices C1, C2, D1 and D2.

Device	J at 7.0 V (mA cm ⁻²)	Luminance (cd m ⁻²)		EL efficiencies ^[a] (% , cd A ⁻¹ , lm W ⁻¹)	
		at 7.0 V	at 10.0 V	at 100 mA cm ⁻²	at 200 mA cm ⁻²
C1	43.77	1146	2960	1.3, 1.8, 0.7	0.9, 1.3, 0.4
C2	54.04	1572	3676	1.7, 2.2, 0.9	1.1, 1.5, 0.5
D1	51.06	981	5436	2.8, 3.5, 1.2	2.5, 3.1, 1.0
D2	59.38	1121	6510	3.1, 3.7, 1.4	2.8, 3.4, 1.1

^[a]: The estimated values of EQE, CE and PE at current densities of 100 and 200 mA cm⁻².

Figure 5.14 (b-d) shows the plots of EL efficiencies (including EQE, CE and PE)-current density in the devices C1, C2, D1 and D2. The maximum EL efficiencies of devices employed 3TPYMB as ETL were 3.37%, 4.21 cd A^{-1} and 2.55 lm W^{-1} for device C1 and 3.84%, 4.41 cd A^{-1} and 2.62 lm W^{-1} for device C2. However, these values dropped to 0.9%, 1.3 cd A^{-1} , 0.4 lm W^{-1} and 1.1%, 1.5 cd A^{-1} , 0.5 lm W^{-1} at a higher current density of 200 mA cm^{-2} , respectively. In contrast, devices D1 and D2 (employing TPBI as ETL) exhibited lower maximum efficiencies, but their roll-off characteristics were much better when current density were getting higher. This is because the electron injection from ETL to EML is much improved by replacing 3TPYMB with TPBI, which leads to a much better charge balance in OLED devices.

Table 5.7 EL performance of devices D1 and D2.

Device	$V_{\text{on}}^{[a]}$ (V)	at 1000 / 3000 $\text{cd m}^{-2[b]}$ (V/%)	$Max L$ (cd m^{-2} , V)	EQE (%)	CE (cd A^{-1})	PE (lm W^{-1})	λ_{max} (nm)	CIE (x, y)
D1	4.1	7.0, 3.0 / 8.5, 2.5	5672, 10.4	3.13	3.64	1.58	459	(0.166, 0.169)
D2	4.1	6.9, 3.3 / 8.2, 2.8	6538, 10.1	3.42	3.86	1.65	455	(0.159, 0.157)

^[a]: Turn-on voltage at which brightness exceeds 1 cd m^{-2} ; ^[b]: The estimated values of driving voltage and EQE of device at brightness of 1000 and 3000 cd m^{-2} .

EL performance of device D1 and D2 is summarized in Table 5.7. Blue emissions centered at 459 nm and 455 nm in accordance with S1-Cz-OXD and S2-Cz-OXD are obtained from device D1 and D2. The corresponding CIE coordinates are (0.166, 0.169) and (0.159, 0.157), respectively. Both devices turned on at a low voltage of 4.1 V due to the bipolar properties of the emitting materials S4-Cz-OXD and S5-Cz-OXD despite big energy barriers existing between PEDOT:PSS and EML. It achieved a maximum brightness of 5672 cd m^{-2} at 10.4 V, a maximum EQE of 3.13%, a maximum CE of 3.64 cd A^{-1} and a maximum PE of 1.58 lm W^{-1} . High efficiency of 3.0% was obtained at high brightness of 1000 cd m^{-2} . D2 exhibited a better device performance than D1, mainly due to the extended conjugated branches in S2-Cz-OXD, which enhanced the solid quantum efficiency of EML. Device D2 realized a maximum brightness of 6538 cd m^{-2} at 10.1 V. The maximum efficiencies of D2 were 3.42%, 3.86 cd A^{-1} and 1.65 lm W^{-1} , respectively,

and a high efficiency of 3.3% still remained at high brightness of 1000 cd m⁻². Moreover, both D1 and D2 showed better roll-off characteristics improved by using TPBI as ETL. These results are among the high efficient solution-processed undoped blue OLEDs.

5.7 Conclusions

In summary, a series of fluorene-free star-shaped blue emitters Sn-Cz-OXD (n = 1~3) with different arm length have been developed. Sn-Cz-OXD (n = 1~3) are composed of a tris(1,3,4-oxadiazole)phenylene (t-OXD) ring as core and three 3,6-di-tert-butylcarbazole (t-BCz) as terminal groups bridged by rigid benzene units, where 'n' means the amount of benzene units in the bridge. Sn-Cz-OXD (n = 1~3) are D- π -A structure bipolar molecules, where the electron-deficient t-OXD core is an acceptor unit and the electron-rich t-BCzs are donor units. Moreover, t-OXD and t-BCz moieties are of high thermal stability and this endowed these emitters with high T_g (above 135 °C), high T_d (above 440 °C) and excellent spectral stability during prolonged (220 hours) heating at 150 °C in ambient air. They were much more stable than many fluorene-based emitters. High quantum efficiencies (Φ_f) of 54%, 58% and 61% as well as pure blue emission at 457 nm, 452 nm and 448 nm were obtained from the neat films of Sn-Cz-OXD (n = 1~3). The improvement in quantum efficiencies and blue shift in emission spectrum were caused by the increasing benzene amount in the bridges because: (1) it would increase the length of the conjugated arms, which could more effectively suppress the intermolecular interaction and reduce the fluorescence quenching, leading to a higher quantum efficiency; (2) it would cause distortion in the conjugated bridge and reduce the charge transfer ability between t-OXD acceptor and t-BCz donors, resulting in a blue shift in PL spectrum and an increase in molecular energy bandgap of these emitters. However, additional of benzene units would also reduce the solubility of the molecules due to the rigid framework. S3-Cz-OXD was almost insoluble in solvents such as CH₂Cl₂ and hexane and was of low solubility in toluene and chlorobenzene therefore it could not be used in OLED device although it exhibited the most saturated blue emission and the highest quantum efficiency.

Undoped OLED devices based on S1-Cz-OXD and S2-Cz-OXD with configuration of **ITO/PEDOT:PSS/EML/3TPYMB/Cs₂CO₃/Al** were fabricated. S1-Cz-OXD based device C1 exhibited much better performance than the control device A1 which was based on L1-Cz-OXD due to the higher solubility (better film forming ability) and higher solid quantum efficiency of S1-Cz-OXD afforded by the star-shaped structure. S2-Cz-OXD based device C2 showed superior EL performance than C1 because of the higher solid quantum efficiency of S2-Cz-OXD provided by its extended conjugated arms. Device C2 achieved a maximum luminance of 4352 cd m⁻², a maximum CE of 4.41 cd A⁻¹, a maximum EQE of 3.84% and a maximum PE of 2.62 lm W⁻¹.

By using TPBI as ETL instead of 3TPYMB, devices D1 and D2 were fabricated. They exhibited less maximum efficiencies but much better roll-off characteristics at high current density compared with C1 and C2, respectively. Device D2 realized a maximum brightness of 6538 cd m⁻² at 10.1 V and maximum efficiencies of 3.42%, 3.86 cd A⁻¹ and 1.65 lm W⁻¹. These results are believed to be among the high efficient solution-processed undoped blue device employing fluorene-free emitting materials.

References

1. X. He, L. Chen, Y. Zhao, S. C. Ng, X. Wang, X. Sun, and X. (Matthew) Hu, *RSC Adv.*, 2015, **5**, 15399–15406.
2. X. He, L. Chen, Y. Zhao, H. Chen, S. C. Ng, X. Wang, X. Sun, and X. “Matthew” Hu, *Org. Electron.*, 2016, **37**, 14–23.
3. L. Deng, X. Wang, Z. Zhang, and J. Li, *J. Mater. Chem.*, 2012, **22**, 19700–19708.
4. W.-Y. Lai, Q.-Y. He, D.-Y. Chen, and W. Huang, *Chem. Lett.*, 2008, **37**, 986–987.
5. B. Liang, S. Hu, Y. Liu, Z. Fan, X. Wang, W. Zhu, H. Wu, and Y. Cao, *Dye. Pigment.*, 2013, **99**, 41–51.
6. Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin, and Y. Cao, *Adv. Funct. Mater.*, 2013, **23**, 1781–1788.
7. C. Liu, Q. Fu, Y. Zou, C. Yang, and J. Qin, *Chem. Mater.*, 2014, **26**, 3074–3083.
8. W.-B. Zhang, W.-H. Jin, X.-H. Zhou, and J. Pei, *Tetrahedron*, 2007, **63**, 2907–2914.

9. D. Tanaka, T. Takeda, T. Chiba, S. Watanabe, and J. Kido, *Chem. Lett.*, 2007, **36**, 262–263.
10. S.-H. Eom, Y. Zheng, E. Wrzesniewski, J. Lee, N. Chopra, F. So, and J. Xue, *Org. Electron.*, 2009, **10**, 686–691.
11. T.-C. Liao, H.-T. Chou, F.-S. Juang, Y.-S. Tsai, L.-A. Hong, and Y.-Y. Ho, *Curr. Appl. Phys.*, 2013, **13**, S152–S155.
12. S. Il Yoo, J.-A. Yoon, N. H. Kim, J. W. Kim, H. W. Lee, Y. K. Kim, G. He, and W. Y. Kim, *Opt. Mater. (Amst.)*, 2015, **39**, 21–25.

Chapter 6

Star-Shaped Blue Emitters Sn-Cz-OXD (n = 4, 5)

This chapter describes all the experiments related to star-shaped blue emitters S4-Cz-OXD and S5-Cz-OXD with extra alkoxy chains, including their molecular design, synthesis methods, basic characterizations, and fabrication of solution-processed devices. The alkoxy chains are added to greatly improve the solubility of these molecules and are beneficial for their film forming ability through spin-coating. They exhibit strong pure blue light with high quantum efficiency above 62% in neat films and have good thermal stability. The solution processed undoped OLED device based on S4-Cz-OXD shows a maximum luminance of 7804 cd m^{-2} , a maximum CE of 4.69 cd A^{-1} , a maximum EQE of 4.20%, and a maximum PE of 2.08 lm W^{-1} with the CIE coordination of (0.150, 0.141).

6.1 Introduction

Although S3-Cz-OXD exhibited the highest quantum yield and the most saturated blue emission, its poor solubility hindered its application in OLEDs. In order to solve this problem, flexible alkoxy chains were introduced to the backbone of S3-Cz-OXD and so emitter S4-Cz-OXD was developed. Considering that star-shaped molecules with longer conjugated branches possess better photoelectric properties, S5-Cz-OXD with extended branches based on S4-Cz-OXD was also developed. Besides, alkoxy chains were supposed to provide extra electron donating ability and better film forming ability to the molecule. High solid quantum efficiency and good spectrum thermal stability of these two emitters were also expected. S4-Cz-OXD and S5-Cz-OXD were successfully synthesized, characterized and fabricated into undoped OLED devices with good performance.¹

6.2 Experimental Methods

6.2.1 Synthesis

The synthesis of emitters S4-Cz-OXD and S5-Cz-OXD, and specific reaction conditions for each step, are shown in Figure 6.1. The specific chemical structures of target emitters are shown in Figure 6.2.

Synthesis of Compound 13:²

15.5 mL of 1-bromohexane (110 mmol), 5.51 g of hydroquinone (compound **12**, 50.00 mmol), 24.98 g of K₂CO₃ (181 mmol) and 121 mL of dry acetone were mixed in a 250 mL round bottom flask and stirred at reflux for 30 hours. After the reaction was completed, plenty of water was added, and the mixture was extracted with Et₂O. The organic layer was washed with aqueous Na₂S₂O₃ and DI water, and dried over anhydrous MgSO₄. After filtration and evaporation, the residue was purified by silica gel column chromatography followed by recrystallization to give final product as crystals (yield 62%).

Figure 6.1 Synthetic route for S1-Cz-OXD ($n = 4, 5$). Specific reaction conditions: i) 1-bromohexane, K_2CO_3 , DMF, heat at $80\text{ }^\circ\text{C}$ for 30 hours; ii) $CHCl_3$, bromine, stir at room temperature for 20 hours; iii) THF, $n\text{-BuLi}$, $-78\text{ }^\circ\text{C}$ to RT, 30 mins; iv) 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $-78\text{ }^\circ\text{C}$ to RT, stir for 24 hours; v) K_2CO_3 , toluene, Aliquid 336, $Pd(PPh_3)_4$, stir in dark, heat at $100\text{ }^\circ\text{C}$ for 20 hours.

Synthesis of Compound **15**:³

Compound **15** was prepared using a similar reaction to that used for the synthesis of compound **6**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 2.18 g of compound **14** (5 mmol), 55 mL anhydrous THF, 6 mL of $n\text{-BuLi}$ (2.0 M, 12 mmol) and 5.3 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13 mmol). The crude product of compound **15** was collected after

filtration and evaporation without further purification and was directly used in the next step.

Figure 6.2 Chemical structures of S4-Cz-OXD and S5-Cz-OXD.

Synthesis of Compound 16:³

Compound **16** was prepared using a similar Suzuki Reaction to that used for the synthesis of compound **S2-Cz-OXD**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 5.3 g of compound **15** (10 mmol), 3.1 g of 1-bromo-4-iodobenzene (11 mmol), 40 mL of 2M solution of K_2CO_3 , 120 mL toluene, three drops of Aliquat 336, and 0.12 g of $Pd(PPh_3)_4$. The reaction yield of this step was 60%.

Synthesis of Compound 17:

Compound **17** was prepared using a similar Suzuki Reaction to that used for the synthesis of compound **S2-Cz-OXD**. For more details please refer to Section 5.2.1. The specific amount of each reagent were: 4.81 g of compound **6** (10 mmol), 4.80 g of compound **14** (11 mmol), 40 mL of 2M solution of K_2CO_3 , 120 mL toluene, three drops of Aliquat 336, and 0.12 g of $Pd(PPh_3)_4$ (0.1 mmol). The reaction yield of this step was 45%. 1H NMR ($CDCl_3$, 500 MHz, δ): 0.86-0.94 (m, 6H), 1.26-1.43 (m, 12H), 1.48 (s, 18H), 1.71-1.89 (m, 4H), 3.94-4.08 (m, 4H), 7.02 (s, 1H), 7.22 (s, 1H), 7.41-7.49 (m, 4H), 7.59, 7.73 (dd,

$J = 8.4$ Hz, 4H), 8.15 (d, $J = 1.4$ Hz, 2H). ^{13}C NMR (CDCl_3 , 400 MHz, δ): 14.2, 22.7, 25.8, 25.9, 29.3, 29.4, 29.8, 31.6, 32.1, 34.9, 69.8, 70.5, 109.4, 111.8, 116.4, 118.5, 123.5, 123.7, 126.2, 130.2, 130.8, 136.5, 137.2, 139.3, 143.0, 150.1, 150.6. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{44}\text{H}_{56}\text{BrNO}_2$: 709.35. Found: 710.04. Anal. Calcd. for $\text{C}_{44}\text{H}_{56}\text{BrNO}_2$: C, 74.35; H, 7.94; N, 1.97. Found: C, 74.36; H, 7.92; N, 2.01.

Synthesis of Compound 18:

Compound **18** was prepared using a similar reaction to that used for the synthesis of compound **6**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 3.55 g of compound **17** (5 mmol), 55 mL anhydrous THF, 3 mL n-BuLi (2.0 M, 6 mmol) and 2.6 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 mmol). The crude compound **18** was collected without further purification and was used directly in the next step. ^1H NMR (CDCl_3 , 500 MHz, δ): 0.86-0.94 (m, 6H), 1.26-1.38 (m, 22H), 1.48 (s, 20H), 1.69-1.85 (m, 4H), 3.98-4.03 (m, 4H), 6.97 (s, 1H), 7.30 (s, 1H), 7.41-7.48 (m, 4H), 7.58, 7.77 (dd, $J = 8.4$ Hz, 2H), 8.15 (s, 2H). ^{13}C NMR (CDCl_3 , 400 MHz, δ): 14.2, 22.8, 25.1, 25.9, 29.5, 29.7, 31.7, 31.9, 32.2, 34.9, 69.7, 70.0, 109.5, 115.6, 116.3, 121.0, 123.7, 126.1, 131.0, 137.4, 139.4, 142.9, 158.6. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd. for $\text{C}_{50}\text{H}_{68}\text{BNO}_4$: 757.52. Found: 754.42. Anal. Calcd. for $\text{C}_{50}\text{H}_{68}\text{BNO}_4$: C, 79.24; H, 9.04; N, 1.85. Found: C, 79.20; H, 9.06; N, 1.83.

Synthesis of Compound 19:

Compound **19** was prepared using a similar Suzuki Reaction to that used for the synthesis of compound **S2-Cz-OXD**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 2.90 g of compound **6** (6 mmol), 4.70 g of compound **16** (8 mmol), 40 mL of 2M solution of K_2CO_3 , 120 mL toluene, three drops of Aliquid 336, and 0.08 g of $\text{Pd}(\text{PPh}_3)_4$ (0.07 mmol). The reaction yield of this step was 42%. ^1H NMR (CDCl_3 , 500 MHz, δ): 0.87-0.91 (m, 6H), 1.28-1.43 (m, 12H), 1.48 (s, 18H), 1.67-1.77 (m, 4H), 3.94-3.98 (m, 4H), 6.98 (s, 1H), 7.06 (s, 1H), 7.42-7.57 (m, 8H), 7.65, 7.86 (dd, $J = 8.4$ Hz, 2H), 7.75 (s, 4H), 8.16 (d, $J = 1.4$ Hz, 2H). ^{13}C NMR (CDCl_3 , 400 MHz, δ): 14.1, 22.7, 25.9, 29.4, 31.6, 32.2, 34.9, 69.8, 69.9, 109.4, 116.1, 116.2, 116.4, 121.2, 123.5, 123.7, 126.8, 127.1, 128.4, 129.7, 130.2, 130.6, 130.8, 131.2, 131.3, 137.4, 137.5,

137.7, 139.0, 139.3, 139.6, 143.0, 150.3, 150.5. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. for $C_{56}H_{64}BrNO_2$: 861.41. Found: 861.25. Anal. Calcd. for $C_{56}H_{64}BrNO_2$: C, 77.94; H, 7.47; N, 1.62. Found: C, 77.92; H, 7.49; N, 1.61.

Synthesis of Compound 20:

Compound **20** was prepared using a similar reaction to that used for the synthesis of compound **6**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 4.30 g of compound **19** (5 mmol), 55 mL anhydrous THF, 3 mL n-BuLi (2.0 M, 6 mmol) and 2.6 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 mmol) The crude compound **20** was collected without further purification and was used directly in the next step. 1H NMR ($CDCl_3$, 500 MHz, δ): 0.86-0.92 (m, 6H), 1.26-1.35 (m, 12H), 1.38 (s, 12 H), 1.48 (s, 18H), 1.66-1.77 (m, 4H), 3.92-3.98 (m, 4H), 7.03 (s, 1H), 7.07 (s, 1H), 7.42-7.50 (m, 4H), 7.64, 7.66 (dd, $J = 2.2$ Hz, 4H), 7.75 (s, 4H), 7.87 (t, $J = 8.6$ Hz, 4H), 8.16 (d, $J = 1.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ): 14.2, 22.7, 25.0, 25.2, 25.9, 29.5, 31.6, 32.2, 34.9, 53.6, 69.8, 69.9, 83.9, 109.4, 116.4, 123.6, 123.8, 126.8, 127.1, 128.4, 129.0, 130.2, 130.6, 131.0, 134.6, 137.5, 137.9, 139.0, 139.4, 139.7, 141.5, 143.0, 150.6. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. for $C_{62}H_{76}BNO_4$: 909.59. Found: 907.50. Anal. Calcd. for $C_{62}H_{76}BNO_4$: C, 81.82; H, 8.42; N, 1.54 Found: C, 81.85; H, 8.27; N, 1.51.

Synthesis of S4-Cz-OXD:

S4-Cz-OXD was prepared using a similar Suzuki Reaction to that used for the synthesis of compound **S2-Cz-OXD**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 1.52 g crude product of compound **18** (2 mmol), 0.37 g of compound **11** (0.5 mmol), 20 mL of 2M solution of K_2CO_3 , 60 mL toluene, three drops of Aliquid 336, and 0.12 g of $Pd(PPh_3)_4$ (0.10 mmol). The reaction yield of this step was 33%. 1H NMR ($CDCl_3$, 400 MHz, δ): 0.88-0.91 (m, 18H), 1.31-1.35 (m, 24H), 1.41-1.47 (m, 12H), 1.49 (s, 54H), 1.75-1.83 (m, 12H), 4.06 (t, $J = 6.4$ Hz, 12H), 7.14 (d, $J = 13.8$ Hz, 6H), 7.45-7.51 (m, 12H), 7.64 (d, $J = 8.4$ Hz, 6H), 7.85, 7.91 (dd, $J = 8.4$ Hz, 12H), 8.17 (d, $J = 1.3$ Hz, 6H), 8.34 (d, $J = 8.3$ Hz, 6H), 9.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 14.0, 14.1, 22.6, 22.7, 25.8, 25.9, 29.3, 29.4, 31.4, 31.5, 32.0, 34.7, 69.8, 109.3,

115.9, 116.0, 116.2, 123.4, 123.6, 126.1, 126.9, 129.4, 130.4, 130.8, 131.0, 136.7, 137.1, 139.2, 142.6, 142.9, 150.5, 162.8, 165.7. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. for $C_{162}H_{183}N_9O_9$: 2398.41. Found: 2398.26. Anal. Calcd. for $C_{162}H_{183}N_9O_9$: C, 81.06; H, 7.68; N, 5.25. Found: C, 81.04; H, 7.63; N, 5.30.

Synthesis of S5-Cz-OXD:

S5-Cz-OXD was prepared using a similar Suzuki Reaction to that used for the synthesis of compound **S2-Cz-OXD**. For more details please refer to Section 5.2.1. The specific amounts of each reagent were: 1.82 g of compound **20** (2 mmol), 0.37 g of compound **11** (0.5 mmol), 20 mL of 2M solution of K_2CO_3 , 60 mL toluene, three drops of Aliquid 336, and 0.12 g of $Pd(PPh_3)_4$ (0.10 mmol). The reaction yield of this step was 27%. 1H NMR ($CDCl_3$, 400 MHz, δ): 0.90 (t, $J = 6.7$ Hz, 18H), 1.30-1.35 (m, 24H), 1.40-1.45 (m, 12H), 1.49 (s, 54 H), 1.73-1.80 (m, 12H), 4.00 (t, $J = 6.2$ Hz, 12H), 7.10 (d, $J = 5.5$ Hz, 6H), 7.42-7.50 (m, 12H), 7.67 (d, $J = 8.3$ Hz, 6H), 7.77-7.81 (m, 24H), 7.88, 7.92 (dd, $J = 8.3$ Hz, 12H), 8.16 (d, $J = 1.1$ Hz, 6H), 8.34 (d, $J = 8.1$ Hz, 6H), 9.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 14.0, 22.6, 25.8, 29.4, 31.5, 32.0, 34.7, 69.7, 109.3, 116.1, 116.2, 122.0, 123.4, 123.6, 126.7, 126.9, 127.7, 127.8, 128.3, 130.1, 130.2, 130.6, 137.4, 137.6, 138.1, 138.9, 139.2, 139.4, 142.9, 144.8, 150.5, 162.8, 165.5. MS (MALDI-TOF, m/z): $[M]^+$ Calcd. for $C_{198}H_{207}N_9O_9$: 2854.60. Found: 2854.78. Anal. Calcd. for $C_{198}H_{207}N_9O_9$: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.21; H, 7.33; N, 4.38.

6.2.2 Device Fabrication and Optimization

The solubility of S4-Cz-OXD and S5-Cz-OXD in different organic solvents was listed in Table 6.1. Compared with S3-Cz-OXD which was almost insoluble in hexane and toluene, S4-Cz-OXD exhibited greatly improved solubility although they were with the same amount of benzene units in the bridges, which could be assigned to the introduced alkoxy chains. S5-Cz-OXD showed poorer solubility than S4-Cz-OXD because of the rigid extended conjugated branches. Undoped devices E4 and E5 with the configuration of **ITO/PEDOT:PSS/EML/TPBI/LiF/Al** were fabricated employing S4-Cz-OXD and S5-Cz-OXD as emitting layer. The procedure of device fabrication was similar with that

of device D1 and D2 (please refer to Section 5.2.2). The specific conditions for all spin-coating layers, the parameters for vacuum deposition for all used source materials and the optimized thickness for each layer are summarized in Table 6.2.

Table 6.1 Solubility of target emitters in different organic solvents.

Compound	Solubility (mg mL ⁻¹)				EML for OLEDs
	CHCl ₃	Toluene	Hexane	toluene : CB (1:1)	
S4-Cz-OXD	~ 20	12	3	15	Spin-coating
S5-Cz-OXD	10	3	< 1	8	Spin-coating

Table 6.2 Optimized condition for deposition of multilayers in device fabrication.

Spin coated	Spin rate / t (rpm / s)	Anneal T / t (°C / min)	Thickness (nm)	Vacuum deposited	Deposit T / I (°C / A)	Thickness (nm)
PEDOT:PSS	4000 / 60	120 / 15	30	TPBI	200 / 1	40
S4-Cz-OXD	3500 / 60	120 / 30	70	LiF	630 / 3.6	0.5
S5-Cz-OXD	2000 / 40	120 / 30	70	Al	>70 / 60	120

6.3 Materials Characterization

The characterization methods for Sn-Cz-OXD (n = 4~5) were almost the same as those applied to L1-Cz-OXD and Sn-Cz-OXD (n = 1~3). For details of the chemical analysis, absorption and photoluminescence spectroscopy, electrochemical and thermal properties, surface morphology, please refer to Section 4.3.

6.4 Device Characterization

Characterization for OLED devices based on Sn-Cz-OXD (n = 4~5) were identical to those applied to L1-Cz-OXD based ones. For details please refer to Section 4.4.

6.5 Results and Discussion for Synthesized Materials

6.5.1 Analysis for Chemical Structure and Molecular Weight

^1H NMR, ^{13}C NMR, EA and MALDI-TOF data of all newly reported compounds including compounds **17**, **18**, **19**, **20**, **S4-Cz-OXD** and **S5-Cz-OXD** are summarized in Section 6.2.1. The spectra for NMR and MALDI-TOF are in the Appendix. The chemical structure and purity of these compounds are proved by the combined results of NMR, EA and MALDI-TOF measurements.

6.5.2 Photophysical Properties

UV-visible absorption and photoluminescence of **S4-Cz-OXD** and **S5-Cz-OXD** were characterized in dilute toluene solution, doped PMMA films and solid neat films. The resultant spectra are shown in Figures 6.3, 6.4, and 6.5, respectively. The photophysical properties of these emitters are summarized in Table 6.3. Figure 6.3 depicts the UV-vis absorption and PL spectra of Sn-Cz-OXD (n = 3~5) in dilute toluene solution. The maximum absorption peaks were located at 348 nm, 350 nm and 349 nm, while and the emission peaks were located at 418 nm, 428 nm and 425 nm for S3-Cz-OXD, S4-Cz-OXD and S5-Cz-OXD. Both spectra of S4-Cz-OXD exhibited red shift compared with those of S3-Cz-OXD. This could be attributed to the introduced alkoxy chains in S4-Cz-OXD because: (1) Alkoxy chains are electron donating groups and this enhances the HOMO energy level of the molecule, leading to a narrower energy bandgap; (2) Alkoxy chains increase the polarity of S4-Cz-OXD, causing a bathochromic shift in toluene solvent. S5-Cz-OXD exhibits a slight blue shift compared with S4-Cz-OXD due to the extended conjugated branches, which was discussed in Chapter 5.

The corresponding onset wavelengths of the absorption were 403 nm, 408 nm and 405 nm for S3-Cz-OXD, S4-Cz-OXD and S5-Cz-OXD. And their optical energy bandgap, estimated from the onset values, were calculated to be 3.08 eV, 3.04 eV and 3.06 eV, respectively. These results were in accordance with their spectra. High quantum

efficiencies (Φ_f) of 79% and 75% were obtained for S4-Cz-OXD and S5-Cz-OXD in dilute toluene solution by using 9,10-diphenylanthracene as a reference. The Φ_f of S4-Cz-OXD was much lower than that of S3-Cz-OXD (87%). This was because the alkoxy chains in S4-Cz-OXD were flexible and free to move in solvent. The free rotation and changes of configuration would reduce the radiative efficiency, leading to low quantum efficiency. S5-Cz-OXD exhibited a lower Φ_f than S4-Cz-OXD due to the reduced steric effect. This trend again was similar to that of Sn-Cz-OXD ($n = 1\sim3$).

Figure 6.3 Normalized absorption (a) and PL spectra (b) of Sn-Cz-OXD ($n = 3\sim5$) in dilute solution.

Doped PMMA films and neat films of Sn-Cz-OXD ($n = 4, 5$) were fully investigated. The packing state of emitting molecules was different in these two types of solid films. Molecules are isolated domains when dispersed in PMMA, while in neat films, they are much closer to each other. Figure 6.4 depicts the UV-vis absorption and PL spectra of S3-Cz-OXD, S4-Cz-OXD and S5-Cz-OXD in doped PMMA films. The absorption peaks are at 352 nm and 351 nm, while the emission peaks at excitation of 355 nm were 447 nm and 445 nm for S4-Cz-OXD and S5-Cz-OXD, respectively. Both absorption and PL spectra exhibit an obvious red shift compared with those of dilute solutions, implying weak aggregation and increased intermolecular interactions in the solid state. Both absorption and PL spectra for a doped PMMA film of S5-Cz-OXD exhibit blue shifts compared with S4-Cz-OXD. These changing trends of S4-Cz-OXD and S5-Cz-OXD are similar to that in their corresponding dilute solutions for the same reasons discussed above. Here, without the bathochromic shift caused by polar solvent, S4-Cz-OXD only

shows a very slight red-shift (1 nm) compared with S3-Cz-OXD, which could be due to the electron donating ability of the introduced alkoxy chains.

Figure 6.4 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD (n = 3~5) in doped PMMA films.

The corresponding Φ_f in doped PMMA films of S4-Cz-OXD and S5-Cz-OXD are calculated to be 81% and 84%, higher than those of Sn-Cz-OXD (n = 1~3), which was quite different from the situation in dilute solution. This is because in solid state, the molecular vibration and single bond rotation were mainly suppressed. Compared with S3-Cz-OXD (79%), Φ_f of S4-Cz-OXD is slightly increased because the introduced bulky alkoxy chains could further suppress the intermolecular interactions in solid state. In contrast to dilute solution, PMMA film of S5-Cz-OXD exhibits a higher Φ_f than that of S4-Cz-OXD due to the longer branches which could prevent intermolecular aggregation more effectively. This trend was similar to that from S1-Cz-OXD to S3-Cz-OXD due to the same reason.

Figure 6.5 shows the UV-vis absorption and PL spectra of Sn-Cz-OXD (n = 3~5) in solid neat films. The absorption peaks are 352 nm and 351 nm, while the emission peaks at excitation of 355 nm are 449 nm and 446 nm for S4-Cz-OXD and S5-Cz-OXD, respectively. The absorption of the neat films were almost the same with their corresponding doped PMMA films.

Figure 6.5 Normalized absorption (a) and PL spectrum (b) of Sn-Cz-OXD (n = 3~5) in neat films.

Table 6.3 Photophysical properties of target molecules.

Emitter	Dilute solution ^[a]				Solid film ^{[c]/[d]}		
	$\lambda_{\text{max}}^{\text{Abs}}/\lambda_{\text{max}}^{\text{PL}}$ (nm)	$\lambda_{\text{onset}}^{\text{Abs}}$ (nm)	E_{opt} (eV)	$\Phi_{\text{f}}^{\text{[b]}}$ (%)	$\lambda_{\text{max}}^{\text{Abs}}$ (nm)	$\lambda_{\text{max}}^{\text{PL}}$ (nm)	$\Phi_{\text{f}}^{\text{[e]}}$ (%)
S4-Cz-OXD	350 / 428	408	3.04	79	352 / 352	447 / 449	81 / 62
S5-Cz-OXD	349 / 425	405	3.06	75	351 / 351	445 / 446	84 / 65

^[a]: Analyzed in dilute toluene solution (10^{-6} M); ^[b]: 9,10-diphenylanthracene is reference material, $\Phi_{\text{f}} = 0.92$ in dilute toluene; ^[c]: Analyzed in doped PMMA films ($<10^{-3}$ M); ^[d]: Analyzed in neat films; ^[e]: 9,10-diphenylanthracene is reference material, $\Phi_{\text{f}} = 0.83$ dispersed in PMMA films ($<10^{-3}$ M).

Generally speaking, the aggregation of emitting molecules in the neat films leads to serious fluorescence quenching and obvious red shift in emission due to the enhanced intermolecular interactions compared with the doped PMMA films where the emitting molecules are isolated. However, the PL spectra of neat films exhibit very slight red shift (only 1 ~ 2 nm) compared with the corresponding doped PMMA films, implying extended branches. These introduced alkoxy chains suppress the intermolecular aggregation effectively. High Φ_{f} of 62% and 65% were obtained for S4-Cz-OXD and S5-Cz-OXD in neat films, indicating their high potential as undoped emitters.

6.5.3 Electrochemical Properties

CV curves of S4-Cz-OXD and S5-Cz-OXD are shown in Figure 6.6. Both S4-Cz-OXD and S5-Cz-OXD exhibit reversible similar oxidation and reduction behavior under positive and negative voltages just like Sn-Cz-OXD ($n = 1\sim2$), indicating their distinct bipolar properties. Different from S4-Cz-OXD ($n = 1\sim3$), two oxidation peaks are observed, located at 1.31 V and 1.51 V for S4-Cz-OXD and at 1.28 V and 1.42 V for S5-Cz-OXD. The peaks at 1.31 V and 1.28 V could be assigned to the oxidation of alkoxy chains on the branches; while the peaks at 1.51 V and 1.42 V could be ascribed to the oxidation of the backbone of S4-Cz-OXD and S5-Cz-OXD, respectively. This suggests the HOMO energy levels of S4-Cz-OXD and S5-Cz-OXD were improved by the introduced alkoxy chains with electron-donating ability.

Figure 6.6 Cyclic voltammograms of Sn-Cz-OXD ($n = 4, 5$).

The onset oxidation potentials ($E_{\text{onset}}^{\text{oxd}}$) are 1.17 V and 1.19 V, while the reduction potentials ($E_{\text{onset}}^{\text{red}}$) are -1.55 V and -1.56 V for S4-Cz-OXD and S5-Cz-OXD, respectively. The onset redox potentials are very similar for these two emitters due to their similar molecular structure. They possess the same donor and acceptor units, which determine the HOMO and LUMO energy level of the molecules, respectively. The HOMO levels estimated from $E_{\text{onset}}^{\text{oxd}}$ are -5.57 eV and -5.59 eV for S4-Cz-OXD and S5-Cz-OXD. These

values are much higher than that of S1-Cz-OXD (-5.66 eV) and S2-Cz-OXD (-5.67 eV), which could be attributed to the alkoxy chains that enhance electron-donating ability of the molecule. Besides, the slight decrease in the HOMO energy level of S5-Cz-OXD compared with that of S4-Cz-OXD is caused by the extended conjugated benzene units, which reduce the charge transfer ability between donor and acceptor moieties. The LUMO levels estimated from $E_{\text{onset}}^{\text{red}}$ are -2.85 eV and -2.84 eV. The resultant energy bandgap calculated from CV curves are 2.72 eV and 2.75 eV for S4-Cz-OXD and S5-Cz-OXD.

Table 6.4 Electrochemical and thermal properties of target molecules.

Compounds	$E_{\text{onset}}^{\text{oxd}} / E_{\text{onset}}^{\text{red}}$ ^[a] (V)	E_{HOMO} ^[b] (eV)	E_{LUMO} ^{[b]/[c]} (eV)	E_{gap} ^{[d]/[f]} (eV)	T_g (°C)	T_d (°C)	RMS ^{[g]/[h]} (nm)
S4-Cz-OXD	1.17 / -1.55	-5.57	-2.85 / -2.53	2.72 / 3.04	137, 151	413	0.54 / 0.52
S5-Cz-OXD	1.19 / -1.56	-5.59	-2.84 / -2.53	2.75 / 3.06	140, 160	421	0.67 / 0.65

^[a]: Performed in 0.1M (C₄H₉)₄NClO₄ in CH₂Cl₂; ^[b]: Estimated from $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ obtained from CV curve with ferrocene calibration; ^[c]: Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt}}$; ^[d]: Determined from CV; ^[f]: Estimated from UV-vis absorption spectrum (E_{opt}); ^[g]: RMS value of non-annealed films and ^[h]: RMS value of annealed films.

As was seen from CV results for other emitters, there is a big difference between E_{gap} calculated from CV curves and E_{opt} calculated from UV-vis spectroscopy for S4-Cz-OXD and S5-Cz-OXD (see Section 4.5.3). A more reliable LUMO energy level is determined by the Equation $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{opt}}$ and the values are -2.53 eV for both S4-Cz-OXD and S5-Cz-OXD. All these results are summarized in Table 6.4.

6.5.4 Thermal Properties

The thermal properties of Sn-Cz-OXD (n = 4~5) are explored by TGA and DSC. The resultant DSC traces and TGA thermogram are shown in Figure 6.7 and the results are summarized in Table 6.4. The DSC curves exhibit two separated T_g at 137 °C and 151 °C for S4-Cz-OXD, at 140 °C and 160 °C for S5-Cz-OXD. The former values (at 137 °C and

140 °C) might correspond to the T_g of the flexible alkoxy chains; the latter ones (at 151 °C and 160 °C) might be ascribed to the T_g of the backbone of S4-Cz-OXD and S5-Cz-OXD molecules, respectively. If only the molecular backbone is considered, it is obvious that the T_g is increasing with the amount of benzene units (T_g values are 137 °C, 141 °C, 145 °C, 151 °C and 160 °C from S1-Cz-OXD to S5-Cz-OXD). However, T_g of S4-Cz-OXD and S5-Cz-OXD are reduced compared with Sn-Cz-OXD ($n = 1\sim3$) because alkoxy chains are flexible and they tend to readily undergo rearrangement processes. The thermal decomposition temperatures (T_d , 5% weight loss) for S4-Cz-OXD and S5-Cz-OXD are 413 °C and 421 °C. T_d of S4-Cz-OXD and S5-Cz-OXD is lower than those of Sn-Cz-OXD ($n = 1\sim3$) because the alkoxy chains are easier to undergo thermal degradation during the heating process. This trend of T_d is the same as that of T_g . S5-Cz-OXD exhibits higher T_d than S4-Cz-OXD due to the larger molecular size. To sum up, both S4-Cz-OXD and S5-Cz-OXD possess high T_g (> 135 °C) and T_d (> 410 °C) temperatures.

Figure 6.7 DSC traces (a) and TGA thermogram (b) of Sn-Cz-OXD ($n = 4, 5$).

6.5.5 Spectrum Thermal Stability

Similar long period annealing experiments were employed to test the stability of the neat films of S4-Cz-OXD and S5-Cz-OXD. The resultant spectra are shown in Figure 6.8. The emission spectra are quite stable after 120 hours of thermal annealing at 150 °C in ambient air. S4-Cz-OXD and S5-Cz-OXD exhibit less

stability than that of Sn-Cz-OXD ($n = 1\sim3$) without alkoxy chains. A very slight increase in the tail of the spectra was observed as time passed, which is probably due to slight aggregation of the molecules. However, the spectral stability of S4-Cz-OXD and S5-Cz-OXD were still much better than fluorene-based materials.

Figure 6.8 Normalized PL spectrum of Sn-Cz-OXD ($n = 4, 5$) during prolonged heating treatment.

6.5.6 Surface Morphology

The excellent heat tolerance of emitters S4-Cz-OXD and S5-Cz-OXD indicates that they could form thermal stable films. Moreover, the introduced alkoxy chains in these two emitters could enhance their solubility and film forming ability, therefore stable amorphous films of these emitters are expected to be obtained from solution-casting. In order to verify this, surface morphology of spin-cast thin films of S4-Cz-OXD and S5-Cz-OXD are evaluated by using AFM and the resultant images of both non-annealed and annealed films are shown in Figure 6.9.

The RMS roughness was 0.54 nm and 0.67 nm for films of S4-Cz-OXD and S5-Cz-OXD without annealing treatment and was 0.52 nm and 0.65 nm for films after annealing. For both non-annealed and annealed films, the roughness of S5-Cz-OXD was larger than that of S4-Cz-OXD due to the extended conjugated branch that enhanced the rigidity of the

molecules and led to a less amorphous film by spin-coating. This could also be proved by AFM images, where the fluctuation range of height is more apparent on the surface of S5-Cz-OXD film. Moreover, the slightly decrease in RMS roughness for the annealed films compared with those non-annealed ones indicates annealing treatment could improve the surface quality of these films. Large particles could be observed on the surface of the non-annealed films, while in the annealed films, the color is much more evenly distributed, illustrating more homogeneous films. Finally, compared with the film of S3-Cz-OXD (RMS = 0.80 nm), S4-Cz-OXD exhibits lower roughness (RMS = 0.52 nm). Particles with higher contrast could be observed in the AFM image of the annealed film of S3-Cz-OXD. For comparison, the height fluctuation in that of S4-Cz-OXD is of low relief, indicating the introduction of alkoxy chains created better surface topography. These results are in accordance with the expectation.

Figure 6.9 AFM images of Sn-Cz-OXD ($n = 4, 5$) films spin-casted from chloroform solution.

6.6 Results and Discussion for OLED Devices

To further investigate the luminescence properties of S4-Cz-OXD and S5-Cz-OXD, solution-processed undoped devices E4 and E5 with configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al were fabricated (E4: EML = S4-Cz-OXD; E5: EML = S5-Cz-OXD). PEDOT:PSS is serving as the hole transporting layer. TPBI is serving as both electron transporting and hole blocking layer, while a thin layer of LiF serves as electron injecting layer in the device. The energy diagram of the devices and the chemical structure of TPBI are shown in Figure 6.10.

Figure 6.10 Energy level diagram of the OLED devices E4 and E5.

Figure 6.11 displays the EL spectra of devices E4 and E5 at different applied voltages. Pure blue emissions at 452 nm and 449 nm with the CIE coordinates of (0.157, 0.146) and (0.150, 0.141) were observed from devices E4 and E5, which were slightly blue shifted compared with that of the device D1. This was in accordance with their PL spectra, indicating the light was from S4-Cz-OXD and S5-Cz-OXD emitting layer. There was no significant difference in the EL spectra under various driving voltages, implying their EL spectra were stable and voltage-independent. Electroluminescence characterization data of devices E4 and E5 are summarized in Table 6.5.

Figure 6.11 Normalized EL spectra of device E4 (a) and E5 (b) at different applied voltages.

Figure 6.12 illustrates the J-V-L characteristics and plots of electroluminescent efficiencies-current density characteristics for devices E4 and E5. The turn-on voltages are 4.0 V for both E4 and E5. These values are slightly lower than those of devices D1 and D2 based on S1-Cz-OXD and S2-Cz-OXD (4.1 V), which could be attributed to the enhanced HOMO energy level of S4-Cz-OXD and S5-Cz-OXD caused by the electron donating alkoxy chains. Device E4 exhibited a maximum luminance of 7804 cd m^{-2} , a maximum EQE of 4.20%, a maximum CE of 4.69 cd A^{-1} , and a maximum PE of 2.08 lm W^{-1} . As shown in Figure 6.12 (a), the luminance of device E5 is higher than that of device E4 under the same current density. This is because S5-Cz-OXD possesses higher solid state quantum efficiency than S4-Cz-OXD. The maximum luminance of device E5 achieved 8213 cd m^{-2} , but it exhibits higher current density than E4 and this became greater at high voltages. A possible reason was the morphology of S5-Cz-OXD emitting layer was not as good as that of S4-Cz-OXD due to its poorer solubility, so a leakage current was generated, leading to lower maximum EL efficiencies of 3.93%, 4.66 cd A^{-1} , and 1.99 lm W^{-1} , respectively. In addition, both of them showed good roll-off characteristics, high efficiency of 3.5% and 3.4% were still obtained at high brightness of 3000 cd m^{-2} for devices E4 and E5. It is believed these results are among the most efficient solution-processed undoped blue OLEDs.

Figure 6.12 EL performance: (a) J-V (solid symbol) and L-V (open symbol) characteristics; (b) EQE-J characteristics; (c) CE-J characteristics and (d) PE-J characteristics of devices E4 and E5.

Table 6.5 Electroluminescence characteristics of the devices.

Device	$V_{on}^{[a]}$ (V)	at 1000 / 3000 cd m ⁻² ^[b] (V/%)	Max L (cd m ⁻² , V)	EQE (%)	CE (cd A ⁻¹)	PE (lm W ⁻¹)	λ_{max} (nm)	CIE (x, y)
E4	4.0	6.3, 4.1 / 7.4, 3.5	7804, 9.7	4.20	4.96	2.08	452	(0.157, 0.146)
E5	4.0	6.3, 3.9 / 7.2, 3.4	8213, 9.6	3.93	4.66	1.99	449	(0.150, 0.141)

^[a]: Turn-on voltage at which brightness exceeds 1 cd m⁻²; ^[b]: The estimated values of driving voltage and EQE of device at brightness of 1000 and 3000 cd m⁻².

6.7 Conclusions

In previous study of blue emitters Sn-Cz-OXD (n = 1~3), solid quantum efficiency of emitters was found to be increased with the benzene amount, i.e., the length of the

branches, and this also caused the blue-shift in their emission spectrum. S3-Cz-OXD with the longest conjugated arms exhibited the highest quantum yield and the most saturated blue emission. However, it had very poor solubility in organic solvents therefore some investigations including CV characterization and device fabrication could not be carried out. For this sake, emitter S4-Cz-OXD was developed based on S3-Cz-OXD by introducing flexible alkoxy chains to the backbone of the molecule to improve the solubility of it. And S5-Cz-OXD with two more benzene units was designed for further study of extending of conjugated arms.

The introduced alkoxy chains Improved solubility. Compared with S3-Cz-OXD, which solubility in CHCl_3 was less than 3 mg mL^{-1} and in mixed toluene : CB (1 : 1) was less than 1 mg mL^{-1} , S4-Cz-OXD exhibited greatly enhanced solubility of 20 and 15 mg mL^{-1} . These values for S5-Cz-OXD were reduced to 15 and 8 mg mL^{-1} due to the increased benzene units in arms. Extra electron donating ability was provided to the molecules, leading to an enhanced HOMO energy level and a red-shift in the emission spectrum. This could be shown by their emission spectra (peaking at 449 nm and 446 nm) and the CV results (E_{HOMO} : -5.57 eV and -5.59 eV for S4-Cz-OXD and S5-Cz-OXD). The alkoxy chains further suppressed the aggregation of molecules in solid state and reduced the fluorescence quenching. Therefore they showed high quantum efficiencies of 62% and 65% in the solid neat films. In addition, S4-Cz-OXD and S5-Cz-OXD showed excellent thermal stabilities with high T_g (above 135°C) and high T_d (above 410°C). Their emission spectra were quite stable during the heat treatment at 150°C for 120 hours in ambient air, much better than many fluorene-based emitting materials.

Undoped OLED devices E4 and E5 based on S4-Cz-OXD and S5-Cz-OXD with configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al were fabricated. Device E5 exhibited poorer performance than device E4 due to the lower solubility (poorer film forming ability) of S5-Cz-OXD with extended rigid conjugated branches. However, E5 showed higher maximum luminance since the solid quantum efficiency of S5-Cz-OXD was higher than that of S4-Cz-OXD. Both E4 and E5 showed good roll-off characteristics due to the well matched energy levels in the devices. Device E4 achieved a maximum

luminance of 7804 cd m⁻², a maximum CE of 4.69 cd A⁻¹, a maximum EQE of 4.20% and a maximum PE of 2.08 lm W⁻¹. These results are believed to be among the highest efficiency solution-processed undoped blue OLED devices employing fluorene-free emitting materials.

References

1. X. He, L. Chen, Y. Zhao, H. Chen, S. C. Ng, X. Wang, X. Sun, and X. “Matthew” Hu, *Org. Electron.*, 2016, **37**, 14–23.
2. S. Maruyama and Y. Kawanishi, *J. Mater. Chem.*, 2002, **12**, 2245–2249.
3. R. Fáber, A. Staško, and O. Nuyken, *Macromol. Chem. Phys.*, , 2000, **201**, 2257–2266.

Chapter 7

Conclusions and Future Plans

This chapter summarizes the overall outcomes of this project and draws together the threads of this thesis. From linear emitter L1-Cz-OXD to star-shaped emitter S1-Cz-OXD, and from S1-Cz-OXD to S3-Cz-OXD and S5-Cz-OXD, a series of bipolar blue undoped emitters were developed with certain modification for improvement in quantum efficiency, color purity and solubility. They all possessed excellent spectra stability. Also, future work relating to this project is also elaborated. Further studies would be carried out on (1) doped OLEDs using the target molecules as the host materials; (2) the relationship between triplet energy and chemical structure of these target materials; and (3) developing novel emitting materials with desired properties.

7.1 Outcomes of This Project

This project was motivated by the lack of highly effective undoped blue electroluminescent materials for solution-processed OLEDs. Recently, undoped blue emitters attracted many interests since they take an important role in high efficient hybrid white OLEDs with relative simple device configurations. According to the literature, one group of the best undoped blue emitting materials is star-shaped oligofluorenes. However, they still have shortcomings (e.g., unstable spectrum) and further improvement. So far, high efficiency undoped star-shaped blue emitters are still quite limited in number. This study aims to develop star-shaped blue emitting materials with enhanced thermal stability, high solid quantum efficiency (undoped property) and improved charge balancing transportation through well-designed molecular structures. Moreover, the prime influence of chemical structure of emitters on their properties was also studied, which will be beneficial for future research into OLEDs materials.

In this project, target molecules (Sn-Cz-OXD, $n = 1\sim5$) were designed, synthesized, characterized and employed in undoped OLED devices for the investigation of their electroluminescent properties. L1-Cz-OXD, a linear counterpart of S1-Cz-OXD was synthesized for comparative study. According to the chemical structure, these target molecules could be divided into three different material systems: (1) L1-Cz-OXD; (2) Sn-Cz-OXD ($n = 1\sim3$); and (3) Sn-Cz-OXD ($n = 4\sim5$). The experimental results and analysis of these emitters were elaborated in Chapters 4, 5 and 6, respectively.

7.1.1 S1-Cz-OXD VS L1-Cz-OXD

The designed emitter S1-Cz-OXD is composed of a tris(1,3,4-oxadiazole)phenylene (t-OXD) ring as the core and three 3,6-di-tert-butylcarbazole (t-BCz) terminal groups bridged by a benzene unit. L1-Cz-OXD consists of an oxadiazole unit (OXD) centered by two t-BCz groups at both ends with a benzene spacer. Both S1-Cz-OXD and L1-Cz-OXD utilize electron-deficient oxadiazole derivatives and electron-rich t-BCz units, which possess good charge transporting ability¹ and high thermal stability, as the acceptor and

donors, respectively. This D- π -A design provides bipolar properties for emitters, leading to improved balanced injection / transportation of charges and recombination efficiency. Low turn-on voltage, high EL efficiencies as well as good spectrum thermal stability are expected. *T-butyl* groups in the periphery could prevent the intermolecular aggregation, while also improve the solubility. Compared with linear L1-Cz-OXD, the highly branched structure of S1-Cz-OXD could more effectively suppress the intermolecular interactions and reduce the concentration quenching in the solid state. Therefore higher solid quantum efficiency is expected for S1-Cz-OXD. The well-defined structure of S1-Cz-OXD also promises high purity and precise analysis.

Material characterization shows both S1-Cz-OXD and L1-Cz-OXD are of good thermal stability with high T_g (137 °C and 141 °C) and high T_d (447 °C and 423 °C). Moreover, the emission spectra of their solid neat films are quite stable after 220 hours of heat treatment at 150 °C in ambient air, which is much better than many fluorene-based emitters. A high quantum efficiency (Φ_f) of 54% in the neat film was obtained for S1-Cz-OXD, which is higher than that of L1-Cz-OXD (41%). S1-Cz-OXD dissolved well in many organic solvents while L1-Cz-OXD was of poor solubility, and the quality of a spin-cast film is superior to one of L1-Cz-OXD. For study of their EL properties, undoped OLEDs with configuration of ITO/PEDOT:PSS/EML/3TPYMB/Cs₂CO₃/Al were fabricated. The device based on S1-Cz-OXD turned on at 3.7 V, realizing a maximum luminance of 3648 cd m⁻² and maximum EL efficiencies of 3.37%, 4.21 cd A⁻¹ and 2.55 lm W⁻¹, which values are much better than the control device based on L1-Cz-OXD. All of the above findings are consistent with the original hypothesis, indicating the molecular design concepts are correct.

The influence of different electron transporting materials on device performance was also studied. An optimized OLEDs device with configuration of ITO/PEDOT:PSS/S1-Cz-OXD/TPBI/LiF/Al is fabricated. By employing TPBI as ETL, this device exhibits less maximum efficiency but higher maximum luminance and much better roll-off characteristics at high current density due to its well-matched energy level. Besides, although the performance of control device based on L1-Cz-OXD is not very good due to

the poor film quality of the solution-cast emission layer, L1-Cz-OXD shows high potential in OLEDs fabricated by vacuum-deposition, indicating it is still a good candidate for deep blue emitting material. An optimized device with configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al is fabricated and it achieves a maximum brightness of 3547 cd m⁻² and a high efficiency of 3.09%. The deep blue emission of this device is located at 429 nm with CIE coordinates of (0.16, 0.07), which is close to the blue coordinate (0.14, 0.08) in the NTSC color gamut.

7.1.2 Sn-Cz-OXD (n = 1 ~ 3)

High solid quantum efficiency is one of the most important parameters for an electroluminescence material. Based on S1-Cz-OXD, molecules S2-Cz-OXD and S3-Cz-OXD were designed with extended branch length by increasing the amount of benzene spacer between t-OXD core and t-BCz terminal groups to achieve increasing quantum efficiency (according to the literatures). This usually causes a red shift in the emission spectrum for most reported star-shaped blue emitting materials due to the extended π conjugation length in the branches. Such a red shift is undesirable since it reduces the color purity or saturation of the blue emission. For designed emitting materials Sn-Cz-OXD (n = 1~3), instead of the undesired red shift, a blue shift is expected with the increasing of branch length due to the D- π -A structure. This is because the charge transferring ability between donor and acceptor is reduced by the increasing distance between them and the distortion of the biphenyl or terphenyl chains.

Just like S1-Cz-OXD, emitters S2-Cz-OXD and S3-Cz-OXD exhibited excellent spectrum stability due to their similar composition of oxadiazole and carbazole moieties which was of high thermal stability. Values of T_g and T_d were 141 °C and 453 °C for S2-Cz-OXD and were 145 °C and 470 °C for S3-Cz-OXD, both of which were increasing with the molecular size. Solid neat films of S2-Cz-OXD and S3-Cz-OXD emitted pure blue light at 452 nm and 448 nm with quantum efficiency of 58% and 61%, respectively. It was obvious that the emission spectrum was blue shifted, while the solid quantum efficiency was enhanced when the conjugated branches were extending. But in the

meantime, their solubility decreased. S3-Cz-OXD was almost insoluble in solvents such as CH_2Cl_2 and hexane and was of low solubility in toluene and chlorobenzene, so it could not be used in OLEDs although it exhibited the most saturated blue emission and the highest quantum efficiency. All of the above findings were consistent with the design expectation.

Undoped OLED devices based on S1-Cz-OXD and S2-Cz-OXD with both configurations of (1) ITO/PEDOT:PSS/EML/3TPYMB/ Cs_2CO_3 /Al and (2) ITO/PEDOT:PSS/EML/TPBI/LiF/Al were fabricated. For different ETL, 3TPYMB based devices exhibited higher maximum EL efficiencies but these values sharply fell down with current density. In contrast, TPBI based devices showed less maximum efficiency but much better roll-off characteristics due to its well-matched energy level in OLEDs which benefit balanced charge injection and transportation, leading to higher recombination efficiency. For different emitting materials, devices based on S2-Cz-OXD showed superior EL performance than those based on S1-Cz-OXD because the solid quantum efficiency of S2-Cz-OXD was higher than S1-Cz-OXD, which was provided by the extended conjugated branch. Among these devices, the one with configuration of ITO/PEDOT:PSS/S2-Cz-OXD/TPBI/LiF/Al showed the best performance. It realized a maximum brightness of 6538 cd m^{-2} and maximum efficiency of 3.42%, 3.86 cd A^{-1} and 1.65 lm W^{-1} . These results were believed to be among the most efficiency solution-processed undoped blue devices employing fluorene-free emitting materials.

7.1.3 Sn-Cz-OXD (n = 4, 5)

S3-Cz-OXD was of poor solubility in organic solvent thus it could not be used in solution-processed OLEDs, although it exhibited the most saturated blue emission and the highest quantum efficiency among Sn-Cz-OXD (n = 1~3). In order to solve this problem, S4-Cz-OXD with introduced flexible alkoxy chains was designed in order to improve the solubility. Besides, enhanced solid quantum efficiency was expected to be obtained from S4-Cz-OXD compared with S3-Cz-OXD because the bulky alkoxy chains would have steric effects, which could further suppress the intermolecular aggregation.

However, considering the electron donating ability of the alkoxy chains, the HOMO energy level of S4-Cz-OXD should be raised and a slight red-shift in the emission spectra of S4-Cz-OXD might be observed. S5-Cz-OXD was designed based on S4-Cz-OXD with further extension in conjugated branch length in order to further improve the solid quantum efficiency and color saturation of the blue emission. Changing from S4-Cz-OXD to S5-Cz-OXD should be similar to those from S1-Cz-OXD to S3-Cz-OXD according to the same molecular design principles.

The solubility of S4-Cz-OXD was greatly improved by the alkoxy chains compared with S3-Cz-OXD and it could be spin-coated into a nice thin film. S5-Cz-OXD exhibited lower solubility but it was still higher than that of S3-Cz-OXD. The calculated value of E_{HOMO} was -5.57 eV and -5.59 eV for S4-Cz-OXD and S5-Cz-OXD, much higher than that of Sn-Cz-OXD ($n = 1\sim 3$). Solid neat films of S4-Cz-OXD and S5-Cz-OXD emitted pure blue emission at 449 nm and 446 nm with high quantum efficiency of 62% and 65%, respectively. It was observed that S4-Cz-OXD showed a slight red shift compared with S3-Cz-OXD, while the PL spectrum of S5-Cz-OXD again showed a blue shift compared with S4-Cz-OXD, which was in accordance with expectations. In addition, S4-Cz-OXD and S5-Cz-OXD showed high thermal stabilities with high T_g and high T_d . Their emission spectra were also quite stable during the heating treatment at 150 °C for 120 hours in ambient air, which was much better than many fluorene-based emitting materials. All of the above findings were consistent with the design expectations.

Undoped OLED devices based on S4-Cz-OXD and S5-Cz-OXD with configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al were fabricated. They were much better than the devices employing the same configuration with S1-Cz-OXD and S2-Cz-OXD as emitting materials. The S5-Cz-OXD based device exhibited poorer performance than the one based on S4-Cz-OXD due to the lower solubility and poorer film forming ability due to extended rigid conjugated branches. However, it showed higher maximum luminance since the solid quantum efficiency of S5-Cz-OXD was higher than that of S4-Cz-OXD. Both devices showed good roll-off characteristics. S4-Cz-OXD based device achieved a maximum luminance of 7804 cd m^{-2} , a maximum CE of 4.69 cd A^{-1} , a maximum EQE of

4.20% and a maximum PE of 2.08 lm W^{-1} . These results were believed to be among the highest efficiency solution-processed undoped blue device employing fluorene-free emitting materials.

7.2 Conclusions

This research focuses on undoped blue electroluminescence materials for OLED applications. The following outcomes were achieved:

- (1) Designed and synthesized a series of star-shaped emitting materials Sn-Cz-OXD ($n = 1\sim 5$), which emit pure blue emission at around 450 nm with high solid quantum efficiency and excellent spectrum thermal stability. Solution-processed undoped OLEDs with the configuration of ITO/PEDOT:PSS/EML/TPBI/LiF/Al are fabricated and characterized. Among them the one based on S4-Cz-OXD exhibits the best device performance.
- (2) L1-Cz-OXD as the linear counterpart for S1-Cz-OXD was also synthesized. It emits deep blue emission at about 430 nm, with high solid quantum efficiency and excellent spectrum thermal stability. An optimized undoped device with configuration of ITO/MoO₃/TCTA/L1-Cz-OXD/TPBI/LiF/Al exhibits good performance. Besides, L1-Cz-OXD exhibits crystallization properties and it could grow into single crystal, which endows it potential to be employed in other applications.
- (3) Investigated the relationship between the chemical structure and the properties of emitting materials. All hypotheses concerning the emitting materials were proved correct by the characterization results, implying the importance of understanding the principles underlying molecular design. These studies will facilitate future research since the relationship between structure and properties is the basis of intelligent molecular design.

7.3 Future Work

In this project, a series of blue fluorescent materials were developed with high fluorescent quantum yield, undoped properties, excellent spectrum thermal stability, good charges transport abilities and their undoped OLEDs achieved good performance. As mentioned, effective blue fluorescent materials are very important for full-color displays. In the future, they could be studied as host materials for red, orange and green dopants. Considering the triplet energy of some of these emitters is sufficient to host green phosphors (> 2.4 eV), their application in white hybrid OLEDs could be partly carried out. Further study on developing of deep-blue emitters with high triplet energy should be continued. On the other hand, blue TADF materials recently presented great progress to achieve above 10% external quantum efficiency by vacuum-deposited multilayer OLEDs.^{2,3} Inspired by this, solution-processed undoped blue fluorescent materials with TADF properties should be developed, which enable not only a high EL efficiency, but also a relatively simple and cheap fabrication technology.

7.3.1 Employing Target Emitters as Host Materials in OLEDs

Target blue emitting materials (except S3-Cz-OXD) have been successfully applied in undoped OLEDs in this thesis. These devices show good performance, especially the one based on S4-Cz-OXD. They have potential to serve as host materials due to their blue emission and wide energy bandgap. Therefore one of the future research directions is using these emitters in doped OLEDs.

For fluorescent devices, commercialized RGB emitters could be used as dopants. Generally speaking, a high degree of overlap between the absorption spectrum of dopant material and PL spectrum of host material guarantees a high efficiency of energy transfer from host material to dopant material. Figure 7.1 shows the absorption spectrum of some commonly used dopants and the PL spectrum of S4-Cz-OXD in dilute toluene solvent, indicating that DPAVB, BCzVBi, C545T, and DMC might be good candidates for dopant materials when using S4-Cz-OXD as host material in OLEDs device.

Figure 7.1 Normalized UV-vis spectra of some commonly used fluorescent dopants and normalized PL spectrum of S4-Cz-OXD.

In the case of phosphorescence OLEDs, an ideal host emitter should possess higher triplet energy (E_T) than dopants in order to generate light from doped green, orange or red phosphorescent emitters. Therefore it is necessary to study their phosphorescence properties. Typical triplet energy for green and red emission is 2.4 eV and 2.2 eV. Figure 7.2 shows the phosphorescence spectrum of six target emitting materials in dilute toluene measured at 77 K. The highest energy phosphorescent emission peaks (λ_{Phos}) are located at 486 nm, 492 nm, 518 nm, 546 nm, 540 nm and 556 nm for L1-Cz-OXD and Sn-Cz-OXD ($n = 1 \sim 5$), respectively. The corresponding triplet energy E_T for them could be estimated from $E_T = 1240/\lambda_{\text{Phos}}$ to be 2.55 eV, 2.54 eV, 2.40 eV, 2.27 eV, 2.30 eV and 2.23 eV. The data is summarized in Table 7.1. Among them, L1-Cz-OXD and S1-Cz-OXD possess the highest triplet energy around 2.55 eV, which are sufficient to host green, yellow and red phosphorescent emitters; S2-Cz-OXD with reduced E_T of 2.40 eV could be served as host for orange and red phosphorescent dopant; while the E_T of S3-Cz-OXD, S4-Cz-OXD and S5-Cz-OXD are too small, therefore they could only be used to host red phosphorescent dopant. In addition, considering the high solid quantum efficiency, pure blue emission and high triplet energy of S1-Cz-OXD, it has potential to be used as a host material in solution-processed hybrid white OLEDs, respectively. Besides, with deep blue emission, L1-Cz-OXD is also a good candidate, although it exhibits lower quantum efficiency.

Figure 7.2 Normalized phosphorescence (Phos.) spectra recorded in toluene solution at 77 K.

Table 7.1 Phosphorescence properties of target molecules.

Emitter	λ_{Phos} (nm)	E_{T} (eV)	E_{opt} (eV)	ΔE_{ST} (eV)
L1-Cz-OXD	486	2.55	3.14	0.59
S1-Cz-OXD	488	2.54	3.00	0.46
S2-Cz-OXD	518	2.40	3.03	0.63
S3-Cz-OXD	546	2.27	3.08	0.81
S4-Cz-OXD	540	2.30	3.04	0.74
S5-Cz-OXD	556	2.23	3.06	0.83

7.3.2 Developing Fluorescent Blue Emitters with High Triplet Energy

The combination of carbazole and oxadiazole moieties is expected to provide a potential bipolar host for triplet emitters due to the sufficiently large triplet energy to confine triplet excitons in the emissive layer as well as their good charge transporting abilities.¹ Therefore target molecules L1-Cz-OXD and Sn-Cz-OXD ($n = 1\sim 5$) are supposed to possess high triplet energy. In the hypothesis, HOMO/LUMO energy bandgap is supposed to be increasing with the extending of the conjugated branches because this

would weaken charge transfer ability between donor and acceptor units, while the triplet energy changes following this trend due to the same reason. However, different from the changing trending of E_{opt} , characterization on phosphorescence spectra of these emitters show the triplet energy (E_{T}) is decreasing from S1-Cz-OXD to S3-Cz-OXD and from S4-Cz-OXD to S5-Cz-OXD with the extending of the conjugated branches. This indicates that E_{T} is influenced by many factors and the principle of this design concept is more complicated than images.

Figure 7.3 A Jablonski diagram showing the electronic states of a molecule and the transitions between them.

It is known that excited states (both 1S_1 and 3T_1) are created with different vibronic excited levels, as shown in Figure 7.3. In a molecule with complicated structure, the whole molecule and all sub-parts of the molecule would have corresponding 3T_1 states. The final E_{T} is decided by the one having the lowest triplet energy. Although carbazole possesses high E_{T} , when combined with conjugated benzene units, the value of E_{T} would be largely reduced due to the delocalization of electrons. Therefore the E_{T} of the branch is decreasing with its conjugation length. As a result, the E_{T} of the whole molecule exhibits a similar trend. One of the evidences is that the E_{T} of L1-Cz-OXD and S1-Cz-OXD is almost of the same value because they possess the same branches. This is one possible reason to explain the experimental result. There are likely more unknown principles that influence the triplet energy for an emitter from the view of molecular design. So far,

effective deep-blue emitting materials with high enough triplet energy to host green phosphors are still limited. Further investigation on this topic should be carried out with the assistance of computer simulation.

7.3.3 Developing Solution-Processable TADF Emitters

Recently, a new type of TADF emitting materials was developed by Adachi et al.⁴ They are a family of molecules that possess a relatively small energy difference (ΔE_{ST}) between the singlet and triplet excited states (< 0.2 eV), which enable the up-conversion of energy from triplet excited state to singlet excited state. In TADF emitters, triplet excitons can be made to fully contribute to luminescence without using rare metals and therefore makes it possible to achieve an IQE of 100%.^{5,6} TADF emitting material is supposed to be the third generation of OLED materials after the general fluorescent materials and phosphorescent materials.⁷ So far, many TADF materials with high efficiency and wide emission region (covers red, green and blue) have been reported.^{6,8-10} For blue emission, they fabricated deep blue OLEDs based on efficient TADF emitters and achieved extremely high EQE of 9.9% and CIE coordinates of (0.15, 0.07).² Later, they reported a pure blue TADF OLEDs based on DMOC-DPS, which exhibited a maximum EQE of 14.5% as well as reduced efficiency roll-off, with the CIE coordinates of (0.16, 0.16).¹¹

Most reported TADF blue emitters are small molecules. Undoped blue OLEDs based on these emitters are usually fabricated by high cost vacuum-deposition technology due to the low solubility or poor film-forming ability of small molecules. Furthermore, many TADF materials based devices employed complex multilayer structures. Based on above discussion as well as the achievements that obtained from this thesis, it would be interesting to develop a novel blue fluorescent material incorporating both advantages of the target molecules Sn-Cz-OXD in this work and the TADF properties. It is reasonable to expect such materials could provide a new approach to fabricate next-generation OLEDs with simple structure and high performance in a cost-effective manner.

References

- (1) Tao, Y.; Wang, Q.; Yang, C.; Zhong, C.; Zhang, K.; Qin, J.; Ma, D. *Adv. Funct. Mater.***2010**, *20*, 304–311.
- (2) Zhang, Q.; Li, J.; Shizu, K.; Huang, S.; Hirata, S.; Miyazaki, H.; Adachi, C. *J. Am. Chem. Soc.***2012**, *134*, 14706–14709.
- (3) Wu, S.; Aonuma, M.; Zhang, Q.; Huang, S.; Nakagawa, T.; Kuwabara, K.; Adachi, C. *J. Mater. Chem. C***2014**, *2*, 421–424.
- (4) Endo, A.; Ogasawara, M.; Takahashi, A.; Yokoyama, D.; Kato, Y.; Adachi, C. *Adv. Mater.***2009**, *21*, 4802–4806.
- (5) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature***2012**, *492*, 234–238.
- (6) Zhang, Q.; Tsang, D.; Kuwabara, H.; Hatae, Y.; Li, B.; Takahashi, T.; Lee, S. Y.; Yasuda, T.; Adachi, C. *Adv. Mater.***2015**, *27*, 2096–2100.
- (7) Adachi, C. *Jpn. J. Appl. Phys.***2014**, *53*, 060101.
- (8) Tanaka, H.; Shizu, K.; Miyazaki, H.; Adachi, C. *Chem. Commun. (Camb)***2012**, *48*, 11392–11394.
- (9) Tanaka, H.; Shizu, K.; Lee, J.; Adachi, C. *J. Phys. Chem. C***2015**, *119*, 2948–2955.
- (10) Zhang, Q.; Kuwabara, H.; Potscavage, W. J.; Huang, S.; Hatae, Y.; Shibata, T.; Adachi, C. *J. Am. Chem. Soc.***2014**, *136*, 18070–18081.
- (11) Wu, S.; Aonuma, M.; Zhang, Q.; Huang, S.; Nakagawa, T.; Kuwabara, K.; Adachi, C. *J. Mater. Chem. C***2014**, *2*, 421–424.

APPENDIX

1. NMR Data for Newly Reported Compounds in This Thesis

Figure A.1 ¹H NMR spectrum of compound 8 (400 MHz, CDCl₃).

Figure A.2 ^{13}C NMR spectrum of compound 8 (400 MHz, CDCl_3).

Figure A.3 ^1H NMR spectrum of compound 17 (400 MHz, CDCl_3).

Figure A.4 ¹³C NMR spectrum of compound 17 (400MHz, CDCl₃).

Figure A.5 ¹H NMR spectrum of compound 18 (400 MHz, CDCl₃).

Figure A.6 ^{13}C NMR spectrum of compound 18 (400MHz, CDCl_3).

Figure A.7 ¹H NMR spectrum of compound 19 (400MHz, CDCl₃).

Figure A.8 ¹³C NMR spectrum of compound 19 (400MHz, CDCl₃).

Figure A.9 ¹H NMR spectrum of compound 20 (400MHz, CDCl₃).

Figure A.10 ¹³C NMR spectrum of compound 20 (400MHz, CDCl₃).

Figure A.11 ^1H NMR spectrum of S1-Cz-OXD (400 MHz, CDCl_3).

Figure A.12 ^{13}C NMR spectrum of S1-Cz-OXD (400 MHz, CDCl_3).

Figure A.13 ¹H NMR spectrum of S2-Cz-OXD (400 MHz, CDCl₃).

Figure A.14 ^{13}C NMR spectrum of S2-Cz-OXD (400MHz, CDCl_3).

Figure A.15 ¹H NMR spectrum of S3-Cz-OXD (400 MHz, CDCl₃).

Figure A.16 ¹³C NMR spectrum of S3-Cz-OXD (400MHz, CDCl₃).

Figure A.17 ^1H NMR spectrum of S4-Cz-OXD (400 MHz, CDCl_3).

Figure A.18 ^{13}C NMR spectrum of S4-Cz-OXD (400MHz, CDCl_3).

Figure A.19 ^1H NMR spectrum of S5-Cz-OXD (400MHz, CDCl_3).

Figure A.20 ^{13}C NMR spectrum of S5-Cz-OXD (400MHz, CDCl_3).

Figure A.21 ¹H NMR spectrum of L1-Cz-OXD (400MHz, CDCl₃).

Figure A.22 ^{13}C NMR spectrum of L1-Cz-OXD (400MHz, CDCl_3).

2. MALDI-TOF data for target compounds

Figure A.23 MALDI-TOF result for S1-Cz-OXD doped in Matrix.

Figure A.24 MALDI-TOF result for S2-Cz-OXD doped in Matrix.

Figure A.25 MALDI-TOF result for S3-Cz-OXD doped in Matrix.

Figure A.26 MALDI-TOF result for S4-Cz-OXD doped in Matrix.

Figure A.27 MALDI-TOF result for S5-Cz-OXD doped in Matrix.

Figure A.28 MALDI-TOF result for L1-Cz-OXD without Matrix.

Figure A.29 MALDI-TOF result for Matrix (sinapic acid).

3. MALDI-TOF data for other newly reported compounds

Figure A.30 MALDI-TOF result for compound 8.

Figure A.31 MALDI-TOF result for compound 17.

Figure A.32 MALDI-TOF result for compound 18.

Figure A.33 MALDI-TOF result for compound 19.

Figure A.34 MALDI-TOF result for compound 20.

Figure A.35 MALDI-TOF result for compound 11.

4. Summary of the structure, physical properties and OLED performance of the five target molecules.

Table A.1

Compound	S1-Cz-OXD	S2-Cz-OXD	S3-Cz-OXD	S4-Cz-OXD	S5-Cz-OXD
Structure					

Physical properties					
$\lambda_{\max}^{\text{Abs [a]}}$ (nm)	369 / 372 / 373	356 / 358 / 359	348 / 349 / 349	350 / 352 / 352	349 / 351 / 351
$\lambda_{\max}^{\text{PL [a]}}$ (nm)	422 / 455 / 457	420 / 450 / 452	418 / 446 / 448	428 / 447 / 449	425 / 445 / 446
$\Phi_{\text{f}}^{\text{[a],[b]}}$ (%)	93 / 72 / 54	91 / 76 / 58	87 / 79 / 61	79 / 81 / 62	75 / 84 / 65
$E_{\text{opt}}^{\text{[c]}}$ (eV)	3.00	3.03	3.08	3.04	3.06
$E_{\text{onset}}^{\text{oxd [d]}}$ (V)	1.26	1.27		1.17	1.19
$E_{\text{onset}}^{\text{red [d]}}$ (V)	-1.51	-1.53		-1.55	-1.56
$E_{\text{HOMO}}^{\text{[e]}}$ (eV)	-5.66	-5.67		-5.57	-5.59
$E_{\text{LUMO}}^{\text{[e],[f]}}$ (eV)	-2.89 / - 2.66	-2.87 / - 2.64		-2.85 / -2.53	-2.84 / -2.53
$E_{\text{g}}^{\text{[g]}}$ (eV)	2.77	2.80		2.72	2.75
T_{g} (°C)	137	141	145	137, 151	140, 160
T_{d} (°C)	447	453	470	413	421
$\text{RMS}^{\text{[h],[i]}}$ (nm)	0.48 / 0.41	0.70 / 0.66	0.82 / 0.80	0.54 / 0.52	0.67 / 0.65
OLED performances (device structure: ITO/PEDOT:PSS/EML/TPBI/LiF/Al)					
$V_{\text{on}}^{\text{[j]}}$ (V)	4.1	4.1		4.0	4.0
$\lambda_{\max}$ (nm)	459	455		452	449
CIE (x, y)	(0.166, 0.169)	(0.159, 0.157)		(0.157, 0.146)	(0.150, 0.141)
Max L (cd m ⁻²)	5672	6538		7804	8213
EQE ^[k] (%)	3.13 / 3.1 / 3.0	3.42 / 3.4 / 3.3		4.20 / 4.2 / 4.1	3.93 / 3.8 / 3.9
CE ^[k] (cd A ⁻¹)	3.64 / 3.6 / 3.6	3.86 / 3.8 / 3.8		4.96 / 4.9 / 4.9	4.66 / 4.6 / 4.6
PE ^[k] (lm W ⁻¹)	1.58 / 1.5 / 1.4	1.65 / 1.6 / 1.5		2.08 / 2.0 / 1.9	1.99 / 1.9 / 1.8

[a] values measured in dilute solution / doped PMMA films / neat films; [b] 9,10-diphenylanthracene is reference material, $\Phi_{\text{f}} = 0.92$ in dilute toluene, $\Phi_{\text{f}} = 0.83$ dispersed in PMMA films ($<10^{-3}$ M); [c] Estimated from UV-vis absorption spectrum of dilute solution; [d] Performed in 0.1M (C₄H₉)₄NClO₄ in CH₂Cl₂; [e]: Estimated from $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ obtained from CV

curve with ferrocene calibration; [f]: Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{opt}}$; [g]: Determined from CV measurement; [h]: RMS value of non-annealed films and [i]: RMS value of annealed films; [j] Turn-on voltage at a brightness of 1 cd m^{-2} ; [k] Maximum value, estimated values at 500 cd m^{-2} and 1000 cd m^{-2} .