

## DOCTORAL THESIS

### Cyclometalated iridium(III) complexes for full-color and near infrared phosphorescent organic light-emitting diodes

Chen, Zhao

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## **Abstract**

Dramatic increase of energy consumption and environmental problems invigorate the development of organic semi-conductive materials to substitute for the conventional inorganic materials in the application of photovoltaic and light-emitting devices. In view of the merits of low driving voltage, high power conversion efficiency, large-area fabrication of thin and light organic films as well as saturated emission, organic light-emitting diodes (OLEDs) have received much more consideration by scientists in the past two decades. And even out of laboratory, the OLEDs are popular among the commercial electronic products for solid-state displays and illumination. Generally, three primary RGB emitters, involving red (R), green (G) and blue (B), are footstones to achieve solid-state displays and illumination because the spectra by compositing RGB emissions match very well with the solar spectrum. Also, the combination of two complementary luminophors, blue and orange or yellow is an alternative approach to simulate the solar spectrum for white light illumination. Except for the full-color light-emitting materials for solid-state displays and illumination, near infrared (NIR) organics are of great importance for applications in information-secured devices, communications, biosensors, and phototherapy. To date, uncountable research works focusing on the emitters for full-color emissions have demonstrated their synthesis, photophysical properties and OLED application, which shows enough efficiency and stability to commercial utility. However, there are still three challenging issues which are needed to be handled urgently. Firstly, the lack of efficient deep blue emitters makes

the external quantum efficiency (EQE) of deep blue OLEDs around 10% when the Commission Internationale de l'Éclairage (CIE) coordinates of  $y$  is smaller than 0.1. On the one hand it is difficult to achieve the deep blue emitters with extremely broad energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). On the other hand the triplet and frontier energy levels of the host, electron transporting layer (ETL) and hole transporting layer (HTL) in the device are required to well match with that of the emitters. Secondly, high energy in the emissive layer (EML) of deep blue OLEDs may degrade the materials used inside the EML, resulting in their short lifetimes. Thirdly, by comparison with other colors, the investigations of NIR emitters, such as their preparation, property study and device fabrications are sparse.

By harvesting both 25% singlet and 75% triplet excited states, iridium(III) [Ir(III)] complexes have been proven to be one of the best candidates to achieve highly efficient phosphorescent OLEDs (PHOLEDs) for solid-state displays and illumination. Herein, based on Ir(III) complexes, 18 phosphors were synthesized to achieve a widely tunable phosphorescence from deep blue to NIR. In this thesis, their synthesis were fully characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography. Further investigations on the photophysical, electrochemical and thermal properties reveal that these phosphors have the possibility of device fabrication. And rational design of device architectures afford the OLEDs with high efficiencies.

Firstly, *N*-heterocyclic carbene ligands (C<sup>∧</sup>C:) were used to elevate the LUMO of phosphors (**Ir1-Ir7**), resulting in true and deep blue emission spanning from 420 to 450

nm. Secondly, the widely tunable phosphorescence from 470 to 614 nm was accomplished by using polyfluorinated 2-phenylpyridine (C<sup>N</sup>) derivatives as cyclometallated ligands of Ir(III) complexes (**Ir10-Ir17**). Interestingly, electron-withdrawing trifluoromethyl (CF<sub>3</sub>) group on the phenyl ring of C<sup>N</sup>-type ligands results in significantly red-shifted emissions of Ir(III) complexes, which distinguishes with the blue-shift effect of fluoride approach. Lastly, by comparison with the reported literature on NIR Ir(III) phosphors with extensive conjugation, the addition of slight conjugation but electron-withdrawing moieties onto the pyridyl ligands is a powerful and convenient avenue to tune the phosphorescence of Ir(III) phosphor into the NIR region, emitting at 729 nm.

Meanwhile, the deepest blue OLED made from **Ir1** showed a peak EQE of 7.1% with CIE of (0.16, 0.11). And the best deep blue OLEDs made from **Ir7** by using single and double electroluminescent (EL) units gave the highest EQE of 19.0% and 31.5% with CIE coordinates of (0.15, 0.19) and (0.15, 0.22), respectively. Such high efficiencies are comparable to and even better than the currently reported deep blue PHOLEDs. Also, the sky blue, green, yellow, orange, red and NIR PHOLEDs fabricated from **Ir10**, **Ir13**, **Ir15**, **Ir16**, **Ir17** and **Ir18** afforded the maximum EQE of 11.2%, 20.1%, 15.4%, 9.9%, 6.8% and 4.0%, respectively. By stacking RGB EML, the white PHOLED (PHWOLED) made by **Ir1**, **Ir13** and **Ir17** gave a peak EQE of 16.0% and CIE of (0.36, 0.47).

All in all, this thesis has successfully combined the materials synthesis and devices design to achieve efficient full-color and NIR PHOLEDs which are of great interest for

solid-state displays and illumination. These works have a great significance in terms of the improvement of efficiency and stability of deep blue OLEDs as well as simplifying the synthesis methods to prepare highly efficient NIR Ir(III) phosphors.

## Table of Contents

DECLARATION	i
Abstract	ii
Acknowledgements	vi
Table of Contents	vii
List of Table	xi
List of Figures	xiii
List of Schemes	xx
List of Abbreviations and Symbols	xxii
Formula Index	xxv
Chapter 1 Introduction	1
1.1 Background	1
1.2 Spectrum of sunlight	2
1.3 Chromophores and luminophors	3
1.4 Fluorescence and phosphorescence	5
1.5 Transition metal complexes	7
1.5.1 Ligands	8
1.5.2 The crystal field	9
1.5.3 The ligand field and frontier orbitals	10
1.6 Ir(III) phosphorescent materials	11
1.6.1 The configurations of Ir(III) complexes	11

1.6.2	The synthesis methods	13
1.6.3	The properties and applications of Ir(III) complexes	20
1.6.4	Full-color and NIR Ir(III) complexes	24
1.6.5	Blue Ir(III) phosphors	26
1.6.6	Green to red Ir(III) phosphors	44
1.6.7	Near infrared Ir(III) phosphors	48
1.7	The concepts of OLEDs	50
1.7.1	The mechanism of electroluminescence	52
1.7.2	Brief definitions in OLEDs	54
1.7.3	Typical PHOLEDs	60
1.8	Conclusion	71
	References	73
Chapter 2 Triscyclometalated Iridium(III) Carbene Complexes as Deep Blue Phosphors:		
	Synthesis and Characteristics	84
2.1	Introduction	84
2.2	Experimental	90
2.2.1	Synthesis of ligands and phosphors	90
2.2.2	X-ray crystallography	92
2.2.3	Photophysical, electrochemical and thermal properties of phosphors	92
2.3	Results and discussion	94
2.3.1	Synthesis of ligands	94
2.3.2	Synthesis of phosphors	103

2.3.3	X-ray crystallography	107
2.3.4	Photophysical properties of these Ir(C <sup>∧</sup> C:) <sub>3</sub> phosphors	115
2.3.5	Electrochemical and thermal properties of these Ir(C <sup>∧</sup> C:) <sub>3</sub> phosphors	121
2.4	Conclusion	125
	References	126
Chapter 3 Facile Tuning of the Phosphorescence Spanning from Blue to Near Infrared by Electron-Withdrawing Substituents on the Cyclometalated Ligands of Iridium(III) Complexes		
		128
3.1	Introduction	128
3.2	Experimental	133
3.2.1	The synthesis of ligands	134
3.2.2	The synthesis of Ir(III) phosphors	135
3.2.3	X-ray crystallography	137
3.2.4	Photophysical, electrochemical and thermal properties of phosphors	138
3.3	Results and discussion	138
3.3.1	The synthesis and characterization of ligands	138
3.3.2	The synthesis and characterization of Ir(III) phosphors	143
3.3.3	The crystal structures of Ir(III) phosphors	148
3.3.4	Photophysical properties of these heteroleptic Ir(III) phosphors	154
3.3.5	Electrochemical and thermal properties of these heteroleptic Ir(III) phosphors	159
3.4	Conclusion	163



References	165
Chapter 4 Efficient Phosphorescent Organic Light-Emitting Diodes with Tunable Emission Colors	168
4.1 Introduction	168
4.2 Experimental	177
4.3 Results and discussion	178
4.3.1 The single-doped deep blue and sky blue PHOLEDs made by <b>Ir2-Ir8</b>	178
4.3.2 Monochromatic and white PHOLEDs by using phosphors <b>Ir1, Ir10-Ir18</b> with tunable electroluminescence colors from deep blue to near infrared	198
4.4 Conclusion	211
References	213
Chapter 5 Summary and Future Prospects	216
List of Publications	220
CURRICULUM VITAE	221