DOCTORAL THESIS

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

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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 (CˆC:) 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^N) derivatives as cyclometallated ligands of Ir(III) complexes (**Ir10**-**Ir17**). Interestingly, electron-withdrawing trifluoromethyl (CF_3) group on the phenyl ring of C^N-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.

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