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# Iridium based Molecular Complexes for OLED Applications

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#### Abstract

The synthesis and photophysical characterization of Ir based molecular complex is reported. UV-visible, Photoluminescence (PL) and PL lifetime studies of Ir(fliq)<sub>3</sub> have been carried out and the results discussed in details. The absorption spectrum shows two absorption bands below 400 nm (spin-allowed ligand-centered (LC)  $\pi$ - $\pi$ \* transitions). The weak absorption shoulders in the visible region are assigned to the metal-to-ligand chargetransfer (<sup>1</sup>MLCT and <sup>3</sup>MLCT) transitions induced by the strong spin-orbit coupling between the singlet and triplet manifolds. PL and PL lifetime (in the film form) is decreased with increasing doping concentration of Ir-G0 in CBP host. This clearly indicates that the dendritic structures are necessary to block quenching of the emitting state by intermolecular interactions effectively. The OLED device shows pure red electroluminescence maximum ~ 650 nm with (EL) performance (Ir-G0: 3007 cd/m<sup>2</sup> and  $\eta_{ext}$  3.62 %) and excellent Commission Internationale de l'Eclairage (CIE) color coordinates (x = 0.67, y = 0.31).

Keywords: Iridium complex, red OLEDs, Organic electronics.

## 1. INTRODUCTION

Recent decades, the photophysics of cyclometalated metal complexes (homo/heteroleptic) has been the theme of broad studies. These complexes have gained much consideration due to their long lived excited states and high luminescence quantum yields. The design and photophysical properties of a range of Os(II) and Ru(II) complexes for utilization in OLED fabrication has been reviewed1 along with lightemitting molecular devices that incorporate Ni(II), Cu(II) and Zn(II) metal complexes<sup>2</sup>. In OLEDs, triplet states constitute 75% of electrogenerated excited states. In general, these triplet states are nonemissive due to their long lifetime (milliseconds to minutes) as well as their spin-forbidden nature for radiative relaxation to the ground states<sup>4</sup>. Therefore, the maximum internal quantum efficiency of OLEDs is normally limited to 25%. To remove such restriction, efforts have been intended for to using transition metal (particularly 4d and 5d metal ions) complexes<sup>5</sup>.

The heavy atom induced spin-orbit coupling caused by heavy metal ions in these complexes results in efficient intersystem crossing from the singlet to the triplet excited state, allowing heavy metal complexes to utilize both singlet and triplet excitons for efficient electrophosphorescence at room temperature. Mixing of the singlet and triplet excited states not only removes the spin-forbidden nature of the radiative relaxation of the triplet state, also significantly shortens the triplet state lifetime. It is very useful since the triplet-triplet (T-T) annihilation is more effectively suppressed. Therefore one can expect that the internal quantum efficiency can theoretically approach 100% for such complexes. Particularly, the significance of phosphorescent Ir<sup>III</sup> based complexes is growing rapidly<sup>6</sup>. Since, it is possible to realize the high luminescence efficiencies and rather short phosphorescence lifetime. Their metal–ligand-based luminescence provides the opportunity to tune the emission color over the entire visible spectrum by varying the attached cyclometalating ligands<sup>7</sup>.

Ir<sup>III</sup> based complexes are shown the most efficient and versatile class of phosphorescent emitters<sup>6</sup>. The strong spin-orbit coupling leads to mixed singlet and triplet, metal-to-ligand charge-transfer (MLCT) states as well as to mixed ligand based emitting states. The metalligand based emission enables an efficient tuning of the emission color and is generally dependent on the choice of cyclometalating ligand or its substituent groups and selection of the ancillary ligands, and therefore, full-color based on phosphorescent IrIII complexes can be realized. A new red phosphorescent cyclometalated IrIII isoquinoline complexes, bearing 9-arylcarbazolyl chromophores is synthesized and optimized the device efficiency/color purity trade-off. OLED with these complexes shows very high efficiencies with a maximum EQE of up to 12 % photons per electron. The excellent performance of these red emitters indicates that the advantage of the carbazole module (improved hole transporting) in the ligand framework7. A series of

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facial homoleptic cyclometalated Ir (III) complexes have been synthesized and studied their phosphorescence8. An OLED device with phosphorescent dopant (Ir(1-phenylisoquinolinato)<sub>3</sub>) produces very high efficiency ( $\eta_{ex} = 10.3\%$  and power efficiency 8.0 lm/W at 100 cd/m<sup>2</sup>) and pure red emission. The detail photophysical studies of Ir(fliq)<sub>3</sub> and their OLED device performance were discussed.

## 2. EXPERIMENTAL SECTION

Syntheses of Ir(fliq)<sub>3</sub> complex were performed under dry and deoxygenated N<sub>2</sub> atmosphere. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents (Sigma Aldrich) were used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC) glass plates. Column chromatography was carried out using silica gel from Aldrich (70 – 230 mesh, 60 Å).

## Synthesis of Ir-G0:

1-(9,9-diethylfluorene-2-yl)isoquinoline (3.04 g 8.69 mmol), [Ir(acac)3] (1.09 g, 2.24 mmol) were added to glycerol (80 ml). The reaction mixture was heated to 230 °C for 36 hr. Then it was cooled to room temperature and water (150 ml) was added and extracted with dichloromethane ( $3 \times 50$  ml) by using separator. The combined organic phase was dried over MgSO4. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with hexane-dichloromethane (7:3).

The product was obtained as a dark red solid.(0.9g, 0.72mmol, 32%), <sup>1</sup>H NMR (500 MHz, CDCl3):  $\delta$  8.95 (3 H, d, J=8.3 Hz), 8.14 (3 H, s), 7.72 (3 H, s), 7.60 - 7.69 (6 H, m), 7.41 (3 H, s), 7.24 (3 H, d, J=7.3 Hz), 7.19 (6 H, t, J=5.9 Hz), 7.13 (3 H, s), 7.05 (3 H, d, J=6.0 Hz), 6.98 (3 H, s), 1.97 - 2.18 (12 H, m), 0.34 - 0.63 ppm (18 H, m), 13C NMR (126 MHz, CDCl3):  $\delta$  168.5, 163.5, 150.8, 144.1, 143.4, 141.9, 140.9, 139.7, 136.5, 129.7, 128.3, 127.7, 127.0, 126.7, 126.4, 126.3, 126.0, 124.4, 122.0, 120.6, 119.2, 55.6, 32.8, 8.4 ppm. Anal. Calcd for C78H66IrN3: C, 75.70; H, 5.38; Ir, 15.53; N, 3.40. Found: C, 75.19; H, 5.56; N, 3.31. m/z (MALDI): 1237

# **OLED** fabrication

Deep red phosphorescent OLEDs were fabricated using the Ir-G0 as emissive materials. [ITO/PEDOT:PSS (40nm)/Ir dendrimers (x mol%):CBP (70 nm)/BCP (10 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (120 nm); PEDOT:PSS (poly(3,4ethylenedioxythiophene): poly(styrene sulfonate)), CBP (4,4'-N,N'-dicarbazolebiphenyl), BCP (2,9dimethyl-4,7-diphenyl-1,10-phenanthroline), and Alq3 (tris(8-hydroxyquinoline)aluminum)]. The Ir complex-CBP-blended active layers were deposited by spincoating to give uniform thin films. The BCP and the Alq3 were used as a hole-blocking layers and electrontransporting layer, respectively. They were processed by high-vacuum (10-7 torr) thermal evaporation. Typically, a thin layer of LiF with a 120 nm thick Al cathode layer was deposited through a shadow mask in a vacuum chamber with a base pressure of 10-6 torr.

Phosphorescence cyclometalated iridium(III) complex dendrimers have been synthesized for the application to OLEDs. As depicted in Scheme 1, L-G0 dendron was prepared from 4,4,5,5-tetramethyl-1,3,2dioxaborolane-fluorene and 1-chloro-isoquinoline by Suzuki-coupling reaction.<sup>9</sup> And subsequently the synthesis of the iridium complex directly carried out with L-G0 ligand and Ir(acac)<sub>3</sub> according to the information found in the literature.<sup>10</sup>



Scheme 1. Synthesis route of Ir-G0.

## 3. RESULT AND DISCUSSIONS:

## **Photophysical Properties:**

Figure shows the absorption 1a and photoluminescence (PL) spectrum of Ir-G0 in The Ir-complex showed two major CH<sub>2</sub>Cl<sub>2</sub>. absorption bands in their UV-Visible absorption spectra. The absorption bands below 400 nm are attributed to spin-allowed ligand-centered (LC)  $\pi$ - $\pi$ \* transitions. The weak absorption shoulders in the visible region are assigned to the metal-to-ligand charge-transfer (1MLCT and 3MLCT) transitions induced by the strong spin-orbit coupling between the singlet and triplet manifolds.

The PL spectra of the Ir dendrimers were shown in Figure 1a. Deep red emission observed for Ir based molecular complex at 660 nm in dichloromethane solution under 440 nm excitation.

The PL spectrum of neat films of Ir-G0 was partially quenched (figure 1b). The Ir-G0 neat film had a substantial red tail to the emission spectrum, which

was not present in its emission spectrum from samples in dilute solution.



**Fig. 1:** (a) UV–visible absorption and photo luminescence spectra of Ir-G0 in  $CH_2Cl_2$  (conc. ~10<sup>-5</sup> M). (b) The PL spectra for the neat films of Ir-G0.

The red tail was ascribed to aggregate/excimer emission which gives broad red-shifted emission spectra, and it can be expected to reduce with the increasing generation, can be understood to arise from the dendron decreasing the intermolecular interactions between the chromophores.<sup>11,12</sup>.

The complex were blended into a 4,4'-bis(Ncarbazolyl)biphenyl (CBP) host at various concentrations from 1.2 mol% to 4.8 mol%, to provide an additional way of tuning the spacing between the phosphorescent cores. The molecular complex films were deposited by spin-coating on precleaned quartz substrates from chlorobenzene solutions. In order to observe the dynamics of triplet exciton diffusion and quenching, the films with different doping concentration of Ir complex in CBP host were characterized by spectrofluorometer and spectrofluorometer time resolved which has picoseconds diode laser emitting wavelength 375 nm. Figure 2 shows the concentration dependence of the PL spectra and PL lifetime (7) of the films. As the concentration of Ir-G0 in CBP host was increased, PL spectra of Ir-G0 films were broaden and shifted to longer wavelength from 655nm to 658nm, and PL intensity of the films dramatically decreased as shown in figure 2.



**Fig 2:** Photoluminescence spectra of Ir-G0 (x mol%):CBP blend films and their normalized PL spectra (inset).

As the concentration of the Ir complex in CBP host was increased and the corresponding  $\tau$  decreased (Figure 3a and b), probably due to an increase in the number of non-radiative pathways available by intermolecular interactions between phosphorescent emitters.<sup>6, 20</sup> In the case of Ir-G0 films, the photoluminescence lifetimes of Ir-G0 films decreased much more than that of IrG1 films with increasing the doping concentration. These results signify the existence of strong interactions among the IrG0 phosphorescent cores at high doping concentrations.



Fig 3: PL lifetime of Ir-G0 (x mol %) :CBP blend films.

#### 4. CONCLUSION

The fully characterized Ir based molecular complex is reported. UV-visible, Photoluminescence (PL) and PL lifetime studies of  $Ir(fliq)_3$  have been carried out and the results are discussed in details. The absorption studies shows two absorption one is below 400 nm (spin-allowed ligand-centered (LC)  $\pi$ - $\pi^*$  transitions). The weak absorption shoulders in the visible region are assigned to the metal-to-ligand charge-transfer (1MLCT and <sup>3</sup>MLCT) transitions induced by the strong spinorbit coupling between the singlet and triplet manifolds. PL and PL lifetime is decreased with increasing doping concentration of Ir-G0 in CBP host for films. This clearly indicates that the dendritic structures is necessary block quenching of the emitting state by intermolecular interactions effectively. The OLED device shows pure red electroluminescence maximum around 650 nm with (EL) performance (3007 cd/m<sup>2</sup> and  $\eta_{ext}$  3.62 %) and excellent CIE color coordinates (x = 0.67, y = 0.31).

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