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Effective Electrophosphorescence Emitting Devices by Using New Type Ir(III) Complex with Bluky Substistuent Spacers

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The new green Ir(III) complex, ***fac****-tris[4-methyl-2-(4′-trimethylsilylph-enyl)pyridine] [Ir(msippy)$_3$], is synthesized and phosphorescent light emitting devices fabricated by using them as triplet emissive dopants. Ir(dsippy)$_3$ in UV-Vis. spectra showed absorption band at 395 nm originating from ^{1}MLCT. The EL devices with configuration of ITO/CuPc (10 nm)/α-NPD (40 nm)/CBP-Ir(msippy)$_3$ (20 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/LiF (1 nm)/Al (100 nm).showed the emission maximum at 516 nm, due to the radiative decay from ^{3}MLCT state to ground state. The 6% doped devices showed the maximum efficiency of 49.9 cd/A and power efficiency 25.3 lm/W. The observed PL quantum efficiency (0.43) of the [Ir(msippy)$_3$] in CH$_2$Cl$_2$ shows slightly higher than that of reported Ir(ppy)$_3$ ($\Phi = 0.40$).*

Keywords: annihilation; iridium; MLCT; photoluminescence

INTRODUCTION

Electrophosphorescent materials incorporating with heavy metals have attracted great attention due to their potential application in low-cost

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full color displays [1]. Among the many different phosphorescent emitter for use in OLED devices, iridium complexes, in particular, have been described the most effective emitter due to their high photoluminescent efficiency and relatively short excited state lifetime [2]. The key factor in these complexes is an effective singlet-triplet mixing caused by the strong spin-orbit coupling due to heavy atom effect. This leads to large splitting of the d-orbitals which can induce emission from the low lying metal-to-ligand charge-transfer (^{3}MLCT) state. One of the important concerns in electrophosphorescent device is to design phosphor in order to achieve effective energy transfer between host and dye, and thus development and synthesis of promising phosphorescent materials with short life times in excited states and high photoluminescent quantum efficiency have been studied continuously by many research group with great interest so far. Especially, the study on development of Ir(III) phosphor having cyclometallated systems because of these reasons. Luminescnt Ir(ppy)$_3$ derivatives have been described fine-tuning band gap between HOMO and LOMO energy level through the modification of ligands, leading to tune emission energy ranging from blue to red [3,4]. Which have been established by Thompson and Forrest groups, emission energy of Ir(ppy)$_3$ derivatives can be tuned by the introduction of electron donor/acceptor as subunit into 2-phenylpyridine frameworks [5]. For example, introduction of electron-donating groups to pyridine ring and electron-withdrawing groups to phenyl ring that can occurs diminution of HOMO and increasing of LUMO level, respectively, allow to give lager band-gap than that of Ir(ppy)$_3$. Although extensive research on investigation of luminescent properties of Ir(ppy)$_3$ derivatives, containing two *o*-chelating ligand and bidentate ancillary ligand (e.g., acac, tmd, bza, dbm) systems, and use as triplet emitter or host in EL device performance has been well carried out for several years, substituent effect depending on position of phenyl or pyridine rings retaining 2-phenylpyridine backbone remain still scarce. The present report aims at designing a new tris-orthometalated Ir(III) complex as a triplet emitter by using modified phenylpyridine system, that is *fac*-tris [4-methyl-2-(4′-trimethylsilylphenyl)pyridine]Ir(III), [Ir(msippy)$_3$]. The introducing of bulky trimethylsilyl substituents is expected to have inhibitors triplet annihilation due to intermolecular interaction.

EXPERIMENTAL

Synthesis of Ligand msippy

2-bromo-4-methylpyridine (3.7 g, 0.021 mol), 3-trimethylsilylbenzneboronic acid (5 g, 0.026 mol), and Pd(PPh$_3$)$_4$ (0.15 g, 0.6 mol%), were dissolved in THF (45 mL). A solution of 2M-K_2CO_3 (15 mL) was added, and the mixture refluxed with stirring for 18 hr in an atmosphere of nitrogen. After being cooled, the mixture was poured into aqueous EDTA and extracted with ether, the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by chromatography on silica gel (EtOAc/hexane, 1/5, v/v) to obtain a colorless oil (4.83 g, 93%).

Synthesis of Complex [Ir(msippy)$_3$]

msippy (3 g, 0.012 mol) and Ir(acac)$_3$ (1.01 g, 2.07 mmol) were dissolved in glycerol(50 mL), and the mixture was heated to reflux under nitrogen for 25 h. The reaction mixture was then cooled to room temperature, 1 N HCl was added, and the mixture filtered to give a crude product, and then flash chromatographed on silica column using dichloromethane to yield 28%. The compound was then further purified by sublimation. 1H-NMR (CDC13): δ 7.62 (2H), 7.25 (1H), 6.84 (1H), 6.65 (1H), 6.55 (1H), 2.35 (3H), 0.01 (9H) ppm. MS (EI): $m/z = 913[M^+]$.

Fabrication of Electroluminescent Device

A glass substrate precoated with indium tin oxide (ITO) was cleaned in an ultrasonic bath of acetone, followed by 2-propanol. Surface treatment was carried out by exposing ITO to a UV ozone plasma. OLEDs with CBP as host material were fabricated as follows. The hole-injecting layer, a 10 nm thick film of CuPc was deposited on the ITO surface by high-vacuum thermal evaporation and a 40 nm thickness α-NPD as hole-transporting layer was deposited onto the CuPc. An [Ir(msipy)$_3$]-doped host CBP layer was thermally co-evaporated

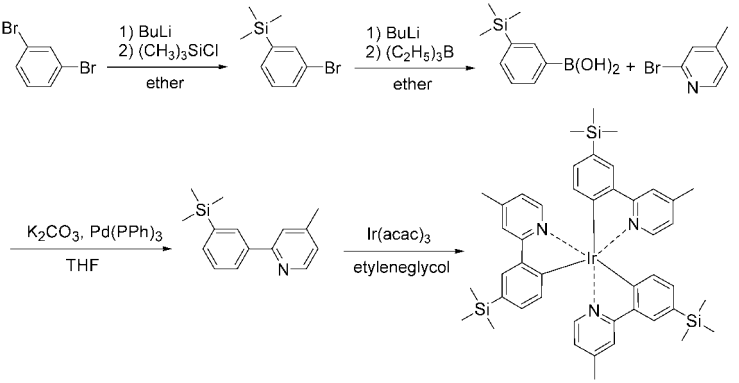

FIGURE 1 Reaction Scheme of [Ir(msippy)$_3$].

onto the α-NPD layer. The [Ir(msippy)$_3$] doping concentration was 6% in CBP. A 10 nm thick BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) layer was then deposited as the exciton-blocking layer, followed by a 40 nm thick Alq$_3$ layer as an electron-transporting layer. Finally, LiF (1 nm) and Al (100 nm) were deposited on top of the organic layers by thermal evaporation. The fabricated multilayer organic light-emitting devices have the structure of ITO/CuPc (10 nm)/α -NPD (40 nm)/CBP-Ir(msippy)$_3$ (20 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/LiF (1 nm)/Al (100 nm).

RESULTS AND DISCUSSION

The newly desiged [Ir(msippy)$_3$] was successfully synthesized. The obtained material was comfirmed by spectroscopic analysis.

The UV-Vis absorption and PL spectra of [Ir(mppy)$_3$] in degassed dichloromethane solution at room temperature are displayed in Figure 2. The strong absorption bands around 286 nm can be assigned to spin allowed π-π^* transitions on the cyclometalated ligands. The broad absorption bands at lower energies are typical for spin allowed metal to ligand charge-transfer (^{1}MLCT) transitions, and the weaker

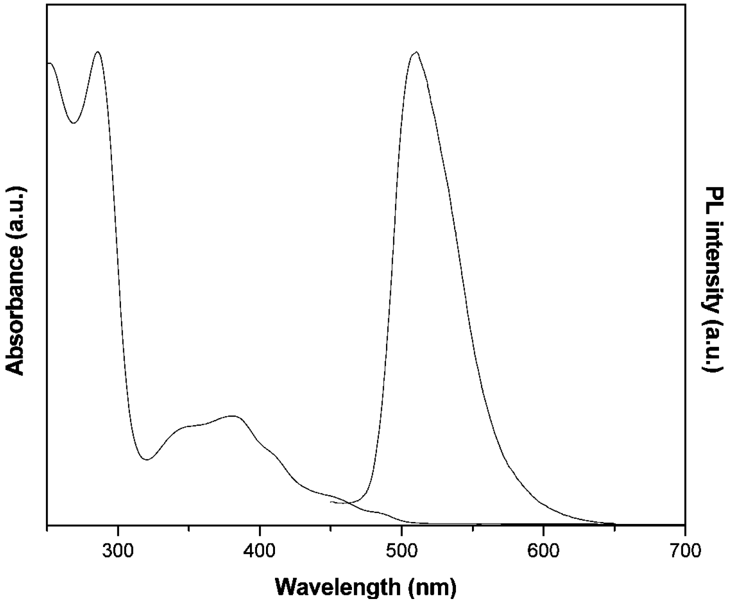

FIGURE 2 UV visible and PL spectra of [Ir(msippy)$_3$].

absorption bands extending into the visible region are assigned to the formally spin-forbidden ^{3}MLCT transitions (480 nm). The emission of the complex, centered at 510 nm is due to the radiative decay from the triplet manifold to the ground state. The observed PL quantum efficiency (0.43) of the [Ir(msippy)$_3$] in CH_2Cl_2 shows slightly higher than that of reported Ir(ppy)$_3$ ($\Phi = 0.40$) [6].

NPD/CBP-Ir(msippy)$_3$/BCP/Alq$_3$/LiF-Al

The EL spectrum of a green phosphorescent device based on [Ir (msippy)$_3$] is shown in Figure 3. The emission peak was located at 516 nm with a sub-peak 541 nm. The EL spectra originating from the triplet-excited states of the phosphors as shown in Figure 2 is coincident with this of the phosphors in a dilute solution. This is no characteristic emission peaks from CBP or Alq$_3$, indicating that the emission originates mostly from the dopant. Furthermore, this result support the proposal that effective energy transfer from the host (CBP) to the dopant (Ir complex) occurs in the emissive layer. The Commission Internationale de L'Eclairage (CIE) coordinates were (0.29, 0.62).

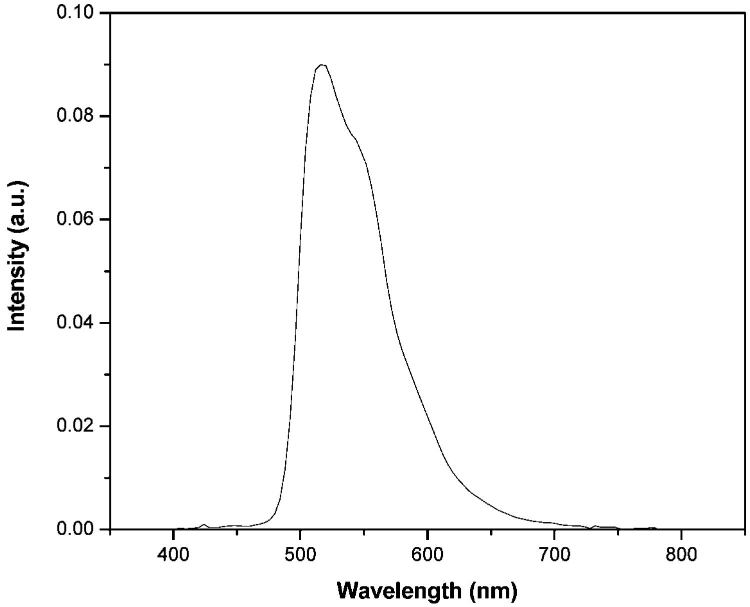

FIGURE 3 EL spectra of [Ir(msippy)$_3$], device structure: ITO/CuPc.

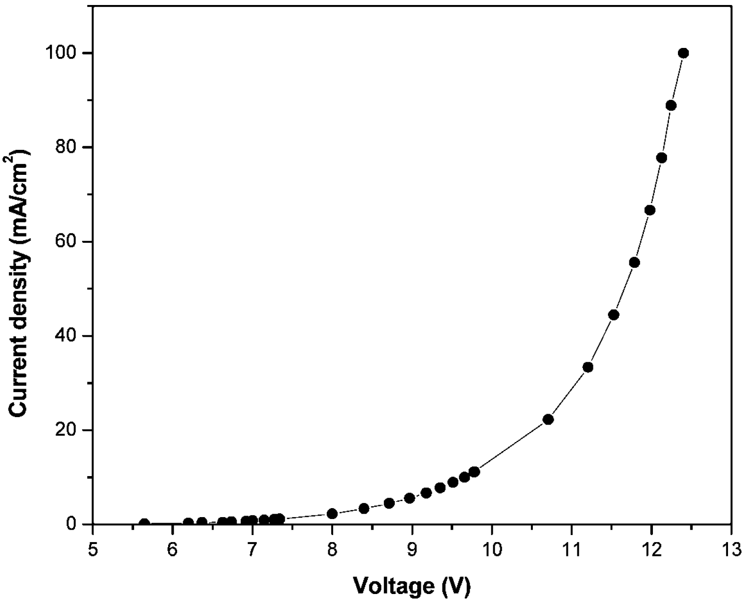

FIGURE 4 Voltage versus current density characteristics of [Ir(msippy)$_3$].

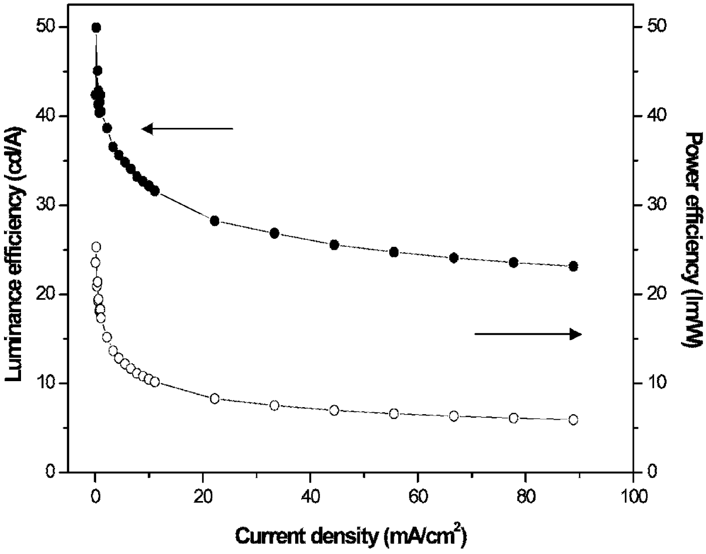

FIGURE 5 Luminance and power efficiency versus current density characteristics of [Ir(msippy)$_3$].

The turn-on voltage (defined as $1\,\text{mA/cm}^2$) of [Ir(msippy)$_3$] is 7.2 V (Figure 4). The ionization potential (Ip) level of [Ir(msippy)$_3$] was investigated cyclic voltammetry. The HOMO, LUMO and band gap of [Ir(msippy)$_3$] was 5.15 eV, 2.67 eV and 2.47 eV, respectively. The luminance reached $20540\,\text{cd/m}^2$ at an applied voltage of 12.3 V.

The luminance efficiency and power efficiency of the green device are shown as a function of current density in Figure 5. The maximum luminance efficiency was 49.9 cd/A, and the power efficiency was 25.3 lm/W.

In conclusion, we have successfully synthesis new ligand, msippy and have used this ligand to synthesis the iridium complex [Ir(msippy)$_3$]. The EL device based on this complex emit green light with high luminance and power efficiency. We believe the efficiency can be further improved by using a more suitable host material for the emitting layer or a more suitable material for the hole blocking layer [7].

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