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# Synthesis and electroluminescent property of highly efficient phosphorescent red dopants based on modulated main ligands

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#### ABSTRACT

Novel red phosphorescent iridium(III) complexes, (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), (PN-MQ)<sub>2</sub>Ir(tmd) were synthesized for red emitter of the phosphorescent organic light-emitting diodes (phOLEDs). The ligands have sites of both the electron donor and acceptor in a molecule. The main ligands consisted of electron-donors ((dimethylamino)phenyl, (diphenylamino)phenyl, (dimethylamino)naphthalene) and electron-acceptor methyl quinoline were synthesized by suzuki coupling reaction. The iridium(III) complexes based on main ligands and 2,2,6,6-tetramethyl-3,5-heptanedione(tmd) ancillary ligand were synthesized by Nonoyama reaction. Their luminescence property was investigated by UV-visible spectroscopy and photoluminescence (PL) spectroscopy. The manufactured PHOLEDs were characterized by investigation of current density-voltage-luminance, luminance efficiency, external quantum efficiency, electroluminescence spectrum. These phosphorescent iridium complexes will be promising candidates for highly efficient red emitters.

#### **KEYWORDS**

Iridium(III) complexes; phosphorescent organic light-emitting diodes; red dopant

#### 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive attention because of their several advantages, such as high efficiency, wider viewing angles, high sense of realness, high definition, fast response time and flexible display. One important requirement for OLED application is the low power consumption and high efficiency. Phosphorescence active matrix organic light emitting diodes (PHAMOLED), expecting as the next generation display because of many advantage. Phosphorescent transition metal complexes as triplet dopant emitters offer a great promise, since the transition metal ions can induce efficient spin–orbit coupling (SOC), which facilitates efficient intersystem crossing (ISC), leading to a higher quantum efficiency [1–6].

Hole and electron transporting layer, an appropriate emission characteristics and the amorphous properties of the organic material, was known to be useful in the manufacture of a light emitting diode. The excitons formed in a device operation are composed of 25% singlets and 75% triplets. The efficiency of the devices limits that contain organic materials as emitter

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Figure 1. Synthetic and chemical structure of complexes.

to 25%. The cyclometalated iridium(III) complexes are considered attractive candidates for electroluminescent devices as they enhance the possibility of reaping both singlet and triplet excitons formed during the device operation. So, phosphorescence might eventually lead to higher efficiency than fluorescence [4–7].

In this paper, we report the synthesis and photo-physical properties of novel phosphorescent red dopants using methyl quinolone and aromatic amine moiety modification of main ligand and 2,2,6,6-tetramethyl-3,5-heptanedione(tmd) of ancillary ligand. Also, red-emitting devices was measured characteristics of electroluminescent properties, respectively

#### 2. Experimental details

Total synthesis of three new red materials is shown in Figure 1. Experimental details are described below.

#### 2.1. Synthesis of the main ligands

All the main ligands were prepared by essentially following the same procedure.

#### 4-(4-methylquinolin-2-yl)-diphenylaniline (DPAP-MQ)

DPAP-MQ was synthesized by Suzuki coupling reaction. A mixture of (4-(diphenylamino)phenyl)boronic acid (2.00 g, 7 mmol), 2-chloro-4-methylquinoline (1.35 g, 7.6 mmol), tetrakis(triphenylphosphine)palladium (0.08 g, 0.07 mmol, 1 mol%), potassium carbonate (10.38 ml, 2M aqueous solution), and tetrahydrofuran (20.75 mL) was handed under a nitrogen atmosphere at 80°C for 24 h. After the reaction, the mixture was cooled to room temperature for 1 h and extracted by liquid-liquid separation (water and dichloromethane) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered concentrated under reduced pressure [2–3]. The compound was purified by a celite-silica gel filtration (solvent: toluene) and column chromatography on silica gel (eluent: hexane/ethyl acetate, 15:1). Yield: 90% (2.4 g); <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 8.15(d, J = 9.5 Hz, 1 H), 8.05(d, J = 9.2 Hz, 2 H), 7.92(d, 8.4 Hz, 1 H), 7.75(t, J = 8.5 Hz, 1 H), 7.58(t, J = 7.5 Hz, 1 H), 7.25(t, J = 7.3 Hz, 4 H), 7.03(s, 1 H), 6.81(t, J = 4.2 Hz, 2 H), 6.62(dd, J = 10.4, 3.4 Hz, 6 H), 2.62(s, 3 H)

#### N,N-dimethyl-4-(4-methylquinolin-2-yl)aniline (DMAP-MQ)

Yield: 91%; <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 8.11(t, J = 8.9 Hz, 3H), 7.95(d, J = 8.3 Hz, 1 H), 7.67(t, J = 5.7 Hz, 2 H), 7.47(t, J = 7.1, 1 H), 6.83(d, J = 8.8, 2 H), 3.05(s, 6 H), 2.73 (s, 3 H)

#### 4-methyl-2-(4-phenylnaphthalen-1-yl)quinolone (PN-MQ)

Yield: 93%; <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 8.67(d, J = 8.5 Hz,1H), 8.47(s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.98(dd, J = 5.4, 2.9 Hz, 2H), 7.95(d, J = 7.4 Hz, 1H), 7.67(q, J = 1.7 Hz, 3H), 7.47(m, 5 H), 7.26(t, J = 3.9 Hz, 1H), 7.18(s, 1H), 2.35(s, 3H)

#### 2.2. Synthesis of the iridium(III) complexes

All the cyclometalated iridium(III) complexes were prepared by essentially following the same procedure.

#### (DPAP-MQ), Ir(tmd)

Dimer [(DPAP-MQ)<sub>2</sub>IrCl]<sub>2</sub> was synthesized using a slightly modified Nonoyama reaction step 1. Iridium(III) chloride hydrate (0.74 g, 2.5 mmol) and DMP-MDCPQ (2.4 g, 6.2 mmol) were dissolved in a mixed solution of 2-ethoxyethanol (36 mL) and water (12 mL). The reaction should be required under a nitrogen atmosphere, refluxed overnight at 135°C. After the reaction, the mixture was cooled to room temperature for 1 h and column chromatography on silica gel (eluent: hexane/ethyl acetate, 15:1). The crude product dimer was obtained by using a solvent (chloroform/methanol, 1:1).

Complex (DPAP-MQ)<sub>2</sub>Ir(tmd) using a slightly modified Nonoyama reaction step 2. [(DPAP-MQ)<sub>2</sub>IrCl]<sub>2</sub> dimer (2.8 g, 1.11 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione(tmd) (1.2 mL), 2-Ethoxyethanol (84 mL) and fine powder of sodium carbonate (1.84 g, 13.3 mmol) is mixed under a nitrogen atmosphere at 130°C for 24 h. After the reaction, the mixture was cooled to room temperature for 1 h. The compound was extracted by liquid-liquid separation (water and dichloromethane) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, washed with brine for the combining organic phase, and filtered concentrated under reduced pressure. Product purified column chromatography on silica gel (eluent: hexane/ethyl acetate, 2:1). The insoluble products were filtered out with methanol and dried. The product was further purified by recrystallization several times for high purity [2–4]. Yield: 74% (1.4 g); <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 8.17(d, J = 9.1 Hz, 2 H), 8.05(d, J = 8.2 Hz, 2 H), 7.92(d, J = 8.7 Hz, 2 H), 7.75(t, J = 7.5 Hz,2H), 7.58(t, J = 7.3 Hz, 2H), 7.18(t, J = 7.6 Hz, 8H),7.02 (s, 2 H), 6.87(tt, J = 4.2, 1.7 Hz, 4H), 6.60(dd, J = 9.2, 2.4 Hz, 12H), 2.62(s, 6H), 0.98(s, 18H)

#### (DMAP-MQ)<sub>2</sub>Ir(tmd)

Yield: 65%; <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 8.11(t, J = 8.2 Hz, 4H), 7.92(d, J = 7.9 Hz, 2H), 7.66(t, J = 5.3 Hz, 4H), 7.15(s, 1H), 6.83(d, J = 8.9 Hz, 4H), 3.12(s, 12H), 2.63(s, 6H), 1.13(s, 18H)

#### (PN-MQ)<sub>2</sub>Ir(tmd)

Yield: 68%; <sup>1</sup>H NMR 500 MHz, CDCl3,  $\delta$ ),  $\delta$ (ppm): 71(d, J = 8.8 Hz,2H), 8.49(s, 2H), 8.21 (d, J = 9.0 Hz, 2H), 7.90(d, J = 8.1 Hz, 2H), 7.76(d, J = 8.2 Hz,2H), 7.52(t, J = 0.9 Hz, 2H),



Figure 2. Schematic illustration and energy level diagram of the red PHOLEDs.

7.47(t, J = 1.0 Hz, 2H), 7.26(p, J = 6.5 Hz, 6H), 7.15(t, J = 2.4 Hz, 6H), 5.3(s, 1H), 4.9(s, 1H), 2.88(s, 6H), 0.69(s, 18H)

#### 2.3. Device fabrication

Indium-tin-oxide (ITO) coated glass substrates, which have a sheet resistance of 10  $\Omega$ /sq and a thickness of 180 nm, were used to fabricate the red PHOLEDs. The cleaning procedure included sequential ultra-sonication in acetone, methyl alcohol, distilled water, and ethyl alcohol at room temperature for 15 min before depositing the organic layers. The pre-cleaned ITO-coated glass substrates were dried in a convection oven at 120°C for 10 min. The ITO substrates were then treated with oxygen plasma at 2 × 10<sup>-2</sup> Torr at 125 W for 2 min. The organic layers were deposited by thermal evaporation through a shadow mask under high vacuum (8 × 10<sup>-7</sup> Torr) condition. The fabricated devices were sealed with UV-epoxy resin and a glass cap in a nitrogen-purged glove box under presence of O<sub>2</sub> and H<sub>2</sub>O at a concentration below 1 ppm. A getter was used to absorb the residue moisture in the encapsulated device.

Figure 2 presents three types of red PHOLEDs with the following structures: ITO (150 nm) as an anode / 4,4',4"-tris(N-(2-naphthyl)-N-phenylamino)-triphenylamine (2-TNATA, 30 nm) as the hole injection layer (HIL) / N,N'-bis(1-naphyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB, 20 nm) as a hole transporting layer (HTL) / 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) doped with three kinds of dopant 8 wt.% as an emitting layer (EML, 30 nm) / 2,2',2"-(1,3,5-tris)tris(1-phenyl)-1H-benzimidazol (TPBi, 40 nm) as an electron transporting layer (ETL) / lithium quinolate (Liq, 2 nm) as an electron injection layer (EIL) / aluminum (Al, 100 nm) as a cathode.

#### 2.4. Measurement

All reagents and solvents were purchased from Aldrich Chemical Co., TCI, and Alpha Aesar, and they were used without further purification. All column chromatography was performed under a standard atmosphere using silica gel (230–400 mesh, Sigma-Aldrich). UV-visible absorption spectra were recorded on an Agilent 8453 UV–Visible spectrophotometer. Photo-luminescence (PL) spectra were obtained using an LS55 fluorescence spectrometer. The 1H NMR spectra were measured using a UNITY-INOVA 500 MHz Nuclear Magnetic Resonance Spectrometer of VARIAN. INC. in a deuterated chloroform solution.

The current density-voltage (J-V) characteristics of the OLEDs were measured using a source measure unit (model 2400, Keithley Instruments Inc., Cleveland, OH, USA). The



Figure 3. UV/PL spectra of complexes.

electroluminescence (EL) performance of the devices including the luminance, luminous efficiency (LE), external quantum efficiency (EQE), Commission International de L'Éclairage (CIE) chromaticity coordinate, and EL spectra were analyzed using a Chroma meter (model CS-1000A, Konica Minolta Holdings, Inc., Chiyoda, Tokyo, Japan). All measurements were carried out at room temperature (about 23°C) under ambient conditions.

#### 3. Results and discussion

Figure 3 is displayed the absorption spectra measured for solutions of  $(DPAP-MQ)_2Ir(tmd)$ ,  $(DMAP-MQ)_2Ir(tmd)$ ,  $(PN-MQ)_2Ir(tmd)$  in Chloroform at room temperature. The main absorption bands are located between 300 and 400 nm. The absorption spectrum can be assigned to the spin-allowed  ${}^1\pi-\pi^*$  transition of the ligands in the Ir(III) complexes. The weak absorption bands were observed in the lower energy range from 400 to 500 nm. The lowest energy absorption peaks are assigned to the spin-allowed metal-ligand charge transfer band ( ${}^1MLCT$ ). And the spin-forbidden metal-to-ligand ( ${}^3MLCT$ ) was transited. Cross point of the  ${}^3MLCT$  absorption and PL emission spectrum was assigned to



Figure 4. EL spectra of CBP doped with (DPAP-MQ)2lr(tmd) or (DMAP-MQ)2lr(tmd) or (PN-MQ)2lr(tmd) within red PHOLED EMLs at 12 V.



Figure 5. (a) Current density-voltage-luminance, (b) LE-luminance, and (inset) EQE-luminance characteristics of the red PHOLEDs.

correspond to the first triplet excited energy  $(T_1)$  level. Because the strong spin-orbital coupling [4, 8–11].

The PL spectra have (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), and (PN-MQ)<sub>2</sub>Ir(tmd) emission with peak wavelength at 590, 598 and 647 nm in Chloroform at room temperature, as shown also in Figure 3. The tuned main ligand could change the phosphorescence peak wavelength. Because of phenyl group is stronger electron-donor group than amino substituents, the electron density of naphtalane in PN-MQ ligand is more increased than the electron density of phenyl in DPAP-MQ, DMAP-MQ ligand. That is why the highest occupied molecular orbital (HOMO) energy level of PN-MQ ligand is higher than others. Therefore, the HOMO-LUMO energy bandgap of (PN-MQ)<sub>2</sub>Ir(tmd) is more decreased than others. So, PL of (PN-MQ)<sub>2</sub>Ir(tmd) is more red-shifted than others.

The normalized EL spectra at 12 V of fabricated red PHOLEDs are shown in Figure 4. The EL spectra have clear (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), and (PN-MQ)<sub>2</sub>Ir(tmd) emission with peak wavelength at 593, 594 and 649 nm for red PHOLEDs. There are no other emission peak from the host or charge transport materials, indicating complete energy transfer from the host of CBP to the (DPAP-MQ)<sub>2</sub>Ir(tmd) or (DMAP-MQ)<sub>2</sub>Ir(tmd) or (PN-MQ)<sub>2</sub>Ir(tmd). In other study, redPHOLEDs are indicated emission of 610~630 nm generally. So, (PN-MQ)<sub>2</sub>Ir(tmd) was observed large wavelength, (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd) was observed small wavelengths as compared with other research [2–7].

Figure 5(a) illustrates the current density-voltage-luminance (J-V-L) characteristics of three red PHOLEDs. The turn-on voltages of red devices using (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), and (PN-MQ)<sub>2</sub>Ir(tmd) were observed with 2.64, 4.30, and 3.60 V at 1.0 cd/m<sup>2</sup>. The maximum luminance of (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), and (PN-MQ)<sub>2</sub>Ir(tmd) red devices were 14,720, 4,526, and 1,770 cd/m<sup>2</sup>. The luminance and LE, EQE characteristic of fabricated devices are shown in Fig. 5(b). The maximum LEs and EQEs of three red PHOLEDs were 16.32, 9.33, and 1.14 cd/A and 9.42, 5.00, and 3.97%, respectively.

The device using  $(DPAP-MQ)_2Ir(tmd)$  show lower turn-on voltage, higher luminance and EQE compared two other devices. It is indicated that the device using  $(DPAP-MQ)_2Ir(tmd)$  in more efficient than two others.

#### 4. Conclusion

The novel phosphorescent red dopants of Ir(III) complexes are using three main ligands. (DPAP-MQ)<sub>2</sub>Ir(tmd), (DMAP-MQ)<sub>2</sub>Ir(tmd), and (PN-MQ)<sub>2</sub>Ir(tmd) were synthesized for highly efficient of PHOLEDs. Ir(III) complexes had emission maxima at 590, 598 and 647 nm.

Because of smaller HOMO-LUMO band gap energy, (PN-MQ)<sub>2</sub>Ir(tmd) had more long wavelength than the others. EL emissions of fabricated red PHOLEDs were 593, 594 and 649 nm. It is indicated completely energy transfer. (DPAP-MQ)<sub>2</sub>Ir(tmd) was higher performance than the others. The maximum luminance is 14,720 cd/m<sup>2</sup>, maximum LE is 16.32 cd/A and maximum EQE is 9.42%. Therefore, it was concluded that (DPAP-MQ)<sub>2</sub>Ir(tmd) is highest dopant in those three dopants and it will be able to use a strong candidate dopant for PHOLEDs.

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