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# Green Phosphorescent Homoleptic Iridium(III) Complexes for Highly Efficient Organic Light-Emitting Diodes

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#### Abstract

Homoleptic Ir(III) complexes, Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub>, based on 2-phenyl-5-(trimethylsilyl)pyridine (ppyTMS) and 2-(1,1'-biphenyl-3'-yl)-5-(trimethylsilyl)pyridine (mPppyTMS) as cyclometalated ligands, respectively, were synthesized for highly efficient green phosphorescent organic light-emitting diodes (OLEDs). The trimethylsilyl and phenyl groups introduced on the 2-phenylpyridine ligand suppressed the intermolecular interactions and the triplet-triplet annihilation process taking place via molecular aggregation, which otherwise decrease the OLED efficiency. The green phosphorescent OLEDs doped with  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  as green emitters exhibited maximum electroluminescent wavelengths of 525 and 529 nm, respectively, at an optimized doping concentration of 5%. The Commission Internationale de L'Eclairage coordinates of these OLEDs were (0.35,0.62) and (0.37, 0.61), respectively, at a luminance of 1000 cd m<sup>-2</sup>. The maximum external quantum efficiency and maximum power efficiency (PE<sub>max</sub>) were 16.6%/66.1 lm  $W^{-1}$  for the Ir(ppyTMS)<sub>3</sub> device and 18.1%/70.3 lm W<sup>-1</sup> for the Ir(*m*PppyTMS)<sub>3</sub> device, which were higher than those of Ir(ppy)<sub>3</sub> without substituents on the 2-phenylpyridine ligand. Moreover, the  $PE_{max}$  value of the  $Ir(mPppyTMS)_3$  device is one of the highest values among the reported devices fabricated using homoleptic Ir(III) complexes for green phosphorescent OLEDs.

Keywords: green phosphorescence; iridium(III) complex; organic light-emitting diodes; power efficiency

#### **1. Introduction**

Iridium(III) complexes have attracted considerable attention as emitters in phosphorescent organic light-emitting diodes (OLEDs) because of their advantages such as 100% theoretical internal quantum efficiency using both singlet and triplet excitons, high external quantum efficiency (EQE), and high power efficiency (PE) [1,2]. In particular, Ir(III) complexes have a short triplet lifetime, good thermal stability, high photoluminescence quantum yields ( $\Phi_{PL}$ ), and can exhibit additional emission wavelengths by ligand tuning in comparison with those of other emitters such as platinum(II), osmium(II), and ruthenium(II) complexes [3-5].

Among the most widely used RGB emitters, the green emitter, Ir(ppy)<sub>3</sub>, was first reported by Watts and co-workers and is a homoleptic Ir(III) complex formed from 2-phenylpyridine using Ir(III) acetylacetonate [Ir(acac)<sub>3</sub>] [6]. Subsequently, Ir(ppy)<sub>3</sub> and Ir(ppy)<sub>3</sub>-derivatives have been prepared and utilized as efficient green phosphorescent emitters with well-defined highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels [7-11]. However, the Ir(ppy)<sub>3</sub> moiety suffers from some drawbacks as a green dopant in phosphorescent OLEDs, including severe self-quenching because of strong bimolecular interactions and triplet-triplet annihilation at high doping concentration arising from their small sizes. These factors result in the diminution of device performances such as luminance and quantum efficiency in phosphorescent OLEDs [12-15]. It has been previously reported that endowing bulkiness to the cyclometalated ligand in Ir(III) complexes can minimize the bimolecular interaction between the molecules, and thus hinder the triplettriplet annihilation in phosphorescent OLEDs [16-20].

In our previous studies, we found that a device comprising a heteroleptic iridium complex containing a 2-phenylpyridine-based ancillary ligand showed improved performances than that comprising the corresponding iridium complex with the acetylacetonate (acac) ancillary

ligand [18,21,22]. Additionally, substitution of a phenyl group on the 5-position of the phenyl ring of the 2-phenylpyridine ancillary ligand efficiently suppressed concentration selfquenching at high doping concentration [22]. Furthermore, it was reported that the introduction of a TMS group on the 5-position of the pyridine ring of the 2-phenylpyridine ligand in heteroleptic Ir(III) complex could be another strategy to improve OLED device performances [23]. The maximum current efficiency and power efficiency of OLED device were increased from 18.0 cd  $A^{-1}/11.1$  lm  $W^{-1}$  to 24.5 cd  $A^{-1}/16.5$  lm  $W^{-1}$  by the TMS substitution. The TMS substituent on the pyridine moiety could impart hindered intermolecular interaction and prevented exciton quenching during OLED operation.

In a continuation of our research efforts toward developing efficient phosphorescent OLEDs, bulky substituents were introduced on the 2-phenylpyridine ligands in homoleptic green phosphorescent Ir(III) complexes to achieve three-dimensional hindered structures by triply bulky cyclometalated ligands. The homoleptic Ir(III) complexes were found to be thermally more stable than the acac-containing heteroleptic complexes, and were thus suitable for fabricating OLED devices via vacuum deposition methods [24]. In this work, we successfully synthesized two green phosphorescent homoleptic Ir(III) complexes, Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub>, containing 2-phenyl-5-(trimethylsilyl)pyridine (ppyTMS) and 2-(1,1'biphenyl-3'-yl)-5-(trimethylsilyl)pyridine (*m*PppyTMS) as ligands, respectively. Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> showed improved thermal stabilities,  $\Phi_{PL}$ , and OLED device performances compared to Ir(ppy)<sub>3</sub>. The effect of endowing bulkiness on the ligands has been described in detail in the results and discussion section.



Scheme 1. Synthesis of Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub>.

#### 2. Experimental

#### 2.1. Materials

2,5-Dibromopyridine, phenylboronic acid, 3-biphenylboronic acid, *n*-butyllithium (2.5 M solution in hexane), trimethylsilyl chloride, tetrakis(triphenylphosphine)palladium(0), and Ir(III) acetylacetonate were purchased from Aldrich and Alfa Aesar. All chemicals were used without further purification.

#### 2.2. Synthesis of Green Phosphorescence Iridium(III) Complexes

#### 2.2.1. Synthesis of 2-bromo-5-(trimethylsilyl)pyridine (1)

Under a nitrogen atmosphere, *n*-BuLi (33.8 mL, 84.4 mmol, 2.5 M solution in hexane) was added dropwise to 2,5-dibromopyridine (20.0 g, 84.4 mmol) in anhydrous diethyl ether (200

mL) at -78 °C. After stirring the mixture at -78 °C for 1 h, trimethylsilyl chloride (12.8 mL, 101.4 mmol) was added. Subsequently, the reaction mixture was allowed to warm to room temperature and stirred for another 12 h. Distilled water was added to the reaction mixture and the organic layer was extracted with ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub>. After filtration to remove MgSO<sub>4</sub>, the solvent was removed under reduced pressure to obtain a crude residue. The crude product was purified by vacuum distillation. The fraction boiling at 87 °C (1.5 mmHg) (1) was collected as a colourless oil (18.5 g, 95.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.40 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 0.28 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 154.85, 154.19, 143.34, 127.57, 127.40, 0.09.

### 2.2.2. Synthesis of 2-phenyl-5-(trimethylsilyl)pyridine (ppyTMS)

Compound **1** (6.0 g, 26.0 mmol), phenylboronic acid (3.2 g, 26.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.9 g, 0.8 mmol) were dissolved in anhydrous tetrahydrofuran (25 mL). An aqueous solution of 2 M K<sub>2</sub>CO<sub>3</sub> (100 mL) and Aliquat 336 (1.1 g, 2.6 mmol) was added, and the mixture was refluxed overnight with stirring under a nitrogen atmosphere. Subsequently, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water and dried over MgSO<sub>4</sub>. After filtration, the solvent was removed under reduced pressure to obtain a crude residue. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane, 1:3  $\nu/\nu$ ) to obtain ppyTMS (3.9 g, 65.7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.78 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 2H), 7.86 (m, 2H), 7.52 (m, 3H), 0.33 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 155.61, 153.76, 140.5, 138.9, 128.5, 129.1, 127.6, 127.3, 121.8, 0.02.

#### 2.2.3. Synthesis of 2-[(1,1'-biphenyl)-3-yl]-5-(trimethylsilyl)pyridine (mPppyTMS)

*m*PppyTMS (4.9 g, 62.1%) was prepared from 3-biphenylboronic acid (5.2 g, 26.0 mmol) and compound **1** using the same procedure as described for ppyTMS. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.83 (s, 1H), 8.31 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.71 (m, 4H), 7.49 (m, 4H), 0.35 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 157.36, 153.93, 142.01, 141.75, 141.05, 139.97, 133.36, 129.23, 128.79, 127.84, 127.53, 127.44, 127.32, 125.83, 120.07, -1.53.

#### 2.2.4. Synthesis of Ir(ppyTMS)<sub>3</sub>

ppyTMS (2.8 g, 12.3 mmol) and Ir(acac)<sub>3</sub> (1.0 g, 2.0 mmol) were dissolved in glycerol (150 mL), and the mixture was stirred at reflux under a nitrogen atmosphere for 25 h. The reaction mixture was then cooled to room temperature and 1 N HCl solution was added. Subsequently, the mixture was filtered to obtain a crude product, which was then purified by silica gel column chromatography (ethyl acetate/hexane, 1:3  $\nu/\nu$ ) to obtain Ir(ppyTMS)<sub>3</sub> (0.8 g, 46%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.84 (d, *J* = 7.5 Hz, 3H), 7.67 (m, 6H), 7.45 (s, 3H), 6.99 (m, 3H), 6.93 (m, 6H), 0.05 (s, 27H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 166.95, 161.76, 150.44, 144.00, 140.75, 137.28, 132.67, 129.99, 124.04, 119.63, 118.18, -1.208. Anal. Calcd. for C<sub>42</sub>H<sub>48</sub>IrN<sub>3</sub>Si<sub>3</sub>: C, 57.89; H, 5.55; N, 4.82; Si, 9.67. Found: C, 57.93; H, 5.51; N, 4.63. MALDI-TOF (M<sup>+</sup>, C<sub>42</sub>H<sub>48</sub>IrN<sub>3</sub>Si<sub>3</sub>): Calcd. 871.28, found 871.65. HPLC purity: 99.7%.

#### 2.2.5. Synthesis of Ir(mPppyTMS)<sub>3</sub>

Ir(*m*PppyTMS)<sub>3</sub> (1.0 g, 43%) was prepared from *m*PppyTMS (3.7 g, 12.3 mmol) using the same procedure as described for Ir(ppyTMS)<sub>3</sub>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.93 (m, 6H), 7.72 (d, *J* = 7.8 Hz, 3H), 7.66 (d, *J* = 7.5 Hz, 6H), 7.52 (s, 3H), 7.42 (t, *J* = 7.5 Hz, 6H), 7.28 (m, 6H), 7.16 (d, *J* = 7.8 Hz, 3H), 0.07 (s, 27H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):

166.81, 161.10, 150.56, 144.68, 142.22, 140.98, 137.64, 133.13, 132.57, 129.04, 128.65, 126.46, 126.03, 122.62, 118.40, –1.211. Anal. Calcd. for C<sub>60</sub>H<sub>60</sub>IrN<sub>3</sub>Si<sub>3</sub>: C, 65.54; H, 5.50; N, 3.82; Si, 7.66. Found: C, 65.65; H, 5.47; N, 3.78. MALDI-TOF (M<sup>+</sup>, C<sub>60</sub>H<sub>60</sub>IrN<sub>3</sub>Si<sub>3</sub>): Calcd. 1099.37, found 1099.74. HPLC purity: 99.8%.

#### 2.3. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using a Varian Mercury 300 (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz) spectrometer. MALDI-TOF mass spectra were obtained using a ZMS-DX303 mass spectrometer (JEOL Ltd.). HPLC was performed using a WatersTM 600 Controller with a WatersTM 486 tunable absorbance detector. TGA was performed using an SDT Q600 V20.9 Build 20 instrument under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. UVvis absorption spectra were recorded using a Shimadzu UV-3600 spectrophotometer, while PL spectra were recorded on a Shimadzu RF 5301 PC fluorometer. CV was performed using a CH Instruments 600D voltammetric analyser at a potential scanning rate of 50–100 mV s<sup>-1</sup> at room temperature in a dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Ag/AgCl reference electrode, platinum wire counter electrode, and ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) internal standard were used. The J-V-L characteristics and EL spectra of the phosphorescent OLEDs were obtained using a Keithley 2400 source measurement unit and CS 1000 spectrophotometer. All devices were fabricated by vacuum thermal evaporation and were encapsulated with a glass lid and CaO getter before device measurements. A Lambertian distribution of light emission was assumed in all EQE measurements.

#### 2.4. Device Fabrication of Green Phosphorescent OLEDs

In order to investigate the EL properties of Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub> as green

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emitters, phosphorescent OLEDs were fabricated. The structure of the phosphorescent OLEDs was ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (30 nm)/TCTA:TPBi:emitter (25 nm, x%)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al (200 nm). In the device, the ratio of TCTA to TPBi in the mixed host was 1:1 and the concentration of the emitter (x%) was either 3%, 5%, or 10%. The ITO substrate was cleaned by sonication in distilled water and isopropyl alcohol, followed by UV/O<sub>3</sub> treatment for 15 min. The PEDOT:PSS layer was spin-coated onto the cleaned ITO substrates. TAPC served as the hole injection (HIL) and transport layer (HTL) and was deposited on the PEDOT:PSS layer. The green emissive layer was prepared by co-evaporation of TCTA, TPBi, and x% of the green emistive layer was prepared by co-evaporation of TCTA, TPBi, and x% of the green emissive layer. Finally, lithium fluoride (LiF) was deposited as an EIL, and aluminium (Al) was deposited by vacuum evaporation on top of the film through a mask at less than 2.0 × 10<sup>-6</sup> Torr.

#### 3. Results and Discussion

#### 3.1. Synthesis and Thermal Properties

The two homoleptic green phosphorescent Ir(III) complexes,  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$ , were synthesized according to the procedure shown in Scheme 1. The trimethylsilyl-substituted cyclometalated ligands, ppyTMS and *m*PppyTMS were prepared by the Suzuki coupling reaction between either phenylboronic acid or (1,1'-biphenyl)-3-ylboronic acid and 2-bromo-5-(trimethylsilyl)pyridine. Next, ppyTMS and *m*PppyTMS were reacted with Ir(III) acetylacetonate [Ir(acac)<sub>3</sub>] in glycerol to afford Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> in 46 and 43% yields, respectively. The prepared complexes were purified by the train sublimation method under vacuum and then fully characterized using <sup>1</sup>H- and

<sup>13</sup>C-NMR, elemental analysis, and matrix-assisted laser desorption/ionization (MALDI-TOF) mass spectrometry (Figure S1). The purities of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> were 99.7 and 99.8%, respectively, as determined by high-performance liquid chromatography (HPLC) (Figure S2).

The thermal properties of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> were investigated using thermogravimetric analysis (TGA). The 5% weight loss temperature ( $T_d$ ) of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> were 373 and 410 °C, respectively (Figure S3). The  $T_d$  values of the trimethylsilyl- and phenyl-substituted homoleptic Ir(III) complexes demonstrated that they were thermally more stable than the Ir(ppy)<sub>3</sub> complex ( $T_d$ = 353 °C), which has no substituents on the 2-phenylpyridine ligands.

#### 3.2. X-ray Crystallography

The results of X-ray crystallographic structure determinations of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$  are shown in Figure 1. The single-crystal structures of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$  show identical *facial* geometrical configurations with distorted octahedral geometry around the iridium atom, typical for homoleptic Ir(III) complexes. The three Ir–C bond lengths in  $Ir(ppyTMS)_3$  (Ir(1)–C(11) 2.006 Å, Ir(1)–C(25) 2.023 Å, Ir(1)–C(39) 2.013 Å) and  $Ir(mPppyTMS)_3$  (Ir(1)–C(10) 2.014 Å, Ir(1)–C(30) 2.010 Å, Ir(1)–C(50) 2.011 Å) were similar to those of  $Ir(ppy)_3$  (Ir(1)–C(8A) 2.018 Å, Ir(1)–C(8B) 2.015 Å, Ir(1)–C(8C) 2.016 Å), whereas the three Ir–N bond lengths in  $Ir(ppyTMS)_3$  (Ir(1)–N(1) 2.116 Å, Ir(1)–N(2) 2.109 Å, Ir(1)–N(3) 2.120 Å) and  $Ir(mPppyTMS)_3$  (Ir(1)–N(1) 2.116 Å, Ir(1)–N(2B) 2.128 Å, Ir(1)–N(2C) 2.126 Å). In other words, the Ir–N bonds of the trimethylsilyl-substituted Ir(III) complexes were stronger than those of  $Ir(ppy)_3$ , (Ir(1)– $N(2P)_3$ ).

and indicated the LUMO stabilization in the  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  complexes [25]. The selected bond lengths (Å) of the single-crystal structures of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$  are summarized in Table 1.

The distances between the two nearest iridium atoms in the crystal-packing structures of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$  are 8.447, 9.651, and 11.626 Å, respectively. These values for  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  are relatively longer than that of  $Ir(ppy)_3$ . In particular, the  $Ir(mPppyTMS)_3$  complex with has an additional phenyl substituent on the 5-position of the phenyl ring, showed a significantly longer distance between the two nearest Ir atoms as compared to  $Ir(ppy)_3$  and  $Ir(ppyTMS)_3$ . This result indicates that  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  had relatively weaker bimolecular interactions between the neighbouring iridium complexes compared to  $Ir(ppy)_3$  because of the sterically bulky trimethylsilyl and phenyl spacers. Detailed crystallographic data (cif) of  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  can be found in the Supporting Information.

#### 3.3. Photophysical Properties

Figure 2 displays the absorption and emission spectra of the synthesized Ir(III) complexes, Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>, and the photophysical data for these materials are summarized in Table 2. Figure 2(a) shows the UV-visible absorption spectra of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> in dichloromethane solutions at 298 K with their absorption maxima at 286, 287, and 292 nm, respectively, which correspond to the spin-allowed <sup>1</sup>LC\* (<sup>1</sup> $\pi$ - $\pi$ \*) transitions of the cyclometalated ligands. In the region above 380 nm, the synthesized Ir(III) complexes showed broad absorption bands in the range of 380–397 nm that corresponded to the metal to ligand charge transfer <sup>1</sup>MLCT\* (<sup>1</sup>d- $\pi$ \*) and weak but detectable <sup>3</sup>MLCT\* (<sup>3</sup>d- $\pi$ \*) transitions in the range of 486–501 nm. The optical energy

bandgaps ( $E_{opt}$ ) of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> were obtained from the absorption edges as 2.56, 2.52, and 2.49 eV, respectively.

The maximum PL emission peaks  $(\lambda_{max})$  of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> in dichloromethane solution were observed at 516, 521, and 527 nm, respectively (Figure 2(b)). Substitution of the trimethylsilyl group on the 5-position of the pyridine ring in Ir(ppyTMS)<sub>3</sub> lead to a bathochromic shift of 5 nm in the emission maximum relative to the  $\lambda_{max}$  of Ir(ppy)<sub>3</sub>. In addition, the introduction of phenyl group on the 4-position of the phenyl ring in  $Ir(mPppyTMS)_3$  led to a bathochromic shift of 6 nm in the emission maximum compared to that of Ir(ppyTMS)<sub>3</sub>. Furthermore, the emission maxima of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(mPppyTMS)<sub>3</sub> in the neat film state, which were observed at 525, 530, and 535 nm, respectively, were bathochromically shifted compared to those observed in the solution state. This could be attributed to the aggregation effects between the Ir(III) complexes in the neat films prepared by drop casting. The maximum low-temperature PL emissions of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> in dilute dichloromethane solution at 77 K are observed at 513, 516, and 523 nm, respectively (Figure S4). At 77 K, the emission maxima ( $\lambda_{max}$ ) of  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  were hypsochromically shifted by 4 and 5 nm, respectively, compared to those of the samples analysed in solution at 298 K, likely owing to the rigidochromic effect [26,27]. The triplet state energies  $(T_1)$  of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and Ir(mPppyTMS)<sub>3</sub> were 2.42, 2.40, and 2.37 eV, respectively, as determined from the emission spectra at 77 K. The relative PL quantum yields ( $\Phi_{PL}$ ) of Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub> in dilute degassed dichloromethane solution  $(10^{-5} \text{ M})$  were compared to that of Ir(ppy)<sub>3</sub>, which was chosen as a standard ( $\Phi_{PL} = 0.40$ ) [28], and determined to be 0.42 and 0.45, respectively, showing slightly higher values than that of  $Ir(ppy)_3$ . The improved  $\Phi_{PL}$  of  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  could be attributed to the reduced free rotation of the compounds by the bulky trimethylsilyl and phenyl substituents.

#### 3.4. Theoretical Calculation

The HOMO and LUMO distributions of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> were determined by density functional theory (DFT) calculations using B3LYP/6-31G(d) basis sets [29]. As shown in Figure 3, the electron densities in the HOMO of Ir(ppy)<sub>3</sub> and Ir(ppyTMS)<sub>3</sub> were similarly distributed and primarily localized over the iridium metal and all phenyl rings of the ppy and ppyTMS ligands, while the HOMO of Ir(*m*PppyTMS)<sub>3</sub> was distributed over the iridium metal and the two phenyl rings of the ppy-backbone in the *m*PppyTMS ligands. For all Ir(III) complexes, the LUMOs were distributed over the pyridine rings and some phenyl rings of the ppy-backbone in ppy, ppyTMS, and *m*PppyTMS. The calculated HOMO/LUMO energy levels of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> were –4.90/–1.41, –4.87/–1.46, and –4.85/–1.57 eV, respectively. The presence of the trimethylsilyl group on the 5-position of the pyridine ring decreased its LUMO level and increased the HOMO level; consequently, the HOMO-LUMO energy band gap was reduced. The calculated HOMO energy level of Ir(*m*PppyTMS)<sub>3</sub>, which has an additional phenyl substituent on the 4-position of the phenyl ring in the *m*PppyTMS ligand compared to ppyTMS, was slightly higher than that of Ir(ppyTMS)<sub>3</sub>.

#### 3.5. Electrochemical Properties

The electrochemical behaviour of the synthesized Ir(III) complexes was studied using cyclic voltammetry (CV) in dichloromethane solution. Figure 4(a) displays the reversible oxidation waves in the cyclic voltammograms of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>. The measured HOMO energy levels of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub> were –5.35, –

5.34, and -5.32 eV (vs. Fc/Fc<sup>+</sup>), respectively (Table 2). The LUMO energy levels calculated from the differences between the HOMO energy level and the optical band gap ( $\Delta E_{\text{band gap}}$ =

 $E_{LUMO} - E_{HOMO}$ ) were found to be -2.79, -2.81, and -2.83 eV for Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>, respectively. The decreasing tendency of the HOMO and LUMO energy levels is consistent with those that were calculated theoretically by DFT calculation. These HOMO and LUMO energy levels are well-matched with the energy levels of the host materials of *tris*(4-carbazoyl-9-ylphenyl)amine (TCTA, HOMO: -6.0 eV, LUMO: -2.70 eV) and 2,2',2''-(1,3,5-benzinetriyl)-*tris*(1-phenyl-1*H*-benzimidazole) (TPBi, HOMO: -6.70 eV, LUMO: -2.70 eV) used for the device fabrication (Figure 4(b)).

#### 3.6. Electrophosphorescent OLEDs

Green phosphorescent OLEDs were fabricated using Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(mPppyTMS)<sub>3</sub> as green emitters with a device configuration of ITO (50 nm)/PEDOT:PSS (60 nm)/ TAPC (30 nm)/TCTA:TPBi:green emitter (25 nm, x%)/ TSPO1 (5 nm)/TPBi (30 nm)/LiF (1.5 nm)/Al (200 nm) [ITO= indium tin oxide; PEDOT:PSS= poly(3,4ethylenedioxythiophene) doped with poly(styrenesulfonic acid; TAPC= 4,4'cyclohexylidenebis(*N*,*N*-bis(4-methylphenyl)benzenamine); TSPO1= diphenyl-(4-(triphenylsilyl)phenyl)phosphine oxide]. TAPC served as both the hole-transport layer (HTL) and an electron-blocking layer (EBL). Both TSPO1 and TPBi acted as high triplet-energy hole-blocking layer (HBL) and electron-transporting layer (ETL). The TCTA:TPBi (1:1) mixture was used as a mixed-host system for efficient carrier injection and charge balance [30]. The electroluminescence (EL) performances of the fabricated green phosphorescent OLEDs were evaluated by the controlling the concentration of the Ir(ppyTMS)<sub>3</sub> and  $Ir(mPppyTMS)_3$  dopants in the range of 3–10%. The optimal doping concentration of the

fabricated devices was 5% of both  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$ . The EL performances of the devices fabricated using  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  as green emitters were significantly improved compared to that of the device with  $Ir(ppy)_3$  at 5% doping concentration. The detailed device characteristics using  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  in various doping concentrations are summarized in Table 3.

Figure 5 shows the EL spectra of the Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices with increasing doping concentrations. As the doping concentration increased from 3% to 10%, the maxima of the EL peaks of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices were red-shifted by 1–4 nm because of dopant aggregation and intermolecular interactions between the Ir(III) complexes. Additionally, the increasing of dopant concentration led to a gradual improvement in EL intensity of emission shoulder at ~570 nm for both Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices. It could be originated by the direct charge injection from the electrode to the dopant due to the increased doping concentration at the electrode interfaces [31]. The increase of the relative EL intensity around 570 nm caused the movement of Commission Internationale de L'Eclairage (CIE) coordinates of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices toward yellow region as shown in Table 3. The emission peak maxima of the Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices at the optimized doping concentration and 1000 cd m<sup>-2</sup> were (0.35,0.62) and (0.37,0.61), respectively.

The current density-voltage-luminance (J-V-L) curves for the Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices with 5% doping concentration are shown in Figure 6(a). The other *J*-*V*-*L* curves of Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices at 3% and 10% doping concentrations are shown in Figure S5. The turn-on voltages of the devices were 2.7 and 2.6

V for Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub>, respectively, at the optimized doping concentration. The Ir(*m*PppyTMS)<sub>3</sub> device showed a higher current density as compared to the Ir(ppy)<sub>3</sub> and Ir(ppyTMS)<sub>3</sub>-based devices, indicating better carrier hopping and charge balance of the Ir(*m*PppyTMS)<sub>3</sub> device [32]. The maximum luminances ( $L_{max}$ ) of the Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> devices were 42213 and 67809 cd m<sup>-2</sup> at 5% doping concentration, respectively, while the  $L_{max}$  of Ir(ppy)<sub>3</sub> device was 40637 cd m<sup>-2</sup> (Figure S7). The highest  $L_{max}$  of the Ir(*m*PppyTMS)<sub>3</sub> device could be attributed to its better recombination efficiency with high  $\Phi_{PL}$  as compared to the Ir(ppy)<sub>3</sub> and Ir(ppyTMS)<sub>3</sub>-based devices.

The EQE-L-PE curves of the  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  devices at optimized doping concentration are shown in Figure 6(b). The maximum external quantum efficiency (EQE<sub>max</sub>) of the Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub> devices were 16.6 and 18.1% at 5% doping concentration, respectively, which are higher than that of the  $Ir(ppy)_3$  device (EQE<sub>max</sub>= 16.3%) (Figure S7). It has been known that the thermally evaporated iridium complex guest would exist as an aggregated form rather than a discrete molecule in the host-guest thin film even at low doping concentration [14]. Therefore, the highest EQE<sub>max</sub> of  $Ir(mPppyTMS)_3$ among the synthesized Ir(III) complexes can be explained by the greatest distance between the neighbouring iridium centres, which leads to a small diffusion length of the triplet exciton by the bulky substituents on the ppy ligands, consequently suppressing the triplet-triplet annihilation in the OLEDs [33]. Furthermore, the high current density of the Ir(mPppyTMS)<sub>3</sub> device at low voltage seemingly affected the efficient charge balance in the emitting layer, leading to high EQE. At a luminance of 1000 cd m<sup>-2</sup>, the EQEs were 14.8% for Ir(ppy)<sub>3</sub>, 15.3% for Ir(ppyTMS)<sub>3</sub>, and 15.8% for Ir(mPppyTMS)<sub>3</sub>. The devices with the trimethylsilyl- and phenyl-substituted homoleptic Ir(III) complexes also showed low efficiency roll-off with increasing luminance as compared to the  $Ir(ppy)_3$  device. The maximum power efficiency  $(PE_{max})$  of the Ir(ppyTMS)<sub>3</sub> and Ir(mPppyTMS)<sub>3</sub> devices at 5% doping concentration were

66.1 and 70.3 lm W<sup>-1</sup>, respectively, while the  $PE_{max}$  of  $Ir(ppy)_3$  was 57.5 lm W<sup>-1</sup>. The  $Ir(mPppyTMS)_3$  device showed a higher  $PE_{max}$  than the  $Ir(ppyTMS)_3$  and  $Ir(ppy)_3$  devices, which is one of the highest PE values reported to date among homoleptic Ir(III) complexes for green phosphorescent OLEDs [34-39]. The driving voltage of the devices were 3.9, 3.8, and 3.6 V for  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$ , respectively. The low driving voltage and high EQE of the  $Ir(mPppyTMS)_3$  device improved the PE value [40].

#### 4. Conclusions

In conclusion, we successfully developed trimethylsilyl- and phenyl-substituted homoleptic Ir(III) complexes, Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub>, for use in highly efficient green phosphorescent OLEDs. The introduction of the bulky substituents, trimethylsilyl and phenyl, on the 2-phenylpyridine (ppy) ligand in these complexes led to a long distance between the neighbouring molecules, suppressing triplet-triplet annihilation in the green phosphorescent OLEDs. Ir(*m*PppyTMS)<sub>3</sub>, which had both trimethylsilyl at the 5-position of pyridine ring and phenyl at the 4-position of the phenyl ring in the ppy ligand, showed the best device performances with the highest EQE,  $L_{max}$ , and PE<sub>max</sub>. The high current density of Ir(*m*PppyTMS)<sub>3</sub> device at low voltage indicated better carrier hopping and charge balance, which led to an efficient recombination of excitons in the emitting layer and consequently, a high external quantum efficiency. The Ir(*m*PppyTMS)<sub>3</sub> complex achieved the highest PE<sub>max</sub> in the green phosphorescent OLED among the synthesized Ir(III) complexes owing to the comprehensive effects of the low efficiency roll-off, high EQE, and low driving voltage.

#### Acknowledgements

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# **Table captions**

Table 1. Selected bond lengths (Å) of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>.

 Table 2. Summary of photophysical and electrochemical properties for trimethylsilyl 

 substituted homoleptic iridium(III) complexes.

Table 3. Summary of performances of green phosphorescent OLEDs.

Ir(ppy) <sub>3</sub>		Ir(ppyT	TMS) <sub>3</sub>	Ir( <i>m</i> PppyTMS) <sub>3</sub>		
Ir(1)-C(8A)	2.018 Å	Ir(1)-C(11)	2.006 Å	Ir(1)-C(10)	2.014 Å	
Ir(1)-C(8B)	2.015 Å	Ir(1)-C(25)	2.023 Å	Ir(1)-C(30)	2.010 Å	
Ir(1)-C(8C)	2.016 Å	Ir(1)-C(39)	2.013 Å	Ir(1)-C(50)	2.011 Å	
Ir(1)-N(2A)	2.137 Å	Ir(1)-N(1)	2.116 Å	Ir(1)-N(1)	2.116 Å	
Ir(1)-N(2B)	2.128 Å	Ir(1)-N(2)	2.109 Å	Ir(1)-N(2)	2.119 Å	
Ir(1)-N(2C)	2.126 Å	Ir(1)-N(3)	2.140 Å	Ir(1)-N(3)	2.122 Å	

Table 1.

	Photophysical						Electrochemical	
Dopant	$\lambda_{abs}$	$\lambda_{em}{}^{a/b}$	Ф <sup>с</sup>	$E_{\rm opt}^{\rm d}$	$T_1$	НОМО	LUMO	
	(nm)	(nm)	$arphi_{ ext{PL}}$	(eV)	(eV)	(eV)	(eV)	
Ir(ppy) <sub>3</sub>	286, 380, 454, 486	516/520	0.40	2.56	2.42	-5.35	-2.79	
Ir(ppyTMS) <sub>3</sub>	287, 390, 460, 492	521/530	0.42	2.52	2.40	-5.34	-2.81	
Ir( <i>m</i> PppyTMS) <sub>3</sub>	292, 397, 467, 501	527/535	0.45	2.49	2.37	-5.32	-2.83	

<sup>a</sup>Maximum PL emission wavelength, measured in dichloromethane solution.

<sup>b</sup>Maximum PL emission wavelength, measured in neat film state.

<sup>c</sup>Measured in degassed dichloromethane solution (10<sup>-5</sup> M) relative to Ir(ppy)<sub>3</sub> ( $\Phi_{PL} = 0.40$ )

<sup>d</sup>Calculated from the absorption edge,  $E_{\rm g} = 1240/\lambda_{\rm abs}$ , onset.

		$\lambda_{max}$	CIE <sup>a</sup>	$V_{\rm t}$	$L_{\max}$	EQE <sup>b</sup>	$\rm PE^{b}$	$LE^{b}$
Device	x%	(nm)	(x,y)	(V)	(cd m <sup>-2</sup> )	(%)	(lm W <sup>-1</sup> )	$(cd A^{-1})$
	3	523	(0.34,0.62)	2.7	38330	16.4/15.0	62.9/46.3	60.1/55.0
Ir (ppyTMS) <sub>3</sub>	5	525	(0.35,0.62)	2.7	42210	16.6/15.3	66.1/47.6	60.9/55.9
(PP)	10	526	(0.36,0.61)	2.7	43740	15.6/14.0	54.7/45.3	58.1/51.1
							AY	
	3	528	(0.36,0.61)	2.6	60680	17.9/15.6	69.8/47.7	66.7/58.3
Ir ( <i>m</i> PppyTMS) <sub>3</sub>	5	529	(0.37,0.61)	2.6	67810	18.1/15.8	70.3/46.7	67.2/58.7
	10	532	(0.38,0.60)	2.6	71060	16.4/14.8	60.6/47.3	63.5/54.8
Ir(ppy) <sub>3</sub>	5	512	(0.32,0.61)	3.0	40640	16.3/14.8	57.5/40.8	54.9/50.3

Table 3.

<sup>a</sup> Value measured at a luminance of 1000 cd m<sup>-2</sup>.

<sup>b</sup> Values measured at maximum efficiency and luminance of 1000 cd m<sup>-2</sup>.

#### **Figure captions**

Figure 1. (a) Single-crystal and (b) crystal packing structures of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS).

Figure 2. (a) UV-visible absorption (in  $CH_2Cl_2$ , inset; expanded spectra from 450 to 550 nm) and (b) PL spectra (left; in  $CH_2Cl_2$ , right; in film) of  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$  at 298 K.

Figure 3. Frontier molecular orbitals HOMO and LUMO of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>.

Figure 4. (a) Cyclic voltammograms and (b) energy diagrams of Ir(ppy)<sub>3</sub>, Ir(ppyTMS)<sub>3</sub>, and Ir(*m*PppyTMS)<sub>3</sub>.

Figure 5. EL spectra of green phosphorescent OLEDs with Ir(ppyTMS)<sub>3</sub> and Ir(*m*PppyTMS)<sub>3</sub> at 5% doping concentration.

Figure 6. (a) Current density-voltage-luminance (*J-V-L*) and (b) external quantum efficiency-*L*-power efficiency (EQE-*L*-PE) curves of the  $Ir(ppy)_3$ ,  $Ir(ppyTMS)_3$ , and  $Ir(mPppyTMS)_3$ devices at 5% doping concentration. Figure 1.



(b)

Ir(III) complex	Crystal-Packing diagram	Ir-Ir distance
Ir(ppy) <sub>3</sub>		8.447 Å
Ir(ppyTMS) <sub>3</sub>		9.651 Å
Ir(mPppyTMS) <sub>3</sub>		11.626 Å





Figure 3.

Complex	Ir(ppy) <sub>3</sub>	Ir(ppyTMS) <sub>3</sub>	Ir(mPppyTMS) <sub>3</sub>
	$\mathbf{E} = -1.41 \text{ eV}$	$\mathbf{E} = -1.46 \text{ eV}$	E = -1.57  eV
LUMO			
номо			
	$\overline{\mathbf{E}} = -4.90 \text{ eV}$	$\mathbf{E} = -4.87 \text{ eV}$	$\mathbf{E} = -4.85 \text{ eV}$

Figure 4.







Figure 6.



## Table of Content (TOC)



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# Highlights

• New green phosphorescent Ir(III) complexes,  $Ir(ppyTMS)_3$  and  $Ir(mPppyTMS)_3$  were synthesized.

• The bulky ppyTMS or *m*PppyTMS ligand effectively suppresses concentration selfquenching.

• Ir(*m*PppyTMS)<sub>3</sub> exhibited high maximum power efficiency of 70.3 lm/W in green OLED.

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