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Orange Phosphorescent OLEDs



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2	2-Phenylbenzothiazole for Solution-Processed Organic
3	Light-Emitting Diodes
4	
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24	

25 Abstract

Orange phosphorescent iridium(III) complexes, (DMBT)₂Ir(acac) and (TBT)₂Ir(acac), 26 either 2-(3,4-dimethylphenyl)benzo[*d*]thiazole 27 based on (DMBT) or 28 2-(4-(trimethylsilyl)phenyl)benzo[d]thiazole (TBT) as the cyclometalated main ligands and acetylacetone (acac) as an ancillary ligand, were synthesized for 29 30 solution-processed organic light-emitting diodes (OLEDs). The Ir(III) complex, $(BT)_2$ Ir(acac), which consists of 2-phenylbenzo[d]thiazole (BT) as the main ligand 31 and acac as the ancillary ligand, was also synthesized as a reference. The 32 photophysical, electrochemical, and electroluminescent (EL) properties of these Ir(III) 33 complexes were investigated. The OLED fabricated using (TBT)₂Ir(acac) exhibited 34 35 significantly improved luminance and external quantum efficiency (EQE) as self-quenching at high doping concentrations was successfully prevented by 36 37 introducing bulky trimethylsilyl groups. The EL spectrum of (TBT)₂Ir(acac) exhibited an emission maximum at 578 nm with a full-width-at-half-maximum of 74 nm and 38 Commission Internationale de L'Eclairage coordinates of (0.55, 0.44) at 1000 cd/m². 39 The device with 7 wt% (TBT)₂Ir(acac) dopant exhibited a maximum luminance of 40 6.837 cd/m^2 , maximum luminous efficiency of 25.26 cd/A, power efficiency of 12.37 41 42 lm/W, and EQE of 9.94%.

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47 Keywords: benzothiazole; iridium(III) complex; organic light-emitting diodes;
48 phosphorescence; bulky substituents

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50 **1. Introduction**

In recent years, phosphorescent organic light-emitting diodes (OLEDs) have attracted considerable attention in academia and industry because of their potential applications as color emitters in solid-state lighting and full-color flat panel displays. Phosphorescent OLEDs exhibit many outstanding properties such as low operating voltages for low power consumption, high brightness, high contrast, and the possibility to produce thin, large-area, and flexible devices [1,2].

The use of phosphorescent emitting materials such as Ir(III) [3–7], Pt(II) [8,9], Ru(II) 57 [10-12], and Os(II) [13,14] complexes in OLEDs has significantly improved their 58 performances because both singlet and triplet excitons can be harvested for light 59 60 emission. This is a result of the strong spin-orbit coupling caused by the presence of 61 heavy metals. Thus, high external quantum efficiencies (EQEs) can be achieved using efficient phosphorescent materials [15–18]. Several research groups have focused on 62 the development of phosphorescent Ir(III) complexes because of their thermal 63 64 stability, high phosphorescence quantum efficiency, short triplet lifetime, and facile control of the emission spectrum [3–7, 19]. 65

Among the iridium complexes, (BT)₂Ir(acac) has been often used as an orange emitter 66 of OLEDs, however, it suffers from problems such as poor thermal stability, low 67 photoluminescence (PL) quantum efficiency (Φ_{PL}), and significant concentration 68 69 self-quenching at high doping concentrations [20–22]. Structural modifications of 70 cyclometalated ligands in Ir(III) complexes have been carried out to address these issues. For instance, the introduction of bulky substituents such as pinene, 71 72 trimethylsilyl (TMS), or phenyl on 2-phenylpyridine (ppy) ligands not only prevented self-quenching at high doping concentrations but also improved the thermal stability 73 of the devices, thus leading to enhanced device performances [24,25]. The bulky 74

substituents in the Ir(III) complex suppressed bimolecular interactions and thuseffectively reduced self-quenching at high doping concentrations.

In this study, we designed new orange phosphorescent iridium(III) complexes, 77 78 $(DMBT)_2Ir(acac)$ and (TBT)₂Ir(acac), based on 2-(3,4-dimethylphenyl)benzo[*d*]thiazole 79 (DMBT) and 2-(4-(trimethylsilyl)phenyl)benzo[d]thiazole (TBT) as cyclometalated main ligands 80 and acetylacetone (acac) as the ancillary ligand. Both (DMBT)₂Ir(acac) and 81 (TBT)₂Ir(acac) exhibited improved electroluminescence (EL) performances in 82 83 phosphorescent OLEDs as self-quenching at high doing concentrations was avoided by the introduction of the bulky dimethyl or TMS groups. Moreover, the dimethyl and 84 85 TMS groups on the cyclometalated ligands of (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) 86 imparted thermal stability and improved solubility in common organic solvents compared to (BT)₂Ir(acac). The detailed synthetic routes and chemical structures of 87 the heteroleptic iridium(III) complexes are outlined in Scheme 1. 88

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90



93 **2. Materials and methods**

94 2.1. Materials

95 Iridium chloride trihydrate (IrCl₃· $3H_2O$), benzaldehyde, 3,4-dimethylbenzaldehyde, 96 4-fluorobenzaldehyde, 2-aminobenzenethiol, *tert*-butyllithium, sodium carbonate, and 97 chlorotrimethylsilane were purchased from Sigma-Aldrich and Alfa Aesar. All 98 chemicals were used without further purification.

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92

- 100 2.2. Synthesis of ligand and phosphorescent iridium complex
- 101 2.2.1. 2-Phenylbenzo[d]thiazole (1)

102 Benzaldehyde (3.00 g, 28.3 mmol) and 2-aminobenzenethiol (3.54 g, 28.3 mmol) 103 were dissolved in DMSO (60 mL) and heated at 120 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane/brine. 104 The combined organic extracts were dried over MgSO₄, filtered, and concentrated in 105 106 vacuo. The resulting solid was recrystallized in methanol to obtain compound 1 as a pale violet solid (4.20 g, 70.4%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.08 (m, 3H), 107 7.89 (d, 1H, J = 7.5 Hz), 7.48 (m, 4H), 7.36 (dd, 1H, J = 8.4, 7.5 Hz); ¹³C NMR (75) 108 MHz, CDCl₃) δ (ppm): 168.1, 154.2, 135.0, 133.4, 131.1, 128.8, 127.5, 126.1, 125.1, 109 123.2, 121.7; MALDI-TOF (M⁺, C₁₃H₉NS): calcd. 211.05, found 211.05. 110

- 111
- 112 2.2.2. 2-(3,4-Dimethylphenyl)benzo[d]thiazole (2)

- same procedure as that for the synthesis of **1**. ¹H NMR (300 MHz, CDCl₃) δ (ppm):
- 115 8.11 (m, 2H), 7.91 (d, 1H, J = 7.5 Hz), 7.50 (m, 4H), 2.08 (s, 3H), 2.01 (s, 3H); ¹³C
- 116 NMR (75 MHz, CDCl₃) δ (ppm): 168.2, 154.0, 138.9, 135.3, 133.5, 131.8, 128.8,

¹¹³ Compound 2 (4.20 g, 78.5%) was prepared from 3,4-dimethylbenzaldehyde using the

117 128.0, 126.3, 125.0, 124.5, 123.0, 121.7, 21.5, 21.3; MALDI-TOF (M^+ , $C_{15}H_{13}NS$):

- 118 calcd. 239.08, found 239.10.
- 119

120 2.2.3. 2-(4-Fluorophenyl)benzo[d]thiazole (3)

- 121 Compound **3** (3.60 g, 64.9%) was prepared from 4-fluorobenzaldehyde using the
- same procedure as that for the synthesis of compound **1**. ¹H NMR (300 MHz, CDCl₃)

123 δ (ppm): 8.07 (d, 1H, J = 8.4 Hz), 7.96 (d, 2H, J = 8.7 Hz), 7.91 (d, 1H, J = 7.5 Hz),

- 124 7.63 (d, 2H, J = 8.7 Hz), 7.51 (dd, 1H, J = 8.4, 7.5 Hz), 7.40 (dd, 1H, J = 8.4, 7.5 Hz);
- ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 166.5, 164.4, 154.0, 136.0, 130.0, 129.6, 126.4,
- 126 125.2, 123.2, 121.7, 116.1; MALDI-TOF (M⁺, C₁₃H₈FNS): calcd. 229.04, found 229.
- 127 03.
- 128
- 129 2.2.4. 2-(4-(Trimethylsilyl)phenyl)benzo[d]thiazole (4)

2-(4-Fluorophenyl)benzo[d]thiazole (3) (3.5 g, 15.3 mmol) was dissolved in 130 tetrahydrofuran and stirred at -70 °C. Addition of *t*-BuLi (10.6 mL, 23.0 mmol, 1.7 M 131 in pentane) over 30 min resulted in a red solution. After stirring for 1 h at this 132 temperature, chlorotrimethylsilane (2.3 mL, 18.1 mmol) was added into the reaction 133 mixture and the solution was stirred for an additional hour. The mixture was then 134 allowed to warm to room temperature and stirred for 4 h. Subsequently, the mixture 135 was extracted with ethyl acetate/brine and the combined organic extracts were dried 136 137 over MgSO₄. After filtration, the solvent was removed under reduced pressure and the resulting liquid was purified by column chromatography on silica gel (ethyl 138 acetate/hexane = 1/7) to obtain compound 4 as a pale yellow liquid (2.73 g, 63%). ¹H 139 NMR (300 MHz, CDCl₃) δ (ppm): 8.10 (m, 3H), 7.90 (d, 1H, J = 8.4 Hz), 7.67 (d, 140 2H, J = 7.5 Hz), 7.50 (dd, 1H, J = 8.4, 7.5 Hz), 7.40 (dd, 1H, J = 8.4, 7.5 Hz), 0.34 (s, 141

142	9H); ¹³ C NMR (75 MHz, CDCl ₃) δ (ppm): 168.0, 154.6, 154.2, 135.2, 131.0, 127.4,
143	126.2, 125.7, 125.1, 123.3, 121.4, 5.82; MALDI-TOF (M ⁺ , C ₁₆ H ₁₇ NSSi): calcd.
144	283.09, found 283.07.

145

146 2.2.5. Synthesis of $Ir(III) \mu$ -chloro-bridged dimer complexes (5–7)

Typical procedure: A mixture of iridium(III) chloride trihydrate (0.50 g, 1.7 mmol) 147 and 2-phenylbenzo[d]thiazole (1) (0.85 g, 4.0 mmol) in 2-ethoxyethanol/water (40 148 mL, 3/1, v/v) was refluxed under nitrogen for 18 h at 120 °C. After cooling to room 149 150 temperature, the precipitate was collected and washed several times with water and petroleum ether to afford a red powder. The solid was dried in vacuo to obtain the 151 iridium(III) μ -chloro-bridged dimer 5 in 77% yield. The other dimers, complexes 6 152 153 (64%) and 7 (59%), were prepared from the corresponding 2-phenylbenzothiazole derivatives 2 and 4, respectively, by following the same procedure. The crude Ir(III) 154 μ -chloro-bridged dimers were used directly in the next step without further 155 156 purification.

157

158 2.2.6. Synthesis of Ir(III) complexes

Typical procedure: A mixture of iridium(III) μ -chloro-bridged dimer 5 (0.5 g, 0.39 159 mmol), 2,4-pentadione (0.15 g, 1.5 mmol), and sodium carbonate (0.38 g, 3.6 mmol) 160 was heated at 135 °C in 2-ethoxyethanol for 24 h under nitrogen atmosphere. After 161 cooling to room temperature, the solvent was removed under reduced pressure. The 162 mixture was then extracted with dichloromethane. The organic extract was dried over 163 164 anhydrous MgSO₄ and the filtrate was evaporated in vacuo. The resulting solid was purified by column chromatography on silica gel using ethyl acetate/hexane (1/5, v/v)165 as the eluent. The resulting solid was recrystallized from dichloromethane/ hexane to 166

167	obtain $(BT)_2Ir(acac)$ as a red solid $(0.35 \text{ g}, 64\%)$. $(DMBT)_2Ir(acac)$ and
168	$(TBT)_2$ Ir(acac) were prepared from the corresponding Ir(III) μ -chloro-bridged dimers
169	6 and 7, respectively, by following the same procedure.

- 170
- 171 (**BT**)₂**Ir**(**acac**) (64%): ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.08 (m, 2H), 7.90 (m,
- 172 2H), 7.64 (d, 2H, J = 7.5 Hz), 7.43 (m, 4H), 6.85 (dd, 2H, J = 7.5, 7.4 Hz), 6.63 (dd,

173 2H, J = 7.8, 7.4 Hz), 6.40 (d, 2H, J = 7.8 Hz), 5.12 (s, 1H), 1.75 (s, 6H); ¹³C NMR (75)

174 MHz, CDCl₃) δ (ppm): 185.5, 180.2, 150.9, 147.6, 142.5, 142.3, 140.2, 131.5, 127.1,

175 125.8, 125.1, 124.4, 122.2, 120.5, 101.6, 28.4; MALDI-TOF (M^+ , $C_{31}H_{23}IrN_2S_2O_2$):

176 calcd. 712.08, found 712.00 (HPLC purity: 99.8%).

(DMBT)₂Ir(acac) (64%): ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.05 (m, 2H), 7.86
(m, 2H), 7.35 (m, 6H), 6.16 (s, 2H), 5.09 (s, 1H), 2.08 (s, 6H), 1.91 (s, 6H), 1.73 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): 185.5, 181.0, 151.0, 144.9, 143.2, 139.7, 136.1, 131.1, 129.5, 127.1, 126.7, 124.6, 122.1, 119.9, 101.6, 28.5, 20.4, 19.5; MALDI-TOF
(M⁺, C₃₅H₃₁IrN₂O₂S₂): calcd. 768.15, found 768.10 (HPLC purity: 99.8%).

182 (**TBT**)₂**Ir**(**acac**) (58%): ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.15 (m, 2H), 7.92 (m,

183 2H), 7.58 (d, 2H, J = 7.5 Hz), 7.42 (m, 4H), 6.97 (d, 2H, J = 7.2 Hz), 5.51 (s, 2H),

184 5.18 (s, 1H), 1.79 (s, 6H), 0.35 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): 185.5, 180.2,

- 185 150.9, 147.6, 142.5, 142.3, 140.2, 131.5, 127.1, 125.8, 125.1, 124.4, 122.2, 120.1,
 186 101.6, 30.2, 28.5; MALDI-TOF (M⁺, C₃₇H₃₉IrN₂O₂S₂Si₂): calcd. 856.16, found
- 186 101.6, 30.2, 28.5; MALDI-TOF (M^+ , $C_{37}H_{39}IrN_2O_2S_2Si_2$): calcd. 856.16, fo 187 856.16 (HPLC purity: 99.7%).
- 188

189 2.3. Fabrication of OLED devices

190 The device structure of the fabricated OLEDs was indium tin oxide (ITO; 50

191 nm)/PEDOT:PSS (40 nm)/TCTA (20 nm)/TCTA:TPBi:orange dopant (50:50:*x*%) (40

192	nm)/TPBi (40 nm)/LiF (1 nm)/Al (120 nm). In these devices, the dopants were
193	$(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$; the doping ratio of
194	tris(4-carbazoyl-9-ylphenyl)amine (TCTA) to
195	2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi) was 1:1, and the
196	concentrations of the dopants (x %) were 3, 5, 7, and 11%. The ITO substrate was
197	cleaned by sonication in acetone and isopropyl alcohol followed by ultraviolet/ozone
198	treatment for 10 min. After treatment with oxygen plasma,
199	poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid)
200	(PEDOT:PSS, AI4083) was spin-coated onto the cleaned ITO substrates. TCTA,
201	which served as the hole-transport layer (HTL), was deposited onto the PEDOT:PSS
202	layer. The emissive layer consisting of TCTA, TPBi, and the Ir(III) complex in the
203	composition ratio of TCTA:TPBi: $Ir(III) = 50:50:x$ was spin-coated onto TCTA layer
204	and then annealed at 120 °C for 30 min to remove the residual solvent. TPBi, which
205	acted as a high triplet-energy exciton blocking layer (HBL) with electron transport
206	properties, was then deposited on the emissive layer. Finally, a layer of lithium
207	fluoride (LiF) as the electron injecting layer (EIL) and that of aluminum (Al) as the
208	cathode were sequentially deposited by thermal evaporation on top of the film through
209	a mask under high vacuum (below 2.0×10^{-6} Torr, 0.27 mPa).

210

211 2.4. Measurements

¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 MHz (75 MHz)
spectrometer in CDCl₃. Thermogravimetric analysis (TGA) was performed using an
SDT Q600 V20.9 Build 20 instrument under nitrogen atmosphere at a heating rate of
10 °C min⁻¹. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF)
mass spectra were obtained using a ZMS-DX303 mass spectrometer (JEOL Ltd.).

217 High-performance liquid chromatographic analysis (HPLC) was performed on a 218 Shimadzu Prominence instrument. UV-Visible absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer, whereas photoluminescence (PL) spectra 219 were recorded on a Shimadzu RF 5301 PC fluorometer. Cyclic voltammetry (CV) 220 measurements were carried out with a CHI600D system at potential scan rate of 221 50–100 mV·s⁻¹ in a dichloromethane (CH₂Cl₂) solution containing 0.1 M 222 tetrabutylammonium perchlorate as the supporting electrolyte at room temperature 223 (Ag/AgNO₃ as reference electrode, Pt wire as counter electrode, Pt disc as working 224 electrode (2 mm diameter), and Cp₂Fe/Cp₂Fe⁺ redox couple as a secondary internal 225 reference). The current density-voltage-luminance (I-V-L) characteristics were 226 measured and electroluminescence (EL) spectra of the phosphorescent OLEDs were 227 recorded using a Keithley 2400 source measurement unit and CS-1000 228 spectrophotometer. All devices were fabricated by solution processing and 229 encapsulated with a glass lid and CaO getter before device measurements. A Keithley 230 2400 source measurement unit and CS-1000 spectroradiometer were used to evaluate 231 the device performances. 232

233

234 **3. Results and discussion**

235 3.1. Synthesis and characterization

heteroleptic Ir(III) 236 The complexes, $(BT)_2$ Ir(acac), $(DMBT)_2$ Ir(acac), and (TBT)₂Ir(acac), were synthesized according to the procedure shown in Scheme 1. The 237 cyclometalated main ligands, BT, DMBT, and TBT were synthesized via a 238 cycloaddition reaction between benzaldehyde derivatives and 2-aminobenzenethiol 239 [20–22]. The Ir(III) μ -chloro-bridged dimers were formed by the reaction of the 240 cyclometalating ligands, BT, DMBT, and TBT, with IrCl₃·3H₂O in a mixture of 241

242 2-ethoxyethanol and water [26]. The Ir(III) μ -chloro-bridged dimers were then reacted with acac as an ancillary ligand in 2-ethoxyethanol to afford the heteroleptic Ir(III) 243 complexes. These complexes were characterized by ¹H- and ¹³C-NMR, and 244 245 MALDI-TOF mass spectroscopy measurements (Figure S1 and S2). The materials were purified by vacuum sublimation before device fabrication. The purity after 246 sublimation was confirmed to be >99.5% based on HPLC (Figure S3). The thermal 247 properties of (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) were investigated 248 by TGA under a nitrogen atmosphere. The 5% weight-loss temperatures (T_d) of 249 (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) were 327, 361, and 338 °C, 250 respectively (Figure S4), indicating that they would be thermally stable under the 251 252 OLED fabrication conditions. The T_d values showed that the Ir(III) complexes with 253 either DMBT or TBT as the cyclometalated ligands were thermally more stable than the corresponding Ir(III) complex containing BT as the main ligand. 254

255

256 *3.2. X-ray Crystallography*

The crystal structure of (DMBT)₂Ir(acac) was investigated using single-crystal X-ray 257 crystallography. The crystallographic refinement parameters, selected bond distances 258 as well as bond angles are summarized in Tables S1–S6 and the crystal structure is 259 shown in Figure S11. The crystallographic data for (DMBT)₂Ir(acac) has been 260 deposited in the Cambridge Structural Database (CCDC 1824937). The iridium atom 261 adopts a distorted octahedral coordination geometry with two C^N cyclometalated 262 ligands and one O^AO ligand. The geometrical configuration of (DMBT)₂Ir(acac) was 263 264 N,N-trans, which is the same configuration as that of $(BT)_2$ Ir(acac) standard material [22]. Although the single crystal sample of (TBT)₂Ir(acac) has not been obtained, a 265 similar conformation can be assumed in view of its structural similarity to 266

267 $(DMBT)_2Ir(acac)$. Detailed crystallographic data (cif) of $(DMBT)_2Ir(acac)$ can be 268 found in the Supporting Information.

269

270 3.3. Photophysical properties

The photophysical properties of the Ir(III) complexes were investigated by conducting 271 UV-Vis absorption and PL spectroscopic measurements of their 272 dilute dichloromethane solutions (10^{-5} M) and thin films at room temperature. The UV-Vis 273 absorption spectra of the Ir(III) complex solutions were almost the same as those of 274 the corresponding films (Figure S5). All the Ir(III) complexes showed a strong 275 276 absorption band below 350 nm and a weak broad absorption band in the longer wavelength region above 380 nm. The absorption band in the shorter wavelength 277 region corresponds to spin-allowed ligand-centered transitions $({}^{1}\pi-\pi^{*})$ of main ligands 278 (Figure 1(a)), and the weak and broad absorption bands in the range of 380–550 nm to 279 metal-to-ligand charge transfer (¹MLCT and ³MLCT) and spin-orbit coupling 280 enhanced ${}^{3}\pi$ - π ^{*}; these assignments were made by comparison with those of 281 previously reported Ir(III) complexes [20–23]. The optical properties of the Ir(III) 282 complexes are summarized in Table 1. Complexes (DMBT)₂Ir(acac) and 283 (TBT)₂Ir(acac) exhibited red-shifted absorption in comparison to that of (BT)₂Ir(acac) 284 because of the substitution of electron-donating dimethyl or trimethylsilyl groups on 285 the phenyl ring of the main ligand. The optical band gap energies (E_{σ}^{opt}) of 286 (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) were determined to be 2.25, 287 2.21, and 2.19 eV, respectively, according to the onset of the absorption edge. 288

The PL maxima of $(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$ were observed at 563, 569, and 576 nm, respectively. These measurements were conducted with dilute dichloromethane solutions of the complexes at room temperature (Figure

292 1(b)). (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) exhibited 7–12 nm red-shifted emission compared to that of (BT)₂Ir(acac) with the same effect as observed in the absorption 293 spectra. The PL quantum yields (Φ_{PL}) of $(DMBT)_2Ir(acac)$ and $(TBT)_2Ir(acac)$ 294 measured using their 10^{-5} M degassed dichloromethane solution and (BT)₂Ir(acac) as 295 a reference ($\Phi_{PI} = 0.26$) were determined to be 0.38 and 0.49, respectively [20–22]. 296 The higher Φ_{PL} values of $(DMBT)_2Ir(acac)$ and $(TBT)_2Ir(acac)$ than that of 297 (BT)₂Ir(acac) were attributed to the reduced free rotation of the compounds because 298 299 of the bulky dimethyl or trimethylsilyl substituents.

300

301 3.4. Theoretical calculations

302 We performed theoretical calculations based on density functional theory (DFT), using the B3LYP/6-31G(d) hybrid exchange-correlation functional and LANL2DZ 303 basis sets, for a better understanding of the effects of DMBT and TBT cyclometalated 304 ligands in iridium(III) complexes. The calculations were conducted using the 305 Gaussian 09 package [27]. Figure 2 shows the electron densities and calculated 306 energy levels of the highest occupied molecular orbitals (HOMOs) and lowest 307 unoccupied molecular orbitals (LUMOs) of (BT)₂Ir(acac), (DMBT)₂Ir(acac), and 308 309 (TBT)₂Ir(acac). The HOMOs of (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) were similarly localized on the phenyl ring of the main ligand and the *d* orbital of the 310 Ir metal. Thus, electron donating substituents on the phenyl ring of the main ligand 311 could be expected to raise the HOMO energy level. The LUMOs in all synthesized 312 Ir(III) complexes were largely localized over the benzothiazole and phenyl rings. 313

The calculated HOMO/LUMO energy levels of (BT)₂Ir(acac), (DMBT)₂Ir(acac), and

315 (TBT)₂Ir(acac) were -5.15/-1.88, -4.94/-1.72 eV, and -5.25/-2.04 eV, respectively.

316 The calculated HOMO energy level of (DMBT)₂Ir(acac) was higher than that of

317 (BT)₂Ir(acac) because of the electron donating dimethyl groups on the phenyl ring. 318 The increased HOMO and decreased LUMO energy levels of the synthesized Ir(III) 319 complexes using DMBT and TBT led to a narrower band gap, and therefore, 320 (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) could be expected to exhibit red-shifted 321 emission compared to that of (BT)₂Ir(acac).

322

323 3.5. Electrochemical properties

The electrochemical properties of the synthesized Ir(III) complexes were investigated 324 325 using CV. The measurements were conducted using their dichloromethane solutions with tetrabutylammonium perchlorate as the electrolyte and the results are shown in 326 Figure 3. Complexes (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) showed 327 328 reversible electron oxidations at positive potentials in the region of 0.50–0.65 V. The onset potentials of the first oxidations (E^{oxi}onset) of (BT)₂Ir(acac), (DMBT)₂Ir(acac), 329 and (TBT)₂Ir(acac) were 0.65, 0.54, and 0.60 V vs. Ag/Ag⁺, respectively. The E^{oxi}_{onset} 330 values of (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) are clearly lower than that of the 331 parent complex (BT)₂Ir(acac). The HOMO energy levels of (BT)₂Ir(acac), 332 (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) were estimated to be -5.35, -5.24, and -5.30 333 eV vs. Fc/Fc^+ , respectively. The LUMO energy levels of $(BT)_2Ir(acac)$, 334 (DMBT)₂Ir(acac), and (TBT)₂Ir(acac), obtained from the differences between the 335 optical band gaps and the HOMO energy levels ($\Delta E_{band gap} = E_{LUMO} - E_{HOMO}$), were 336 found to be -3.10, -3.03, and -3.11 eV, respectively. The HOMO and LUMO energy 337 levels of the synthesized Ir(III) complexes were well matched with those of TCTA 338 (HOMO: -5.8 eV, LUMO: -2.50 eV) and TPBi (HOMO: -6.30 eV, LUMO: -2.70 339 eV) as host materials. The electrochemical properties of the Ir(III) complexes are 340 summarized in Table 1. 341

342

343 3.6. Electrophosphorescent OLEDs

The performances of the Ir(III) complexes in the phosphorescent OLEDs were 344 345 evaluated by fabricating multi-layered devices with the structure ITO (50 nm)/PEDOT:PSS (40 nm)/TCTA (20 nm)/TCTA:TPBi:dopant (50:50:x%) (40 346 nm)/TPBi (40 nm)/LiF (1 nm)/Al (120 nm). We fabricated devices using TCTA and 347 TPBi as mixed-hosts in the emissive layer for efficient carrier injection and charge 348 balance [28]. Doping concentrations of 5 wt% for (BT)₂Ir(acac), 7 wt% for 349 (DMBT)₂Ir(acac), and 7 wt% for (TBT)₂Ir(acac) gave the optimal device 350 performances (Table 2). The optimized doping concentrations of (DMBT)₂Ir(acac) 351 352 and (TBT)₂Ir(acac) were higher than that of (BT)₂Ir(acac), which suggested that the 353 introduction of relatively bulky dimethyl or trimethylsilyl groups on the phenyl ring of main ligand effectively suppressed self-quenching, even at high concentrations. 354 The electroluminescent (EL) spectra of the optimized phosphorescent OLEDs 355 fabricated using (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) (Figure 4) 356 showed emission maxima at 563, 571, and 578 nm, respectively. The emission 357 maxima of the (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) devices were changed by only 1 358 359 nm as the dopant concentration was increased from 3 to 11% while the (BT)₂Ir(acac) device showed a red-shift of 2 nm under the same conditions. This indicated that the 360 361 (BT)₂Ir(acac) device had a higher degree of dopant aggregation and stronger intermolecular interactions at a high dopant concentration than (DMBT)₂Ir(acac) and 362 (TBT)₂Ir(acac) devices. (Figure S7) The Commission Internationale de L'Eclairage 363 364 (CIE) coordinates of the (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) devices 365 at the optimal doping concentrations were (0.49,0.50), (0.52,0.47), and (0.55,0.44), respectively, at 1.000 cd/m^2 . 366

367 Figure 5(a) shows the current density-voltage-luminance (J-V-L) curves of the phosphorescent OLEDs. The current densities of the OLEDs increased with 368 increasing concentration of (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) dopants because of 369 improved charge hopping at high dopant concentrations [29]. The $V_{\text{turn-on}}$ and L_{max} 370 values of the Ir(III) complexes with bulky substituents on the cyclometalated ligands 371 were 4.5 V/4.532 cd/m² for the (DMBT)₂Ir(acac) device and 4.5 V/6.837 cd/m² for 372 the $(TBT)_2Ir(acac)$ device. The highest L_{max} of the $(TBT)_2Ir(acac)$ device could be 373 attributed to its better recombination efficiency with higher Φ_{PL} as compared to the 374 (DMBT)₂Ir(acac) and (BT)₂Ir(acac)-based devices. The (DMBT)₂Ir(acac) and 375 (TBT)₂Ir(acac) devices exhibited higher maximum external quantum efficiencies 376 (EQE_{max})/maximum current efficiencies (CE_{max}) of 7.8%/21.4 cd/A and 9.9%/25.3 377 cd/A, respectively, compared to that of (BT)₂Ir(acac) (4.4%/13.0 cd/A) (Figure 5(b)). 378 The low driving voltage and high EQE of the (TBT)₂Ir(acac) device improved the PE 379 value to 12.37 lm/W, which was the highest value among the three Ir(III) 380 381 complex-based devices.

These results showed that the (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) complexes with 382 bulky substituents on the phenyl ring of the cyclometalated main ligands significantly 383 improved the device performances such as EQE, CE, and PE as compared to the 384 (BT)₂Ir(acac)-doped device. Introduction of bulky substituents on the phenyl ring of 385 (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) complexes could effectively prevent the 386 concentration self-quenching at high doping concentrations and suppress the 387 triplet-triplet annihilation in the device [24,25]. In particular, a trimethylsilyl 388 substituent on the 4-position of the phenyl ring led to better device performances than 389 390 the dimethyl substituents on 3,4-position of the phenyl ring. The device characteristics at other doping concentrations of (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac) 391

are shown in Figures S8, S9, and S10.

393

394 **4. Conclusions**

395 In this study, we successfully synthesized dimethyl- and trimethylsilyl-substituted 2-phenylbenzothiazole-based heteroleptic Ir(III) complexes, (DMBT)₂Ir(acac) and 396 (TBT)₂Ir(acac), for their application in solution-processed orange phosphorescent 397 OLEDs. Compared to (BT)₂Ir(acac), the synthesized (DMBT)₂Ir(acac) and 398 399 (TBT)₂Ir(acac) complexes exhibited improved thermal stability and emission quantum 400 efficiency. The introduction of bulky dimethyl and trimethylsilyl substituents on the phenyl ring of the main ligand in these complexes led to reduced molecular 401 402 aggregation in the emissive layer of the device fabricated by solution processing. 403 Consequently, the triplet-triplet annihilation in the orange phosphorescent OLEDs was effectively suppressed. The devices fabricated using (DMBT)₂Ir(acac) and 404 (TBT)₂Ir(acac) showed better performances than those fabricated using (BT)₂Ir(acac). 405 The device based on the (TBT)₂Ir(acac) complex, which had a trimethylsilyl 406 substituent on the phenyl ring, exhibited the best performance with the highest EQE, 407 L_{max}, CE, and PE_{max}. In particular, among all the fabricated phosphorescent OLEDs, 408 409 the (TBT)₂Ir(acac) device exhibited the highest CE of 25.26 cd/A at a high doping concentration of 7%. 410

411

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526

527

528 Table captions

- Table 1. Optical and electrochemical properties of the synthesized iridium(III)complexes.
- Table 2. Performances of the orange phosphorescent OLEDs.

532 **Table 1.**

	Optical						Electrochemical	
	$\lambda_{abs}{}^a$	$\lambda_{em}{}^{a/b}$	FWHM ^a	$\Phi_{PL}{}^{c}$	E_g^{d}	HOMO ^e	LUMO ^f	
Dopant	(nm)	(nm)	(nm) (%)		(eV)	(eV)	(eV)	
(\mathbf{PT}) $\mathbf{Ir}(\mathbf{a},\mathbf{a},\mathbf{a},\mathbf{c})$	313, 326, 356, 404,	562/564	78	0.26	2.25	-5.35	2 10	
$(\mathbf{D}\mathbf{I})_{2}\mathbf{II}(\mathbf{acac})$	440, 480	505/504					-3.10	
(DMBT)-Ir(acac)	321, 331, 359, 404,	569/571	74	0.38	2 21	-5.24	-3.03	
(DIVID I) ₂ II(acac)	448, 483	507571	74	0.50	2.21	-5.24	-5.05	
	319, 333, 364, 415,			0.40	. 10	5.00	2.10	
$(\mathbf{1B1})_2$ lr(acac)	453, 504	5/6/5/8	/6	0.49	2.18	-5.30	-3.10	

533

534 ^a Maximum PL emission wavelength measured in 1×10^{-5} M CH₂Cl₂ solution.

^bMaximum PL emission wavelength measured in the neat film state.

 $\label{eq:solution} {}^{c} \text{Values were measured using (BT)}_{2} \text{Ir}(\text{acac}) \ (\Phi_{PL} = 0.26) \ \text{as a reference in } 1 \times 10^{-5} \ \text{M CH}_{2} \text{Cl}_{2} \ \text{solution}.$

^dEnergy gap calculated from the onset of the absorption edge.

538 ^eEstimated from the cyclic voltammogram.

- $539 \qquad {}^{\rm f} {\rm Estimated \ from \ the \ HOMO \ energy \ level \ and \ the \ band \ gap.}$
- 540

541

Table 2. 542

Dopant	<i>x</i> %	λ _{max} , FWHM (nm)	$CIE^{a}(x,y)$	V _{turn} ^b (V)	$L_{max} (cd/m^2)$	EQE ^c (%)	CE ^c (cd/A)	PE ^c (lm/W)
	3	561, 70	(0.49, 0.50)	4.5	2,711	2.74/2.52	7.03/6.45	3.51/2.90
	5	562, 72	(0.49, 0.50)	4.5	4,948	4.38/4.38	12.96/12.96	7.29/6.79
$(B1)_2$ ir (acac)	7	562, 73	(0.50, 0.49)	4.5	2,443	3.63/2.67	10.91/8.00	4.90/3.35
	11	563, 75	(0.50, 0.49)	4.5	3,678	3.28/2.79	9.90/8.40	5.57/4.06
	3	570, 70	(0.52, 0.47)	4.5	2,535	4.02/3.70	11.30/10.40	5.63/4.67
	5	571, 72	(0.52, 0.47)	4.5	3,881	4.76/3.94	13.02/10.78	7.44/5.21
(DMBT) ₂ Ir(acac)	7	571, 72	(0.52, 0.47)	4.5	4,532	7.76/7.76	21.43/21.43	11.10/10.36
	11	571, 72	(0.52, 0.47)	4.5	3,567	6.67/5.81	18.26/16.18	10.00/7.26
	3	578, 74	(0.55, 0.44)	4.5	3,551	4.27/3.57	10.33/8.63	5.08/3.62
	5	578, 74	(0.55, 0.44)	4.5	4,958	5.17/4.48	12.49/10.83	8.38/5.67
$(1B1)_2$ Ir(acac)	7	578, 74	(0.55, 0.44)	4.5	6,837	9.94/9.94	25.26/25.26	12.37/12.21
	11	579, 76	(0.55, 0.44)	4.5	4,351	7.92/6.97	18.63/16.40	9.74/7.36

543 544 545

 ^a Values measured at a luminance of 1,000 cd/m².
 ^b Values measured at a luminance of 1 cd/m².
 ^c Values measured at maximum efficiency and luminance of 1,000 cd/m². n

Figure captions

Fig. 1. (a) UV-Visible absorption and (b) PL spectra of $(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$.

Fig. 2. Frontier molecular orbitals HOMO and LUMO of $(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$.

Fig. 3. Cyclic voltammograms of $(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$.

Fig. 4. EL spectra of orange phosphorescent OLEDs fabricated using (BT)₂Ir(acac), (DMBT)₂Ir(acac), and (TBT)₂Ir(acac).

Fig. 5. (a) Current density-voltage-luminance (J-V-L) and (b) external quantum efficiency–current density–current efficiency (EQE-J-CE) curves of $(BT)_2Ir(acac)$, $(DMBT)_2Ir(acac)$, and $(TBT)_2Ir(acac)$ -based devices.

26



Fig	2.
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Fig. 3.



Fig. 4.







Highlights

- New orange phosphorescent (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) were synthesized.
- (DMBT)₂Ir(acac) and (TBT)₂Ir(acac) effectively suppress concentration self-quenching in

the fabricated devices.

• The device using $(TBT)_2 Ir(acac)$ exhibited a L_{max} of 6,837 cd/m² and CE_{max} of 25.26 cd/A.