

## Supporting Information

### Synthesis and Characterization of Perfluorinated Phenyl Substituted Ir(III) Complexes for Color Pure Green Emission

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## 1. Synthesis of characterization of the materials

### *Synthesis of 3'-bromo-3,5-bis(trifluoromethyl)biphenyl (2)*

n-BuLi (11.70 mL, 29.32 mmol, 2.5 M solution in hexane) was added dropwise to a solution of substituted 1,3-bis(trifluoromethyl)-5-bromobenzene (10.3 g, 35.01 mmol) in dry diethyl ether (50 mL) at - 80 °C and the reaction mixture was stirred under nitrogen for 1 h whereupon trimethyl borate (5.54 mL, 48.87 mmol) was added and the reaction mixture was stirred at room temperature for an additional 4 h. The reaction was quenched with the addition of diluted 2N HCl (80 mL). The resulting mixture was extracted with diethyl ether (100 mL), and organic layers were washed with water (100 mL) and dried over anhydrous MgSO<sub>4</sub>. The 3,5-bis(trifluoromethyl)phenylboronic acid (1) was obtained in form of white solids. The crude product was used for next step without any purification. A mixture of 3',5'-bis(trifluoromethyl)biphenyl-3-yl-boronic acid (5.0 g, 19.38 mmol), and 1,3-dibromobenzene (4.5 g, 19.38 mmol) was dissolved in dioxane (50 mL). After 10 mL of 2 M aqueous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) was added through syringes to the mixture, the reaction mixture was degassed. Finally, 0.67 g of tetrakis(triphenylphosphine)palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub>(0)) was added to the mixture. The mixture was vigorously refluxed under nitrogen for 12 h. The reaction mixture was cooled and extracted with dichloromethane (100 mL). The organic extract was washed with water and brine then dried over MgSO<sub>4</sub>. After the solvent was evaporated, the crude product was purified by column chromatography (eluent = n-hexane). Yield: 5.5 g (78%); IR (KBr): 3068, 1621, 1463, 1376, 1137 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ (ppm)): 7.96 (s, 2H), 7.88 (s, 1H), 7.73 (t, 1H), 7.54 (m, 2H), 7.37 (t, 1H).

### *Synthesis of 2-(3,5-bis(trifluoromethyl)biphenyl-3-yl)pyridine, L1 (4)*

n-BuLi (11.70 mL, 29.32 mmol, 2.5 M solution in hexane) was added dropwise to a solution of substituted 3'-bromo-3,5-bis(trifluoromethyl)biphenyl (2) (9.02 g, 24.43 mmol) in dry diethyl ether (40 mL) at -80 °C and the reaction mixture was stirred under nitrogen for 1 h whereupon trimethyl borate (5.54 mL, 48.87 mmol) was added and the reaction mixture was stirred at room temperature for an additional 4 h. The reaction was quenched with diluted 2N HCl (80 mL). The resulting mixture was extracted with diethyl ether (100 mL), and organic layers were washed with water (100 mL) and dried over anhydrous MgSO<sub>4</sub>. The crystallization process was repeated twice. The 3',5'-bis(trifluoromethyl)biphenyl-3-yl-boronic acid was obtained in form of white solids. The crude product was used for next step without any purification. A mixture of (3',5'-bis(trifluoromethyl)biphenyl-3-yl)boronic acid (3) (3.10 g, 9.28 mmol), and 2-bromopyridine (1.33 g, 8.44 mmol)

was dissolved in dioxane (50 mL). After 2 M aqueous  $K_2CO_3$  (15 mL) was added through syringes to the mixture, the reaction mixture was degassed. Finally,  $Pd(PPh_3)_4(0)$  (0.32 g, 0.27 mmol) was added to the mixture. The mixture was vigorously refluxed under nitrogen for 12 h. After cooling to room temperature the reaction mixture was extracted with dichloromethane (100 mL). The organic extract was washed with water and brine then dried over  $MgSO_4$ . After the solvent was evaporated, the crude product was purified by column chromatography (eluent = n-hexane). Yield: 5.5 g (78%); m.p: 72 °C; IR (KBr): 3022, 1585, 1463, 1376, 1276, 1126  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$  (ppm)): 8.74 (hex, 1H), 8.27-8.28 (m, 1H), 8.09 (s, 2H), 8.03 (hex, 1H), 7.88 (s, 1H), 7.80 (hex, 2H), 7.60-7.64 (m, 2H), 7.28 (dd, 1H).

*Synthesis of di[2-(3',5'-bis(trifluoromethyl)biphenyl-3-yl)pyridiene]iridium-(acetylacetonate), [(mtfppy)<sub>2</sub>Ir(acac)] (6)*

A mixture of 2-(3,5-bis(trifluoromethyl)biphenyl-3-yl)pyridine (4) (1.30 g, 3.54 mmol), iridium(III) chloride hydrate (0.50 g, 1.69 mmol), 2-ethoxyethanol (15 mL), and water (5 mL) was deoxygenated and then heated to reflux under nitrogen for 24 h at 120 °C. After cooling to room temperature, the mixture was filtrated and washed with ethanol to give product Ir(III)- $\mu$ -chloride-bridged dimer. A mixture of the Ir(III)- $\mu$ -chloride-bridged dimer (1.72 g, 0.89 mmol), 2,4-pentanedione (0.46 mL, 4.49 mmol),  $Na_2CO_3$  (0.95 g, 8.99 mmol), and ethoxyethanol (15 mL) was deoxygenated and heated to reflux under nitrogen for 24 h at 120 °C. After cooling to room temperature, the mixture was evaporated under vacuum and extracted with dichloromethane (50 mL). The organic extract was washed with water and dried over  $MgSO_4$ . The solvent was evaporated, and the crude product was purified by column chromatography (eluent = dichloromethane). Yield (0.70 g, 40 %). M.p.:285 °C; IR (KBr): 3040, 1691, 1582, 1382, 1378, 1278, 1132. ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$  (ppm)): 8.57 (d, 2H), 8.01 (d, 2H), 7.92 (s, 4H), 7.83 (t, 2H), 7.73 (d, 4H), 7.24 (s, 2H), 6.93 (d, 2H), 6.43 (d, 2H), 5.27 (s, 1H), 1.83 (s, 6H).

*Synthesis of fac-tris[2-(3',5'-bis(trifluoromethyl)biphenyl-3-yl)pyridiene]iridium, [Ir(mtffppy)<sub>3</sub>] (7)*

A mixture of 2-(3,5-bis(trifluoromethyl)biphenyl-3-yl)pyridine (4) (0.32 g, 0.88 mmol), di[2-(3',5'-bis(trifluoromethyl)biphenyl-3-yl)pyridiene]iridium(acetylacetonate) (6) (0.60 g, 0.59 mmol) and glycerol (20 mL) was deoxygenated and then heated to reflux under nitrogen for 24 h. After cooling to room temperature the

reaction mixture was extracted with dichloromethane (50 mL). The organic extract was washed with water then dried over MgSO<sub>4</sub>. The solvent was evaporated, and the crude product was purified by column chromatography (eluent = dichloromethane). Yield (0.40 g, 53%). M.p.: 400 °C; IR (KBr): 3060, 1602, 1470, 1373, 1278, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ (ppm)): 8.08 (d, 3H), 8.03 (s, 6H), 7.89 (s, 3H), 7.73 (t, 6H), 7.63 (d, 3H), 7.12 (d, 3H), 7.02 (d, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ(ppm)): 165.92, 162.32, 147.28, 144.96, 144.38, 137.88, 136.68, 132.16, 131.08, 130.28, 128.71, 126.31, 123.71, 123.52, 121.75, 119.32. HRMS (FAB) Calculated for C<sub>57</sub>H<sub>30</sub>F<sub>18</sub>IrN<sub>3</sub>, 1291.1782 (m/z), Found ;1291.1741

## 2. Thermal property of Ir(mtfppy)<sub>3</sub>

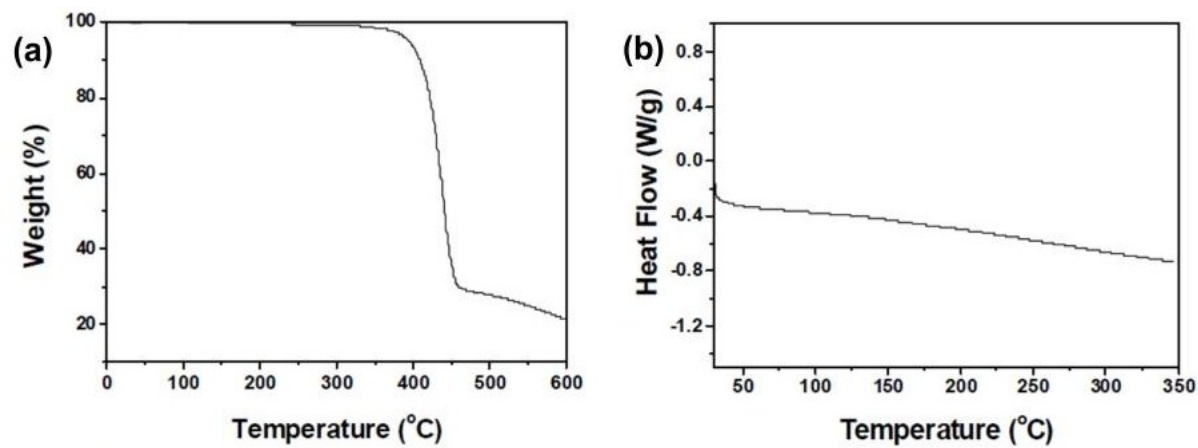
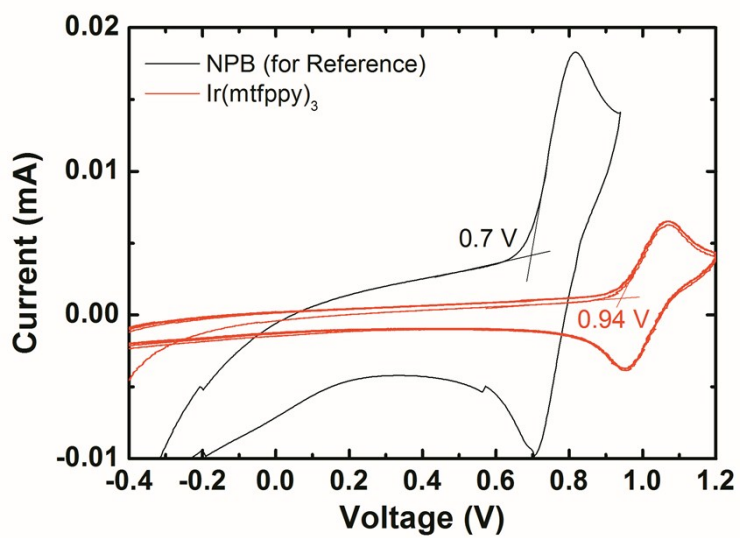


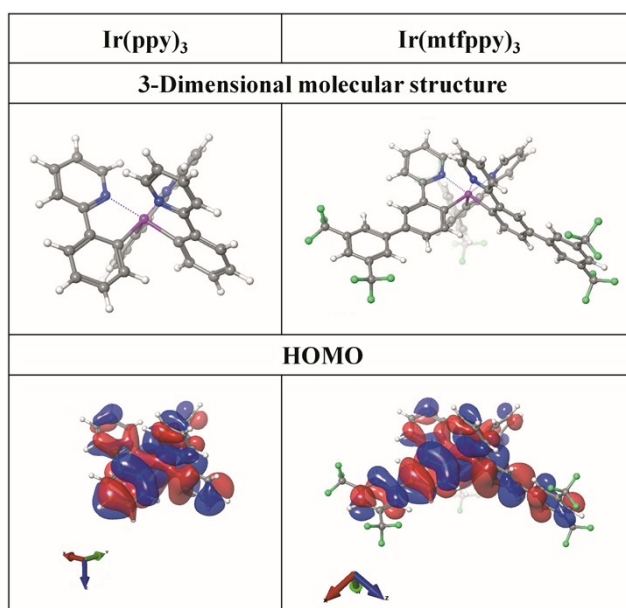
Fig. S1 TGA and DSC thermograms of Ir(mtfppy)<sub>3</sub>

### 3. Cyclic voltammogram of Ir(mtfppy)<sub>3</sub>



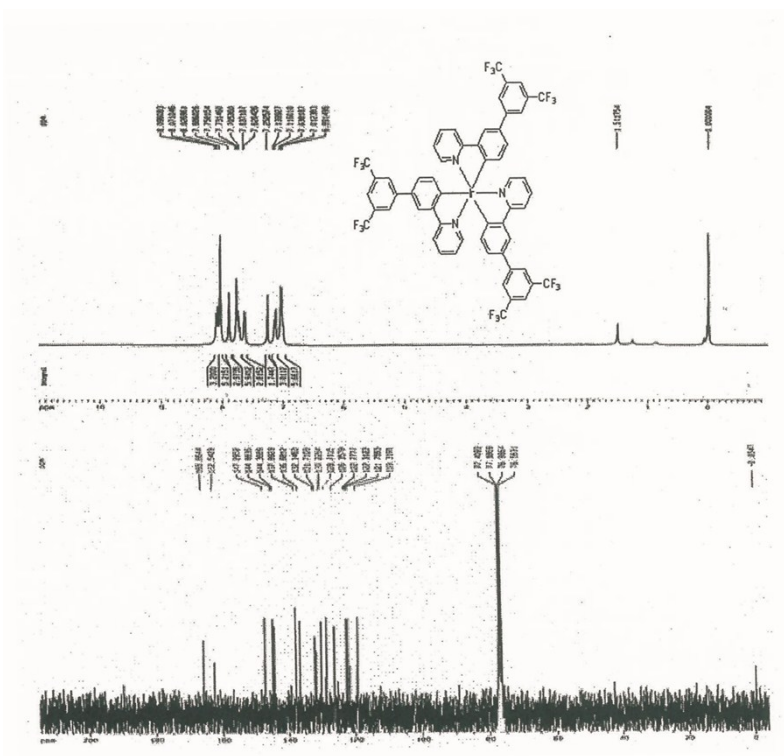
**Fig. S2** Cyclic voltammogram of Ir(mtfppy)<sub>3</sub> in dichloromethane containing 0.1 M TBAPF<sub>6</sub> as electrolyte.

#### 4. Frontier molecular orbitals of Ir complexes



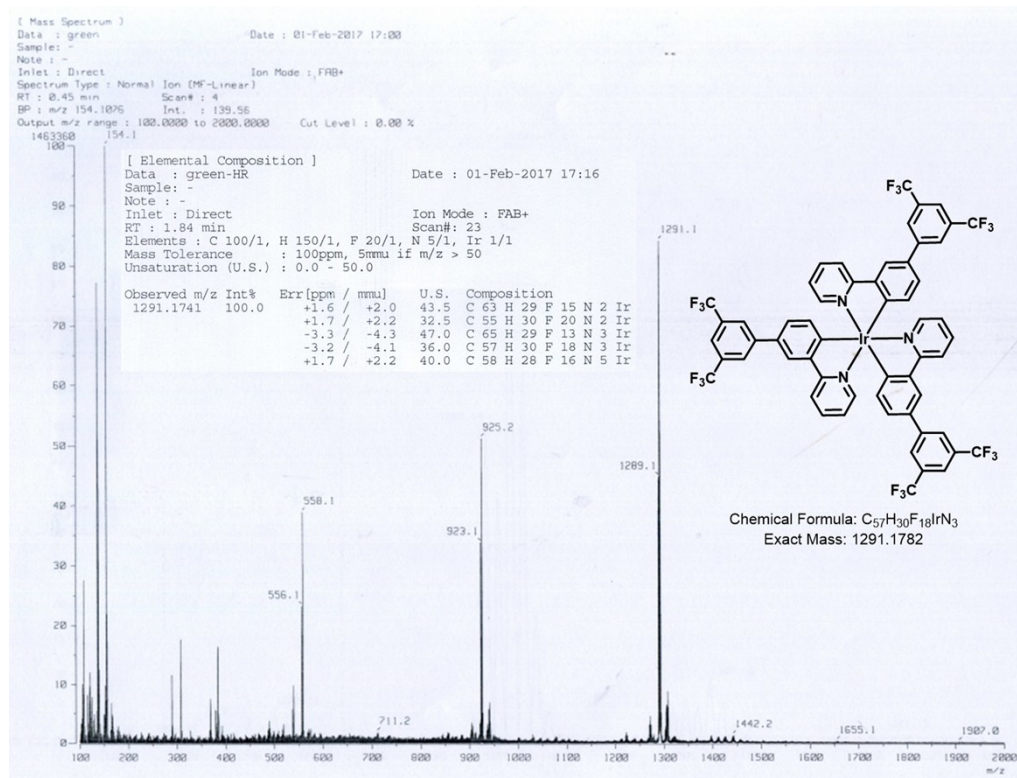
**Fig. S3** 3-Dimensional molecular structure and the frontier molecular orbitals of the Iridium complexes

#### 4. NMR of Ir complexes





## 5. Mass spectra of Ir complex



MS (FAB-HR) m/z: calcd for C<sub>57</sub>H<sub>30</sub>F<sub>18</sub>IrN<sub>3</sub>: 1291.1782; found, 1291.1741.