

Supporting Information

Synthesis of 2-bromo-1-(2,4-dichloro)-ethanone: Synthesis was carried out according to the literature procedure (Ogata, Matsumoto et al. 1987) by combining dropwise 0.262 mL Br₂ (26.45 mmol) in 7 mL chloroform with a solution of 5 g 2,4-dichloroacetophenone (26.45 mmol) in 25.0 mL chloroform and stirring at room temperature for 1 h. This mixture was diluted with ice water and aqueous Na₂S₂O₃ to destroy excess bromine and extracted with CH₂Cl₂. The organic layer was washed with H₂O, dried over NaSO₄, and evaporated under reduced pressure to yield an orange-brown oil.

Synthesis of 1-[2-(2,4-dichloro-phenyl)-2-oxo-ethyl]-pyridinium bromide: 2-bromo-1-(2,4-dichloro)-ethanone was dissolved in 30 mL pyridine and stirred at room temperature for 2 h. The white-orange solid was precipitated by addition of 50 mL diethyl ether and collected via suction filtration.

Synthesis of 1-[2-(2,4-difluoro-phenyl)-2-oxo-ethyl]-pyridinium bromide: This product was prepared analogously to 1-[2-(2,4-dichloro-phenyl)-2-oxo-ethyl]-pyridinium bromide from the appropriate ethanone.

Synthesis of 5-methyl-2-(2,4-dichloro-phenyl)-pyridine: A mixture of 2-methyl-2-propenal (5.5 mmol), 1-[2-(2,4-dichloro-phenyl)-2-oxo-ethyl]-pyridinium bromide (5.5 mmol) and ammonium acetate (55.0 mmol) was dissolved in methanol (25.0 mL) and refluxed with stirring for 15 h. The product was precipitated upon addition of 200 mL of ice-cold water and collected via suction filtration. [Cl₂-mppy].

Synthesis of 5-methyl-2-(2,4-difluoro-phenyl)-pyridine: This product was prepared analogously to 5-methyl-2-(2,4-dichloro-phenyl)-pyridine. [F₂-mppy].

Synthesis of [(4,7-diphenyl-1,10-phenanthroline)-bis-(2-phenylpyridine)-iridium(III)] hexafluorophosphate: The iridium 2-phenylpyridine dichloro-bridged dimer (0.093 mmol, 100 mg) was refluxed at 150 °C with 4,7-diphenyl-1,10-phenanthroline (0.19 mmol, 68.2 mg) in ethylene glycol (10 mL) with constant stirring for 15 h. Upon cooling to room temperature, the orange solution was transferred to a separatory funnel with water and washed three times with 20 mL diethyl ether. Excess ether was removed by heating to 50 °C. 10 mL aqueous ammonium hexafluorophosphate solution (1.0 g in 10 mL H₂O) was added to the reaction mixture and the precipitate was collected by suction filtration and dried under reduced pressure at 100 °C to obtain [Ir(ppy)₂(dphphen)](PF₆).

Synthesis of [(2,2'-bipyridine)-bis-(5-methyl-2-(5-fluoro-phenyl)-pyridine)-iridium(III)] hexafluorophosphate: The synthesis and work-up of this product, using the 5-methyl-2-(5-fluoro-phenyl)-pyridine dichloro-bridged dimer (0.087 mmol, 104 mg) and 2,2'-bipyridine (0.19 mmol, 29.7 mg), was carried out analogously to [Ir(ppy)₂(dphphen)](PF₆), to yield the crystalline product, [Ir(F-mppy)₂(bpy)](PF₆).

Synthesis of [(1,10-phenanthroline)-bis-(5-methyl-2-(5-fluoro-phenyl)-pyridine)-iridium(III)] hexafluorophosphate: The synthesis and work-up of this product, using the 5-methyl-2-(5-fluoro-phenyl)-pyridine dichloro-bridged dimer (0.084 mmol, 101 mg) and 1,10-phenanthroline (0.18 mmol, 33.3 mg), was carried out analogously to [Ir(ppy)₂(dphphen)](PF₆), to yield the crystalline product, [Ir(F-mppy)₂(phen)](PF₆).

Synthesis of [(4,7-diphenyl-1,10-phenanthroline)-bis-(5-methyl-2-(5-fluoro-phenyl)-pyridine)-iridium(III)] hexafluorophosphate: The synthesis and work-up of this product, using the 5-methyl-2-(5-fluoro-phenyl)-pyridine dichloro-bridged dimer (0.072

mmol, 86 mg) and 4,7-diphenyl-1,10-phenanthroline (0.16 mmol, 52.6 mg), was carried out analogously to $[\text{Ir}(\text{ppy})_2(\text{dphphen})](\text{PF}_6)$, to yield the crystalline product, $[\text{Ir}(\text{F-mppy})_2(\text{dphphen})](\text{PF}_6)$.

Structural Identification:

$\text{Cl}_2\text{-mppy}$: ^1H (CDCl_3 , 500 MHz): δ 8.57 (pyridyl- H_6 , 1H, s), 7.58 (3H, m), 7.51 (phenyl- H_3 , 1H, d, $J = 1.83$), 7.36 (phenyl- H_5 , 1H, dd, $J = 8.24$, 1.83), 2.42 (3H, s).

$\text{F}_2\text{-mppy}$: ^1H (CDCl_3 , 500 MHz): δ 8.56 (pyridyl- H_6 , 1H, s), 7.99 (phenyl- H_6 , 1H, m) 7.67 (pyridyl- H_3 , 1H, dd, $J = 7.94$, 1.53 Hz), 7.59 (pyridyl- H_4 , 1H, dd, $J = 7.94$, 1.22 Hz), 7.01 (phenyl- H_5 , 1H, m), 6.93 (phenyl- H_3 , 1H, m), 2.41 (3H, s).

$[\text{Ir}(\text{ppy})_2\text{dphphen}](\text{PF}_6)$: ^1H NMR (CDCl_3 , 500 MHz): δ 8.33 (2H, d, $J = 5.19$ Hz), 8.17 (2H, s), 7.95 (2H, d, $J = 7.94$ Hz), 7.77 (4H, m), 7.70 (2H, d, $J = 5.19$ Hz), 7.63 (2H, d, $J = 6.41$ Hz), 7.57 (12H, m), 7.08 (4H, m), 7.00 (2H, t, $J = 7.33$ Hz), 6.46 (2H, d, $J = 7.33$ Hz). ^{13}C NMR (CDCl_3 , 500 MHz): δ 167.9, 151.4, 150.6, 150.4, 149.4, 147.6, 144.1, 138.4, 135.8, 132.2, 131.0, 130.1, 130.0, 129.9, 129.4, 127.0, 126.7, 125.0, 124.0, 123.0, 119.8. MS (m/z ; ESI): 834 (100%, $\text{M}^+ - \text{PF}_6^-$).

$[\text{Ir}(\text{F-mppy})_2\text{bpy}](\text{PF}_6)$: ^1H NMR (CDCl_3 , 500 MHz): δ 8.91 (2H, d, $J = 7.94$ Hz), 8.25 (2H, t, $J = 7.94$ Hz), 7.95 (2H, d, $J = 5.50$ Hz), 7.78 (2H, d, $J = 8.24$ Hz), 7.66 (4H, m), 7.48 (2H, t, $J = 6.11$ Hz), 7.19 (2H, s), 6.80 (2H, td, $J = 8.55$, 2.44 Hz), 5.91 (2H, dd, $J = 9.47$, 2.44 Hz), 1.80 (6H, s). ^{13}C NMR (acetone- d_6 , 500 MHz): δ 164.3, 156.3, 151.1, 148.8, 140.9, 140.1, 140.0, 134.2, 132.4, 128.9, 126.9, 126.9, 125.2, 119.9, 117.6, 109.6, 17.3. MS (m/z ; ESI): 721 (100%, $\text{M}^+ - \text{PF}_6^-$).

$[\text{Ir}(\text{F-mppy})_2\text{phen}](\text{PF}_6)$: ^1H NMR (CDCl_3 , 500 MHz): δ 8.82 (2H, dd, $J = 7.94$, 1.22 Hz), 8.36 (2H, s), 8.30 (2H, dd, $J = 5.19$, 1.22 Hz), 7.91 (2H, dd, $J = 8.25$, 5.19 Hz), 7.78 (2H, d, $J = 8.25$ Hz), 7.73 (2H, dd, $J = 8.55$, 5.50 Hz), 7.57 (2H, dd, $J = 6.41$, 1.22 Hz), 7.00 (2H, s), 6.84 (2H, td, $J = 8.55$, 2.44 Hz), 6.00 (2H, dd, $J = 9.16$, 2.44 Hz), 2.04 (6H, s). ^{13}C NMR (acetone- d_6 , 500 MHz): δ 164.3, 151.7, 149.0, 147.2, 141.2, 140.1, 139.2, 135.7, 134.1, 132.0, 128.8, 127.3, 126.9, 119.8, 118.0, 115.0, 109.7, 17.2. MS (m/z ; ESI): 745 (100%, $\text{M}^+ - \text{PF}_6^-$).

$[\text{Ir}(\text{F-mppy})_2\text{dphphen}](\text{PF}_6)$: ^1H NMR (CDCl_3 , 500 MHz): δ 8.36 (2H, d, $J = 5.19$ Hz), 8.27 (2H, s), 7.82 (2H, d, $J = 8.55$ Hz), 7.79 (2H, d, $J = 5.50$ Hz), 7.75 (2H, dd, $J = 8.55$, 5.50 Hz), 7.62 (12H, m), 7.19 (2H, s), 6.84 (2H, td, $J = 8.86$, 2.44 Hz), 6.02 (2H, dd, $J = 9.16$, 2.44 Hz), 2.12 (6H, s). ^{13}C NMR (acetone- d_6 , 500 MHz): δ 164.5, 159.6, 153.1, 151.4, 149.0, 147.9, 147.7, 141.2, 140.1, 136.0, 134.1, 130.2, 130.1, 129.7, 129.4, 17.5, 127.0, 126.6, 120.3, 119.9, 117.6, 17.2. MS (m/z ; ESI): 898 (100%, $\text{M}^+ - \text{PF}_6^-$).