## Appendix B

### SYNTHESIS AND CHARACTERIZATION

The following is a representative, but not completely comprehensive, list of the corrole and azaporphyrin syntheses I developed while at Caltech. It should give the reader a good idea of how these compounds are made without a lot of tedious reference to online Supporting Information files. Some NMR and/or UV-vis characterization data is included for each compound as well. X-ray structures for compounds **1-Ir(tma)**<sub>2</sub>, **1b-Ir(tma)**<sub>2</sub>, **1-Ir(dmap)**<sub>2</sub>, and **1-Ir(NH**<sub>3</sub>)<sub>2</sub> are included in Appendix C.

5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III) (bis)trimethylamine, 1-Ir(tma)<sub>2</sub>: H<sub>3</sub>tpfc (80 mg), [Ir(cod)Cl]<sub>2</sub> (335 mg), and K<sub>2</sub>CO<sub>3</sub> (140 mg) were dissolved/suspended in 150 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min (until corrole fluorescence was negligible to the eye upon longwavelength irradiation with a hand-held lamp). Tma *N*-oxide (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the black mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) provided an auburn solution, from which purple crystals of **1-Ir(tma)<sub>2</sub>** (30 mg, 27% yield) could be grown by slow evaporation. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.99 (d, 2H, J = 5.4), 8.67 (d, 2H, J = 6.0), 8.55 (d, 2H, J = 6.0), 8.23 (d, 2H, J = 4.8), -2.95 (s, 18H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -138.38 (m, 6F), -154.89 (m, 3F), -163.27 (m, 6F). MS (ESI): 1105.1 ([M<sup>+</sup>]), 1046.0 ([M<sup>+</sup>-tma]), 986.5 ([M<sup>+</sup>-2tma]). UV-vis (toluene, nm,  $\varepsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ):



Figure B-1: <sup>1</sup>H NMR of **1-Ir(tma)**<sub>2</sub> in CD3CN



Figure B-2: UV-vis of 1-Ir(tma)<sub>2</sub> in toluene



Figure B-3: ESI-MS of 1-Ir(tma)<sub>2</sub>

2,3,7,8,12,13,17,18-Octabromo-5,10,15-(tris)pentafluorophenylcorrolatoiridium(III) (bis)trimethylamine, 1b-Ir(tma)<sub>2</sub>: Br<sub>2</sub> (70 µL) and 1-Ir(tma)<sub>2</sub> (15 mg) were dissolved in 20 mL of MeOH and stirred overnight. Column chromatography (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) of the red mixture provided a ruddy solution from which purple crystals of 1b-Ir(tma)<sub>2</sub> (15 mg, 63% yield) could be grown by addition of methanol followed by slow evaporation. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  -2.60 (s, 18H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -137.78 (d/d, 2F, <sup>3</sup>J = 35.1, <sup>4</sup>J = 18.3), -138.54 (d/d, 4F, <sup>3</sup>J = 33.9, <sup>4</sup>J = 17.1), -152.89 (m, 3F), -163.38 (m, 4F), -163.70 (m, 2F). MS (ESI): 1616.4 ([M<sup>+</sup> - 2tma]). UV-vis (toluene, nm, nm,  $\varepsilon \times 10^{-3}$  M<sup>-1</sup> cm<sup>-1</sup>): 404 (54.0), 424 (62.8), 582 (13.9), 656 (6.15). Emission (toluene, nm): 795. XRD: See Appendix C.



Figure B-4: <sup>19</sup>F NMR of **1b-Ir(tma)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-5: ESI-MS of 1b-Ir(tma)<sub>2</sub>



Figure B-6: UV-vis of 1b-Ir(tma)<sub>2</sub> in toluene

**5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** (bis)pyridine, 1-Ir(py)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. Pyridine (1 mL) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the forest green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 3:2 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a bright green solution, from which thin, green crystals of **1-Ir(py)**<sub>2</sub> (26 mg, 50% yield) could be grown by addition of methanol followed by slow evaporation. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.84 (d, 2H, J = 4.5), 8.53 (d, 2H, J = 4.8), 8.32 (d, 2H, J = 4.8), 8.17 (d, 2H, J = 4.5), 6.21 (t, 2H, J = 7.8), 5.19 (t, 4H, J = 7.0), 1.72 (d, 4H, J = 5.1). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -138.68 (m, 6F), -154.84 (t, 2F, J = 22.2), -155.20 (t, 1F, J = 22.2), -163.28 (m, 4F), -163.65 (m, 2F). MS (ESI): 1144.1 ([M<sup>+</sup>]). UV-vis (toluene, nm,  $\varepsilon \times 10^{-3}$  M<sup>-1</sup> cm<sup>-1</sup>): 392 (46.1), 412 (68.3), 584 (19.4), 621 (10.6). Emission (toluene, nm): 792. XRD: See Appendix C.







Figure B-8: <sup>19</sup>F NMR of **1-Ir(py)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-10: UV-vis of 1-Ir(py)<sub>2</sub> in toluene

**5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** triphenylphosphine, 1-Ir(PPh<sub>3</sub>): H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. Triphenylphosphine (260 mg dissolved in 5 mL THF) was added, and the solution was heated at reflux for another half hour under laboratory atmosphere before being allowed to cool to room temperature. Column chromatography of the deep green mixture (silica, 3:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a bright red-orange solution, which could be evaporated to give **1-Ir(PPh<sub>3</sub>)** (30 mg, 64% yield) as a ruby-colored solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.67 (d, 2H, J = 4.5), 8.36 (d, 2H, J = 5.1), 8.18 (d, 2H, J = 5.1), 8.00 (d, 2H, J = 4.5), 6.98 (t, 3H, J = 7.2), 6.69 (t, 6H, J = 6.9), 4.52 (d/d, 6H, <sup>3</sup>J = 19.5, <sup>4</sup>J = 3.6). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -137.44 (m, 6F), -154.05 (m, 3F), -162.54 (m, 3F). MS (ESI): 1248.1 ([M<sup>+</sup>]). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\varepsilon \times 10^{-3}$  M<sup>-1</sup> cm<sup>-1</sup>): 398 (66), 554 (8.8), 588 (6.7)



Figure B-11: <sup>1</sup>H NMR of **1-Ir(PPh<sub>3</sub>)** in CDCl<sub>3</sub>



Figure B-13: ESI-MS of 1-Ir(PPh<sub>3</sub>)



Figure B-14: UV-vis of 1-Ir(PPh<sub>3</sub>) in CH<sub>2</sub>Cl<sub>2</sub>

**5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** (bis)-4-cyanopyridine, 1-Ir(cnpy)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Cyanopyridine (105 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dichroic red/green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 2:3 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a bright red solution, which upon evaporation yielded 1-Ir(cnpy)<sub>2</sub> (36 mg, 66% yield) as a purple solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.91 (d, 2H, J = 4.5), 8.60 (d, 2H, J = 5.1), 8.39 (d, 2H, J = 4.8), 8.26 (d, 2H, J = 4.5), 5.43 (d/d, 4H, <sup>3</sup>J = 6.9, <sup>4</sup>J = -4.2), 1.75 (d/d, 4H, <sup>3</sup>J = 6.9, <sup>4</sup>J = -3.9). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -138.38 (d/d, 2F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.4), -138.95 (d/d, 4F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.4), -153.75 (t, 2F, J = 22.5), -154.11 (t, 1F, J = 22.2), -162.48 (m, 4F). -162.84 (m, 2F). MS (ESI): 1089.0

([M+-cnpy]), 986.1 ([M+-2(cnpy)]) UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm, ε x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 388 (8.8), 406 (14), 580 (4.2), 608 (2.8). Emission (toluene, nm): 788





Figure B-16: <sup>19</sup>F NMR of **1-Ir(cnpy)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-18: UV-vis of 1-Ir(cnpy)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

**5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** (bis)-4-methoxypyridine, 1-Ir(meopy)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg),  $[Ir(cod)Cl]_2$  (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Methoxypyridine (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dark green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 2:3 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a bright red solution, which upon evaporation yielded **1-Ir(meopy)**<sub>2</sub> (28 mg, 50% yield) as a green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.81 (d, 2H, J = 4.2), 8.49 (d, 2H, J = 4.5), 8.31 (d, 2H, J = 4.5), 8.12 (d, 2H, J = 3.9), 4.69 (d/d, 4H, <sup>3</sup>J = 7.2, <sup>4</sup>J = -4.5), 2.93 (s, 6H), 1.56 (m, 4H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -138.40 (d/d, 2F, <sup>3</sup>J = 35.7, <sup>4</sup>J = 17.4), -138.64 (d/d, 4F, <sup>3</sup>J = 35.7, <sup>4</sup>J = 17.4), -154.98 (t, 2F, J = 22.5), -155.35 (t, 1F, J = 22.4), -163.33 (m, 4F). -163.69 (m, 2F). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 394, 412, 584, 624



Figure B-19: <sup>1</sup>H NMR of **1-Ir(meopy)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-20: UV-vis of 1-Ir(meopy)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

#### 5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III) (bis)[3,5-

(**bis**)**trifluoromethyl]pyridine**, **1-Ir**(**cfpy**)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-(bis)trifluoromethylpyridine (215 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the deep green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 100% CH<sub>2</sub>Cl<sub>2</sub>) afforded a dichroic red/green solution, which upon evaporation yielded **1-Ir(cfpy)**<sub>2</sub> (13 mg, 20% yield) as a purple-red solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.00 (d, 2H, J = 4.2), 8.70 (d, 2H, J = 4.8), 8.44 (d, 2H, J = 4.8), 8.38 (d, 2H, J = 4.2), 6.65 (s, 2H), 1.97 (s, 4H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  = -64.29 (t, 12F, J = 7.5), -138.47 (m, 6F), -153.52 (t, 2F, J = 22.2), -153.82 (m, 1F), -162.35 (m, 6F). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\epsilon$  x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 384 (9.7), 406 (15), 580 (4.5), 602 (2.8)



Figure B-21: <sup>1</sup>H NMR of  $1-(cfpy)_2$  in CDCl<sub>3</sub>. There is a small impurity owing to what appears to be an equilibrium with the five-coordinate species 1-(cfpy).



Figure B-22: <sup>19</sup>F NMR of  $1-(cfpy)_2$  in CDCl<sub>3</sub>. The large downfield peak corresponds to the fluorine atoms in the  $-CF_3$  groups on the axial ligands.



**5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** (bis)-3,5-dichloropyridine, 1-Ir(clpy)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-Dichloropyridine (150 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dark green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 100% CH<sub>2</sub>Cl<sub>2</sub>) afforded a vivid green solution, which upon evaporation yielded 1-Ir(clpy)<sub>2</sub> (27 mg, 47% yield) as a green microcrystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.91 (d, 2H, J = 4.2), 8.64 (d, 2H, J = 4.5), 8.40 (d, 2H, J = 4.5), 8.30 (d, 2H, J = 4.2), 6.16 (t, 2H, J = 1.8), 1.52 (d, 4H, J = 1.8). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -137.49 (d/d, 2F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.7), -137.71 (d/d, 4F, <sup>3</sup>J = 34.8, <sup>4</sup>J = 17.1), -153.87 (t, 2F, J = 22.5), -154.28 (t, 1F, J = 22.2), -162.39 (m, 4F). -162.82 (m, 2F). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\varepsilon$  x 10<sup>-3</sup> M<sup>-1</sup>cm<sup>-1</sup>): 390 (26), 406 (38), 580 (12), 608 (7.3)



Figure B-25: <sup>19</sup>F NMR of **1-(clpy)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-26: UV-vis of 1-(clpy)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

## 5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III) (bis)-4-(N,N-

**dimethylamino)pyridine, 1-Ir(dmap)**<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-dimethylaminopyridine (220 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dark green mixture (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 2:3 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a green solution, which upon evaporation yielded **1-Ir(dmap)**<sub>2</sub> (30 mg, 49% yield) as a green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.76 (d, 2H, J = 4.2), 8.44 (d, 2H, J = 4.8), 8.27 (d, 2H, J = 4.2), 8.05 (d, 2H, J = 4.2), 4.25 (d, 4H, J = 7.5), 2.09 (s, 12H), 1.41 (d, 4H, J = 7.5). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 393, 417, 585, 642. Emission (toluene, nm): 788. XRD: See Appendix C.



Figure B-27: <sup>1</sup>H NMR of **1-Ir(dmap)**<sub>2</sub> in CDCl<sub>3</sub>



Figure B-28: UV-vis of 1-Ir(dmap)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

# **5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III)** (bis)ammine, 1-Ir(NH<sub>3</sub>)<sub>2</sub>: H<sub>3</sub>tpfc (40 mg), [Ir(cod)Cl]<sub>2</sub> (170 mg), and K<sub>2</sub>CO<sub>3</sub> (70 mg) were dissolved/suspended in

75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. The solution was then exposed to the atmosphere, followed by saturation with gaseous ammonia for 15 minutes while cooling occurred. Column chromatography of the turbid green mixture (silica, 3:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub> followed by 1:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) afforded a dark green solution, which upon evaporation yielded **1-Ir(NH<sub>3</sub>)<sub>2</sub>** (20 mg, 39% yield) as a green microcrystalline solid. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO):  $\delta$  8.72 (d, 2H, J = 4.2), 8.47 (d, 2H, J = 4.8), 8.37 (d, 2H, J = 4.8), 8.01 (d, 2H, J = 4.2), -4.057 (s, 6H). MS (ESI): 1019.7 ([M<sup>+</sup>]), 1001.7 ([M<sup>+</sup> - 1NH<sub>3</sub>]), 986.0 ([M<sup>+</sup> - 2NH<sub>3</sub>]). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 394, 413, 584, 624. Emission (toluene, nm): 801. XRD: See Appendix C.



Figure B-29: <sup>1</sup>H NMR of **1-Ir(NH<sub>3</sub>)**<sub>2</sub> in d<sup>6</sup>-DMSO



Figure B-30: ESI-MS of 1-Ir(NH<sub>3</sub>)<sub>2</sub>. Positive and negative peaks overlaid so all three peaks are visible



Figure B-31: UV-vis of 1-Ir(NH<sub>3</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>

2,3,7,8,12,13,17,18-octabromo-5,10,15-(tris)Pentafluorophenylcorrolatoiridium(III) (bis)ammine, 1b-Ir(NH<sub>3</sub>)<sub>2</sub>: Br<sub>2</sub> (30  $\mu$ L) and 1-Ir(NH<sub>3</sub>)<sub>2</sub> (50 mg) were dissolved in 50 mL of C<sub>6</sub>H<sub>6</sub> and stirred overnight. Column chromatography (silica, 1:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) of the dark green mixture provided a green solution from which green microcrystals of **1b-Ir(NH<sub>3</sub>)<sub>2</sub>** could be recovered in essentially quantitative yield by slow evaporation. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -4.03 (s, 6H, J(<sup>15</sup>N) = 71 Hz). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): 408, 427, 594, 640. Emission (toluene, nm): 808



Figure B-32: <sup>1</sup>H NMR of **1b-Ir(NH<sub>3</sub>)**<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>



Figure B-33: UV-vis of 1b-Ir(NH<sub>3</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>