

## Supplementary Information

### Photocatalytic Hydrogen Generation from Water Reduction Using Orchestrated Photosensitizers

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### Synthesis of Ligand 3

4,4'-dibromo-2,2'-bipyridine (104 mg, 0.33 mmol), 4-vinylphenylboronic acid (148 mg, 1.0 mmol) and sodium carbonate (380 mg) were dissolved in a mixed solvent of tetrahydrofuran (25 mL) and water (3 mL). The mixture was deoxygenated and then tetrakis(triphenylphosphine)palladium(0) (39 mg, 0.03 mmol) was added. The resultant mixture was refluxed at 80 °C under nitrogen protection for 48 h. When cooled, water (50 mL) was added and the two layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent was completely removed. The residue was purified by column chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (1: 0 to 1: 1) as eluent to give compound **3** as a white solid (65 mg, 55%); mp 233-234 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.34 (d, 2H, J=11.31), 5.85 (d, 2H, J=17.64), 6.74-6.83 (m, 2H), 7.53-7.58 (m, 6H), 7.76-7.78 (m, 4H), and 8.74-8.76 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 114.90, 118.93, 121.42, 126.85, 127.30, 136.14, 137.43, 138.39, 148.83, 149.61, and 156.58. *m/z* [ESI]: 361.2 ([M+H]<sup>+</sup>). Anal. Cal. For C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.53; H, 5.72; N, 7.91.

### Synthesis of 4-Styrenyl-Ir

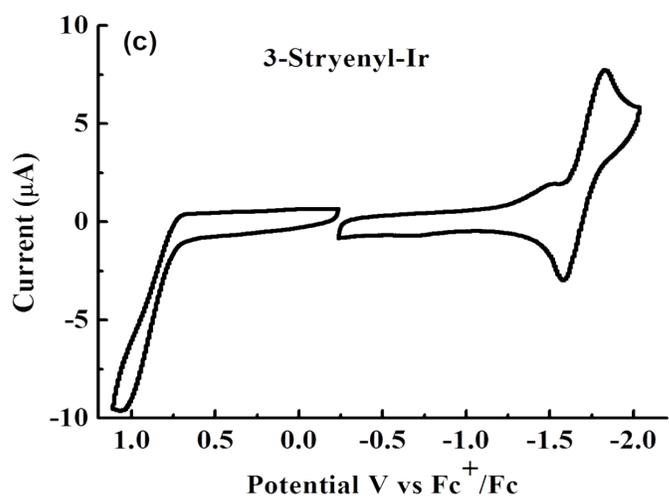
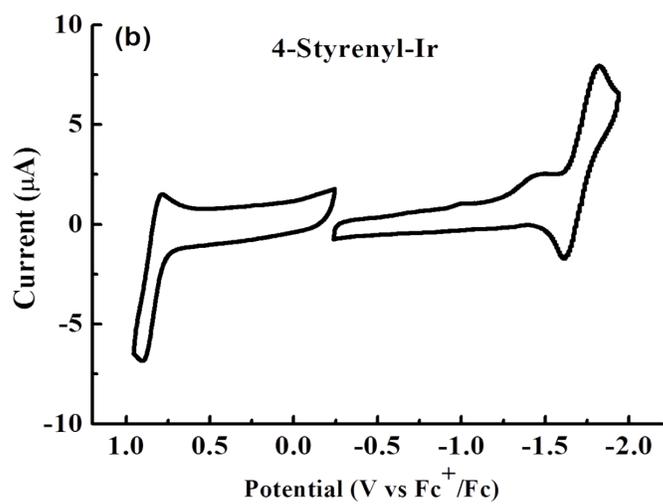
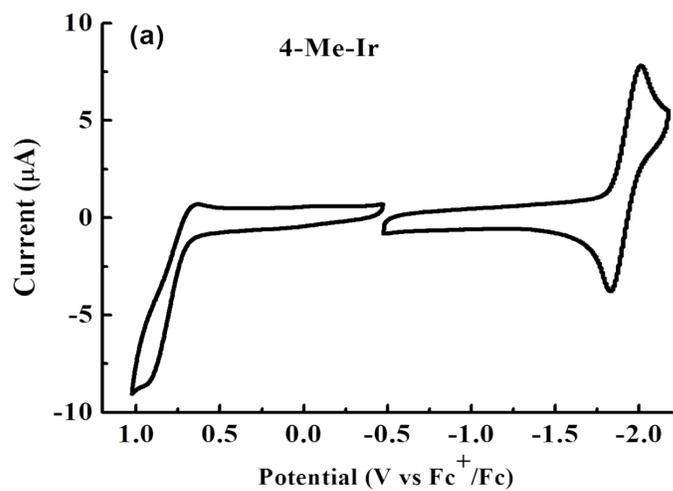
A iridium dimer [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> (ppy = phenylpyridine) (54 mg, 0.05 mmol) and ligand **3** (36 mg, 0.10 mmol) were dissolved in a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10 mL/6 mL) and stirred at 55 °C under nitrogen protection for 16 h. When cooled, the solvent was removed under reduced pressure and then redissolved in 10 mL of CH<sub>3</sub>OH. KPF<sub>6</sub> (120 mg, 0.65 mmol) in 7 mL H<sub>2</sub>O was added to get precipitation, which was filtered and washed subsequently by distilled H<sub>2</sub>O (250 mL), CH<sub>3</sub>OH (10 mL) and diethyl ether (250 mL). The purification was performed through recrystallization by vapor diffusion of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether to give **4-Styrenyl-Ir** as an orange solid (68 mg, 68%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 5.41 (d, 2H, J=11.48), 6.03 (d, 2H, J=17.64), 6.23 (dd, 2H, J=7.56&0.92), 6.82-6.89 (m, 2H), 6.93 (dt, 2H, J=7.40&1.16), 7.04 (dt, 2H, J=7.56&1.16), 7.20 (dt, 2H, J=5.92&1.28), 7.72-7.74 (m, 4H), 7.76-7.78 (m, 2H), 7.89 (d, 2H, J=5.88), 7.93-7.98 (m, 4H), 8.08-8.10 (m, 6H), 8.29 (d, 2H, J=4.83), and 9.36 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 116.46, 120.05, 122.15, 122.26, 124.01, 125.11, 125.54, 126.95, 128.03, 130.27, 131.08, 134.43, 135.76, 138.77, 139.34, 143.86, 149.08, 149.47, 149.86, 150.86, 156.01, and 166.85. *m/z* [ESI]: 861.1 ([M-PF<sub>6</sub>]<sup>+</sup>). Anal. Cal. For C<sub>48</sub>H<sub>36</sub>F<sub>6</sub>IrN<sub>4</sub>P: C, 57.31; H, 3.61; N, 5.57. Found: C, 57.54; H, 3.42; N, 5.80.

### Synthesis of Ligand 5

5-bromo-2-(pyridin-2-yl)pyridine (235 mg, 1.0 mmol), 4-styrenylphenylboronic acid (222 mg, 1.5 mmol) and sodium carbonate (420 mg) were dissolved in a mixed solvent of tetrahydrofuran (25 mL) and water (3 mL). The mixture was deoxygenated and then tetrakis(triphenylphosphine)palladium(0) (116 mg, 0.10 mmol) was added. The resultant mixture was refluxed at 80°C under nitrogen protection for 48 h. When cooled, water (50 mL) was added and the two layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent was completely removed. The residue was purified by column chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (1:0 to 1:1) as eluent to give compound **5** as a white solid (180 mg, 70%); mp 112-113 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.32 (d, 1H, J=10.84), 5.83 (d, 1H, J=17.60), 6.74-6.81 (m, 1H), 7.26-7.33 (m, 1H), 7.52-7.54 (m, 2H), 7.62-7.64 (m, 2H), 7.83 (dt, 1H, J= 7.64&1.76), 8.02 (dd, 1H, J=8.28&2.32), 8.43-8.48 (m, 2H), 8.69-8.71 (m, 1H), and 8.93 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 114.55, 120.95, 121.01, 123.65, 126.91, 127.10, 134.91, 135.94, 136.12, 136.81, 136.90, 137.48, 147.42, 149.21, 154.88, 155.82. *m/z* [ESI]: 259.1 ([M+H]<sup>+</sup>). Anal. Cal. For C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.77; H, 5.66; N, 10.91.

### The Synthesis of 3-Styrenyl-Ir

The iridium dimer [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> (107 mg, 0.10 mmol) and ligand **5** (52 mg, 0.20 mmol) were dissolved in a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10 mL/6 mL) and stirred at 55 °C under nitrogen protection for 16 h. When cooled, the solvent was removed under reduced pressure and then re-dissolved in 10 mL of CH<sub>3</sub>OH. KPF<sub>6</sub> (240 mg, 1.30 mmol) in 7 mL H<sub>2</sub>O was added to form precipitation, which was filtered and washed subsequently by distilled H<sub>2</sub>O (250 mL), CH<sub>3</sub>OH (10 mL) and diethyl ether (250 mL). The purification was performed through recrystallization by vapor diffusion of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether to give **3-Styrenyl-Ir** as an orange solid (160 mg, 89%). <sup>1</sup>H NMR (400 MHz, DMSO/d<sub>6</sub>) δ 5.33 (d, 1H, J=11.08), 5.95 (d, 1H, J=17.72), 6.24-6.30 (m, 2H), 6.72-6.79 (m, 1H), 6.90-6.98 (m, 2H), 7.02-7.09 (m, 2H), 7.14-7.20 (m, 2H), 7.37-7.39 (m, 2H), 7.56-7.58 (m, 2H), 7.67 (d, 1H, J=5.24), 7.70 (t, 1H, J=6.64), 7.82 (d, 1H, J=5.32), 7.89-7.96 (m, 5H), 8.04 (d, 1H, J=2.12), 8.26-8.30 (m, 3H), 8.60 (dd, 1H, t=8.52&2.08), 8.92 (s, 1H), and 8.94 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO/d<sub>6</sub>) δ 116.15, 119.96, 120.10, 122.27, 122.40, 123.98, 124.06, 125.04, 126.77, 127.14, 128.57, 130.20, 130.29, 131.17, 133.42, 135.54, 136.74, 138.44, 138.73, 138.78, 138.86, 139.66, 143.85, 143.91, 146.93, 148.94, 149.36, 149.85, 150.24, 150.62, 153.98, 155.09, 166.68, and 166.71. *m/z* [ESI]: 759.5 ([M-PF<sub>6</sub>]<sup>+</sup>). Anal. Cal. For C<sub>40</sub>H<sub>30</sub>F<sub>6</sub>IrN<sub>4</sub>P: C, 53.15; H, 3.35; N, 6.20; Found: C, 53.55; H, 3.63; N, 6.41.



**Figure S1.** CV plots for the as-synthesized 4-Me-Ir, 4-Styrenyl-Ir and 3-Styrenyl-Ir.