

## Energetic Requirements for Iridium(III) Complex Based Photosensitisers in Photocatalytic Hydrogen Generation

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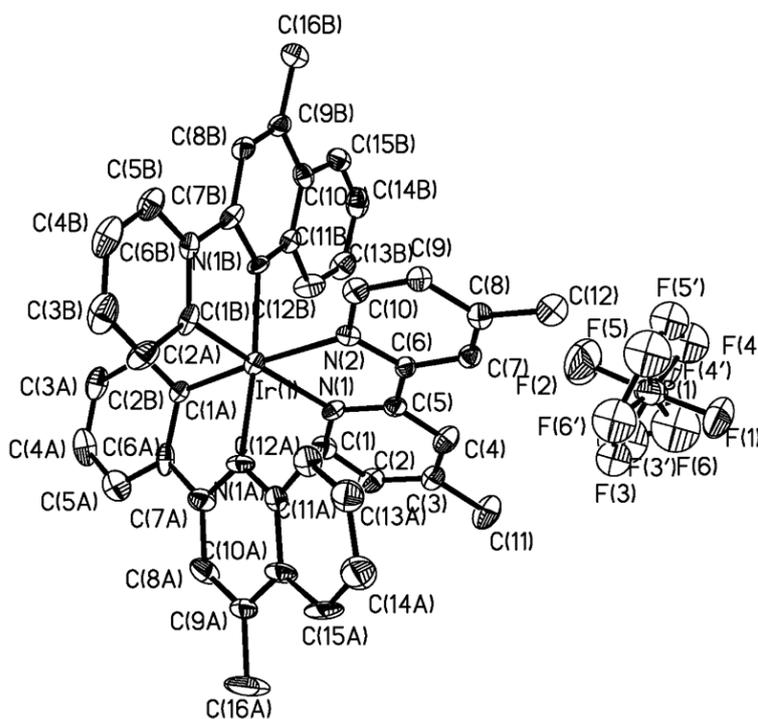
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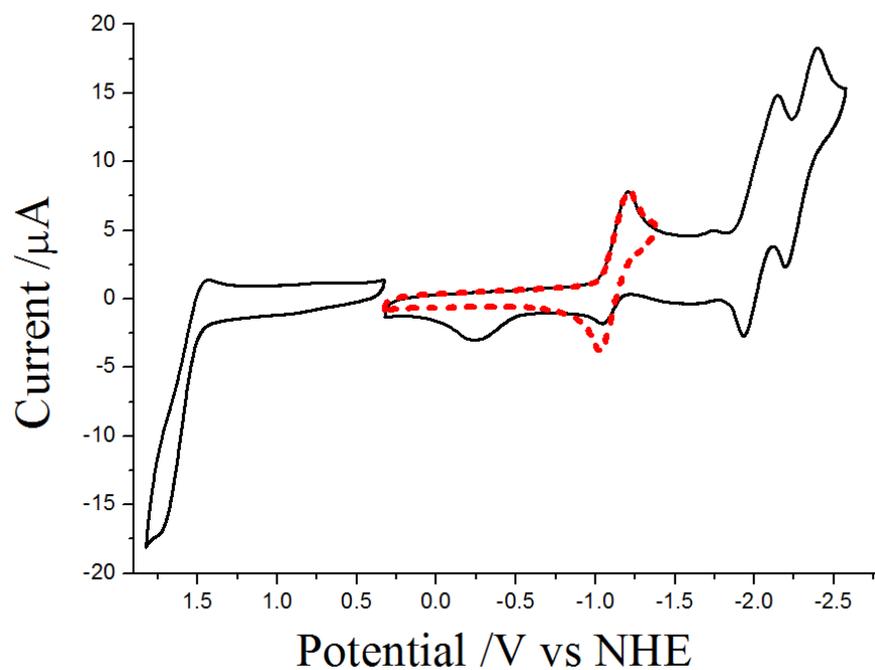
**L5.** A mixture of 2-chloro-4-methylquinoline (500 mg, 2.81 mmol), pyren-1-yl-1-boronic acid (1.03 g, 4.20 mmol), sodium carbonate (2.06 g, 19.4 mmol), toluene (30 mL), ethanol (10 mL) and water (10 mL) was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (233 mg, 0.20 mmol). The mixture was heated in an oil bath held at 100 °C under argon for 48 h. The reaction was cooled to room temperature. Water (50 mL) was added to the mixture and the two layers formed were separated. The aqueous layer was extracted with diethyl ether (3 x 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellowish solid. The crude solid was purified by column chromatography over silica using ethyl acetate/hexane (1:20) as eluent to give **L5** as a light yellow solid (950 mg, 99%); mp 170–171 °C.  $\lambda_{\text{max}}$ (dichloromethane)/nm: 237 (log $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.80), 269sh (4.56), 280 (4.60), 329sh (4.29), 349sh (4.50), 352 (4.51). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =2.85 (s, 3H), 7.62–7.69 (m, 1H), 7.71 (s, 1H), 7.77–7.84 (m, 1H), 8.03 (t, J=7.5, 1H), 8.08 (d, J=9.3, 1H), 8.11–8.16 (m, 3H), 8.18–8.24 (m, 2H), 8.25–8.33 (m, 3H), 8.45 (d, J=9.3, 1H). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$ =19.04, 123.92, 124.60, 125.00, 125.04, 125.26, 125.29, 125.32, 125.54, 126.20, 126.56, 127.16, 127.62, 127.88, 128.10, 128.26, 129.05, 129.69, 130.53, 131.11, 131.56, 131.69, 136.28, 144.56, 148.33, 159.62. *m/z* [ESI<sup>+</sup>]: 344.1 ([M+H]<sup>+</sup>). Anal. Cal. for C<sub>26</sub>H<sub>17</sub>N: C, 90.9; H, 5.0; N, 4.1. Found: C, 90.7; H, 5.1; N, 4.0.

**L6.** A mixture of 2-chloro-4-methylquinoline (500 mg, 2.81 mmol), 9-methyl-9*H*-carbazol-3-yl-3-boronic acid (1.10 g, 4.89 mmol), sodium carbonate (2.06 g, 19.4 mmol), toluene (30 mL), ethanol (10 mL) and water (10 mL) was deoxygenated before and after the addition of

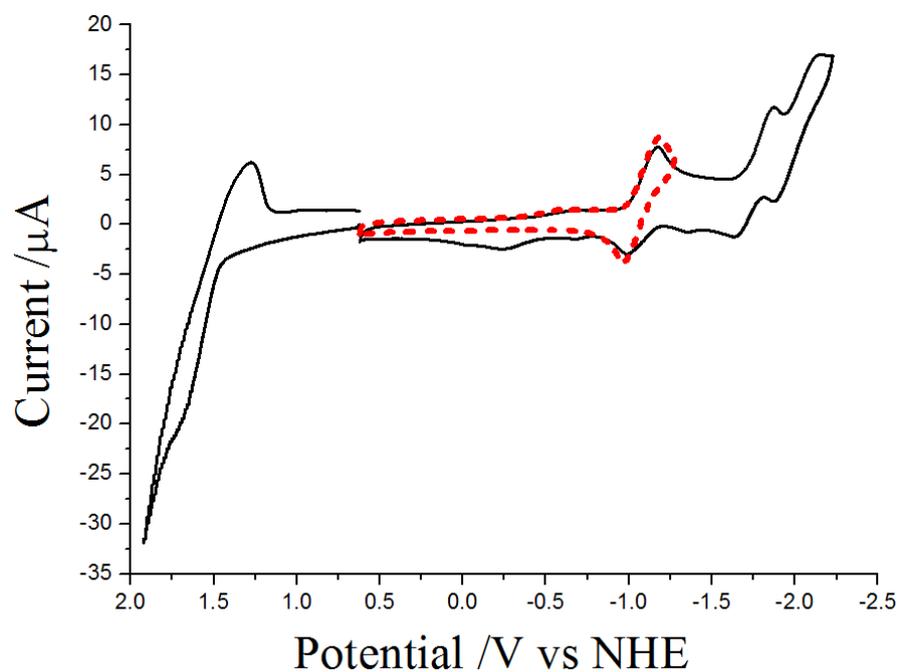
tetrakis(triphenylphosphine)palladium(0) (233 mg, 0.20 mmol). The mixture was heated in an oil bath held at 100 °C under argon for 20 h. The reaction was cooled to ambient temperature. Water (50 mL) was added to the mixture and the two layers formed were separated. The aqueous layer was extracted with diethyl ether (3 x 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was collected and the solvent was removed *in vacuo* to give a yellowish solid. The crude was purified by column chromatography over silica using ethyl acetate/hexane (1:20) as eluent to give **L6** as a white solid (858 mg, 91%); mp 177–178 °C.  $\lambda_{\text{max}}$ (dichloromethane)/nm: 245 (log $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 4.69), 252sh (4.66), 287 (4.62), 339 (4.40), 355sh (4.37), 370sh (4.28). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.81 (s, 3H), 3.91 (s, 3H), 7.29 (dt, J=7.0 & 1.0, 1H), 7.44 (d, J=8.0, 1H), 7.50–7.56 (m, 3H), 7.73 (dt, J=7.8 & 1.5, 1H), 7.89 (s, 1H), 8.01 (dd, J=8.0 & 1.5, 1H), 8.23 (dt, J=8.5 & 1.0, 1H), 8.36 (dd, J=8.5 & 2.0, 1H), 8.93 (d, J=2.0, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.21, 29.38, 108.76, 108.78, 119.41, 119.88, 119.97, 120.78, 123.33, 123.42, 123.77, 125.65, 125.69, 126.07, 127.14, 129.39, 130.12, 130.86, 141.69, 141.96, 144.69, 148.38, 157.91. *m/z* [ESI<sup>+</sup>]: 323.2 ([M+H]<sup>+</sup>). Anal. Cal. for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>: C, 85.7; H, 5.6; N, 8.7. Found: C, 85.9; H, 5.4; N, 8.5.

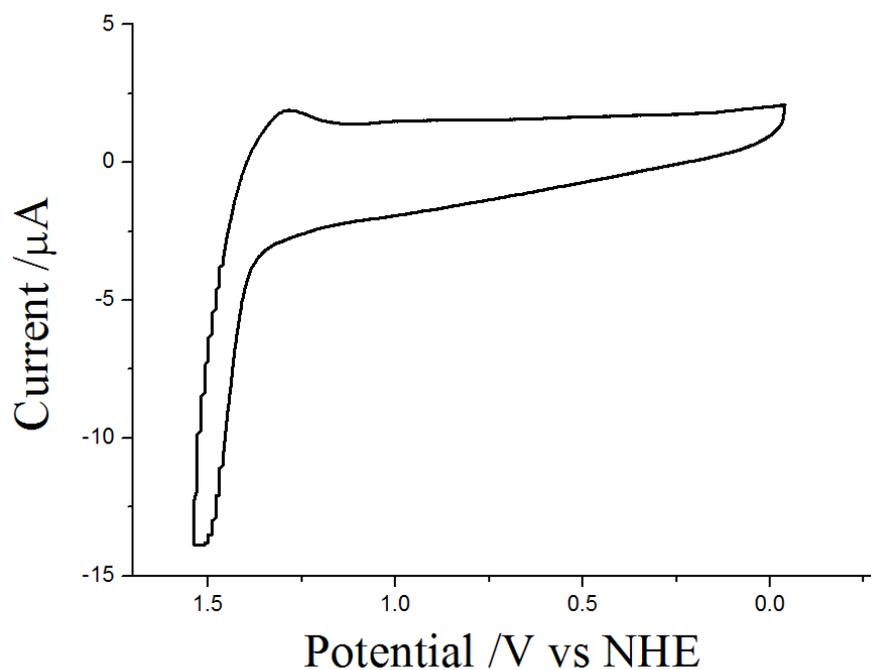


**Fig. S1.** Molecular structure of **PS3** with thermal ellipsoids at 30% probability level. Atom-numbering schemes are shown; the hydrogen atoms are omitted for clarity. Crystallographic data are available from CCDC988597 via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



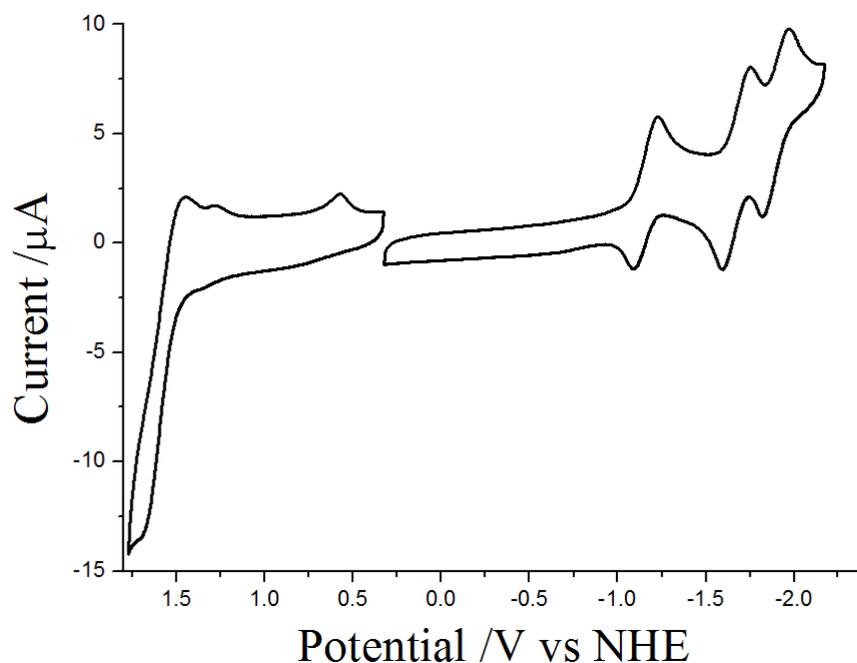
**Fig. S2.** Redox CV of Ir(III) complex **PS1**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire. The red dot curve shows the first reduction CV wave.



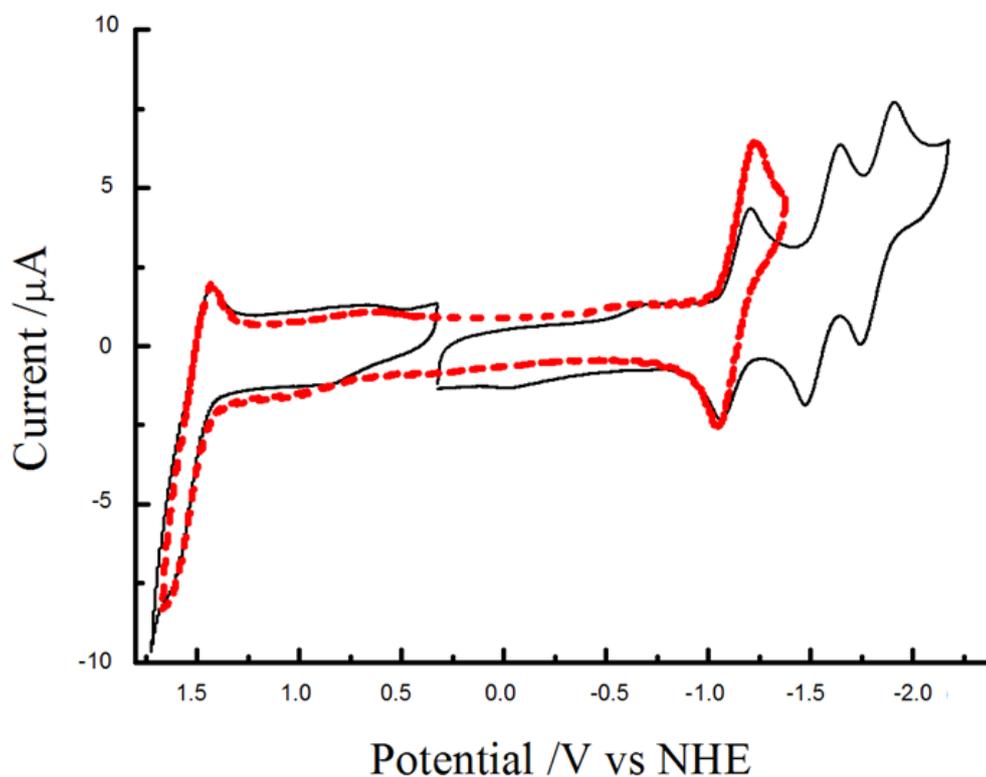


**Fig. S3.** Top: redox CV of Ir(III) complex **PS2**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire. The red dot curve shows the first reduction CV wave.

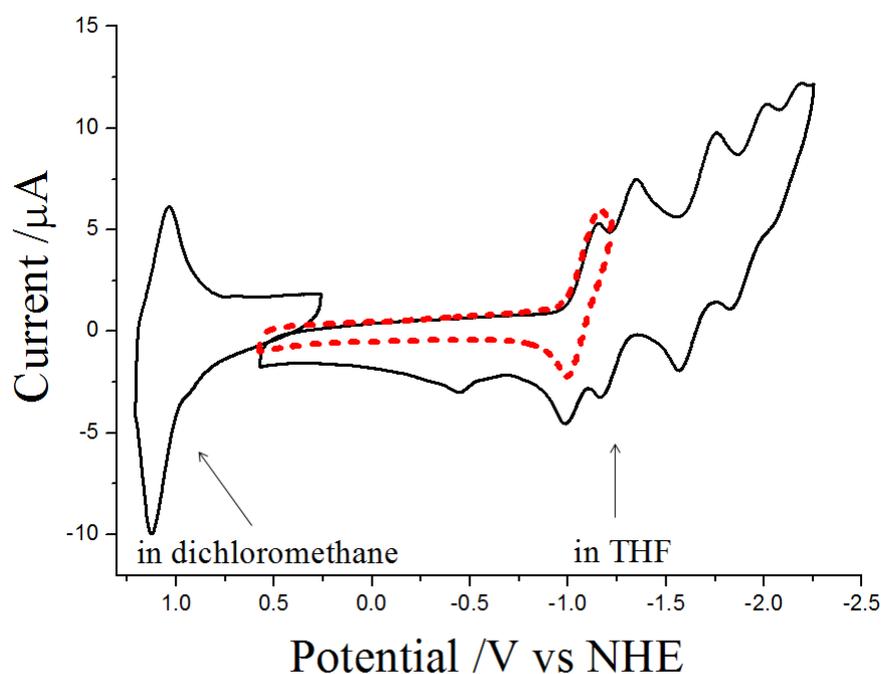
Bottom: oxidation CV of Ir(III) complex **PS2**; in 1 mM of dichloromethane solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire.



**Fig. S4.** Redox CV of Ir(III) complex **PS3**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire.

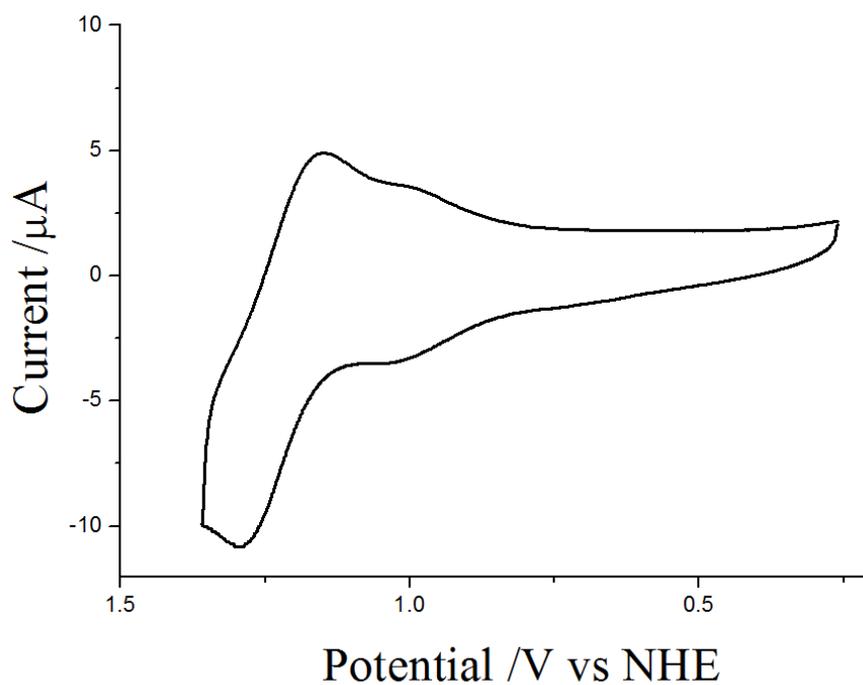
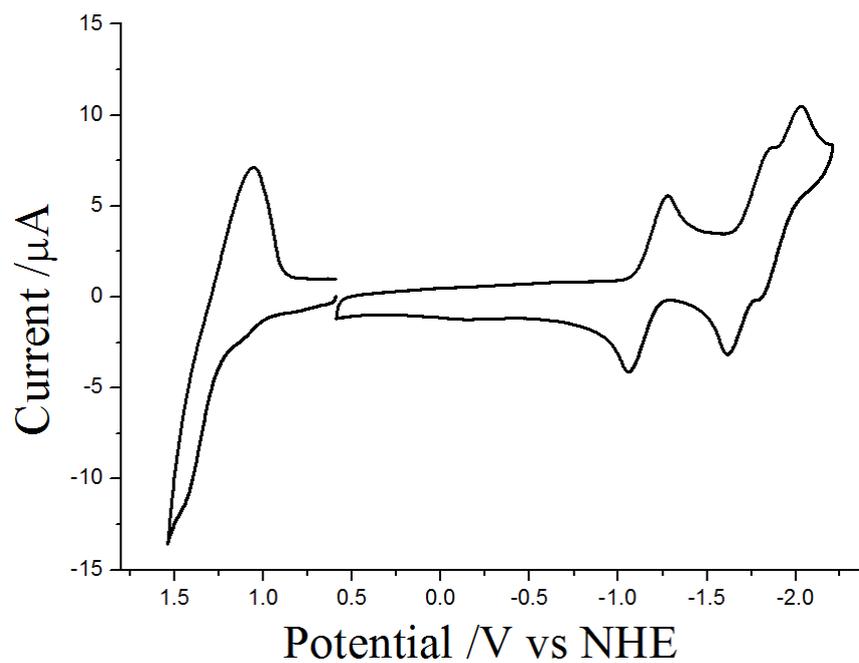


**Fig. S5.** Redox CV of Ir(III) complex **PS4**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire. The red dot curves show the first redox CV waves.



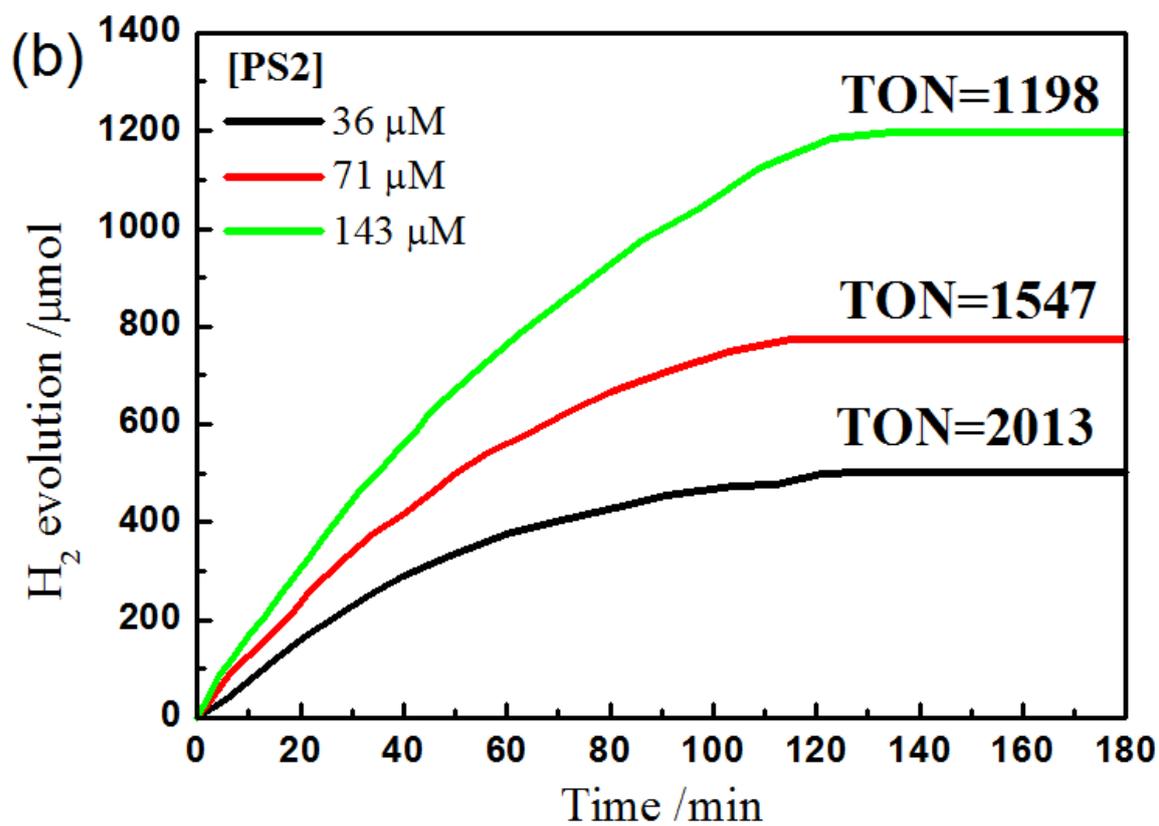
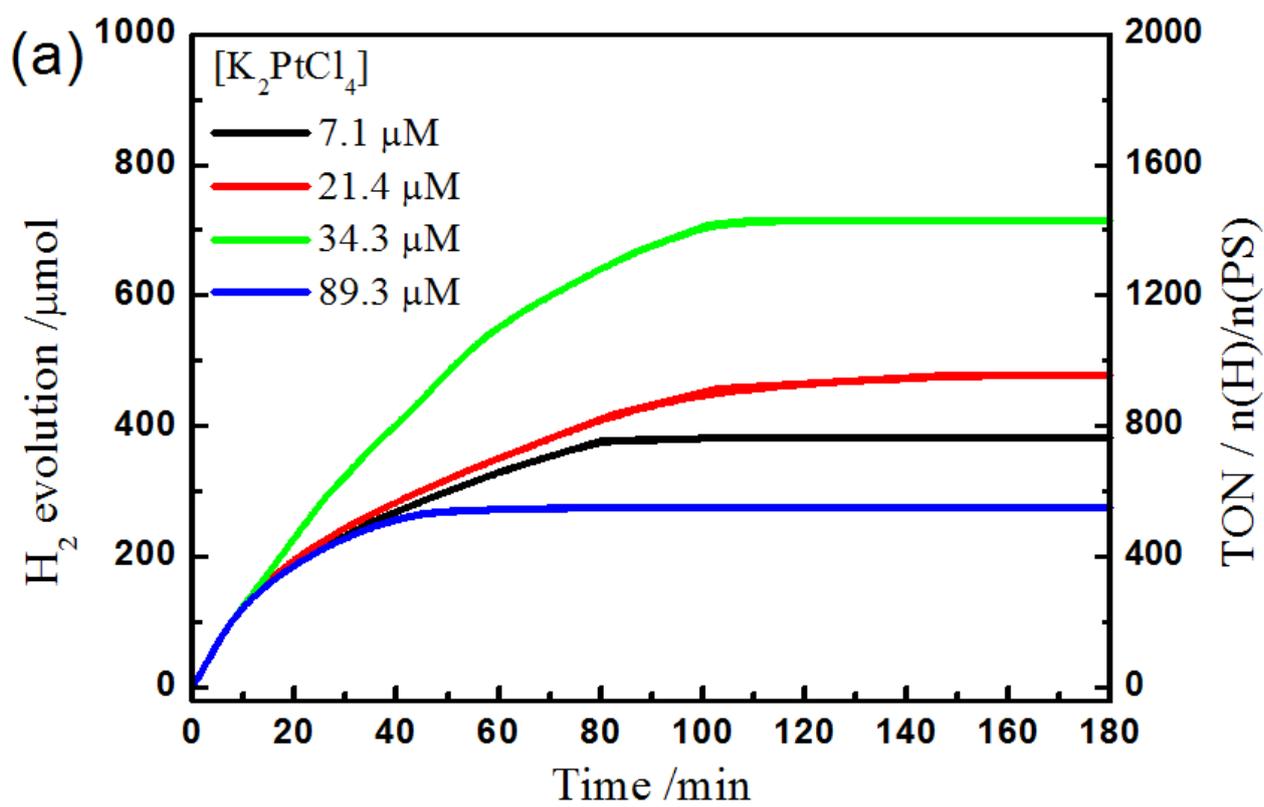
**Fig. S6.** Oxidation CV of Ir(III) complex **PS5**; in 1 mM of dichloromethane solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire.

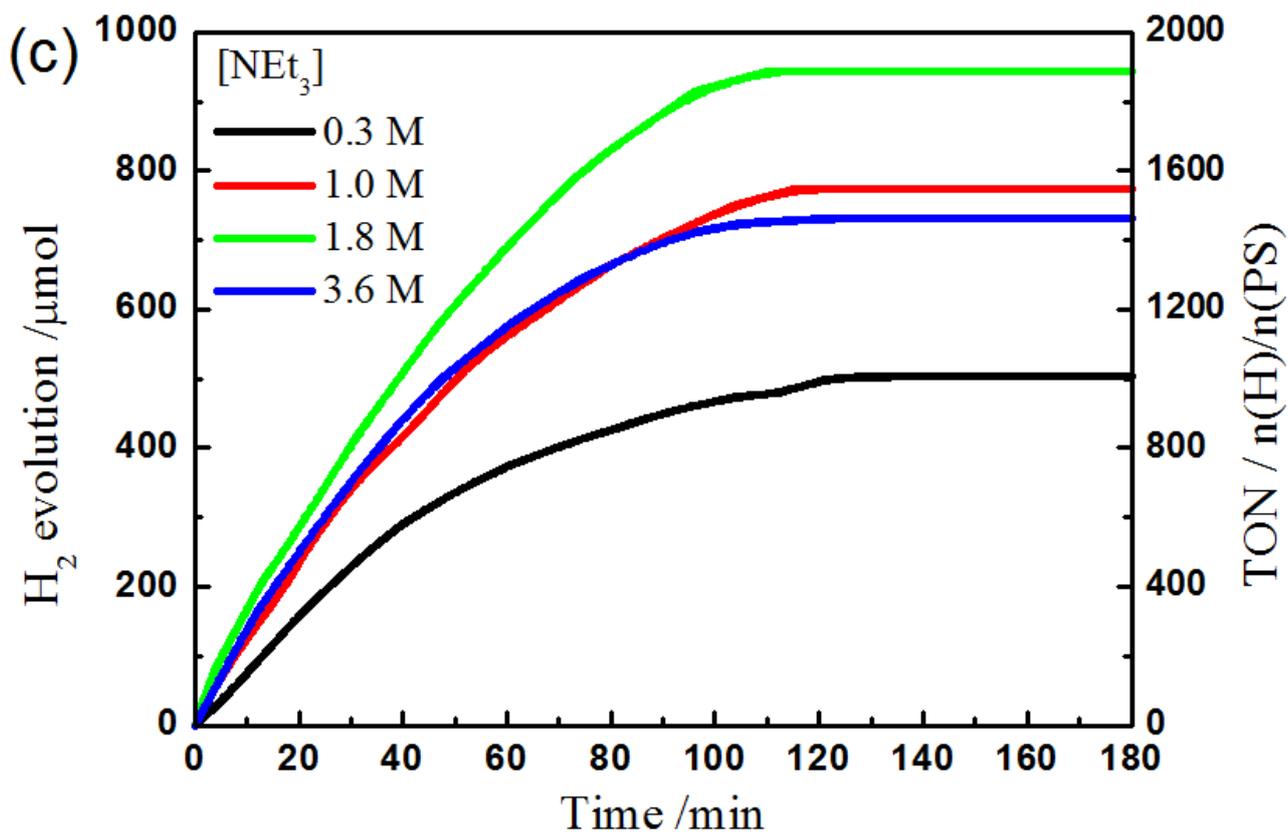
Reduction CVs of Ir(III) complex **PS5**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire. The red dot curve shows the first reduction CV wave.



**Fig. S7.** Top: redox CV of Ir(III) complex **PS6**; in 1 mM of THF solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire.

Bottom: oxidation CVs of Ir(III) complex **PS6**; in 1 mM of dichloromethane solution with 0.1 M of TBAH, scan rate =  $100 \text{ mV s}^{-1}$ , working electrode = glass carbon, counter electrode = platinum, and reference electrode = silver wire.





**Fig. S8.** Hydrogen generation in THF (10 mL)/H<sub>2</sub>O (2 mL): (a) effects of K<sub>2</sub>PtCl<sub>4</sub> concentrations in a system containing 1.0 μmol of PS2 and 2 mL of triethylamine; (b) effects of PS2 concentrations using 0.48 μmol of K<sub>2</sub>PtCl<sub>4</sub> and 2 mL of triethylamine; (c) effects of triethylamine concentrations using 1.0 μmol of PS2 and 0.48 μmol of K<sub>2</sub>PtCl<sub>4</sub>.