Electronic Supporting Information

Intrinsic Hydrogen Evolution Capability and Theoretically Supported Reaction Mechanism of Paddlewheel-type Dirhodium Complex

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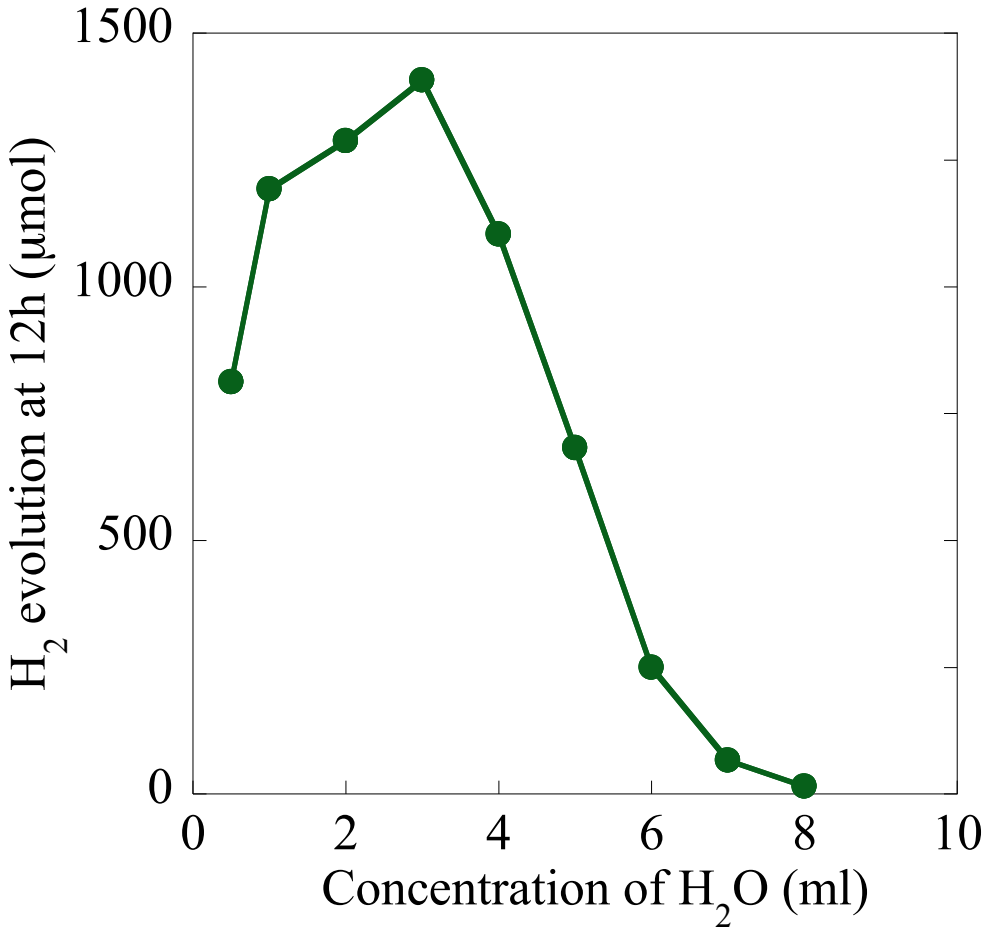

Figure S1. Total amount of hydrogen evolution at 12 h of irradiation versus concentration of H_2O (*n* mL) in the AP system. Here, the AP systems comprise 0.50 mM **[Ir-PS-1]**, 50.0 μM **[1(H$_2$O)$_2$]**, 0.5 mL TEA, *n* mL H_2O, and 9.5 – *n* mL THF.

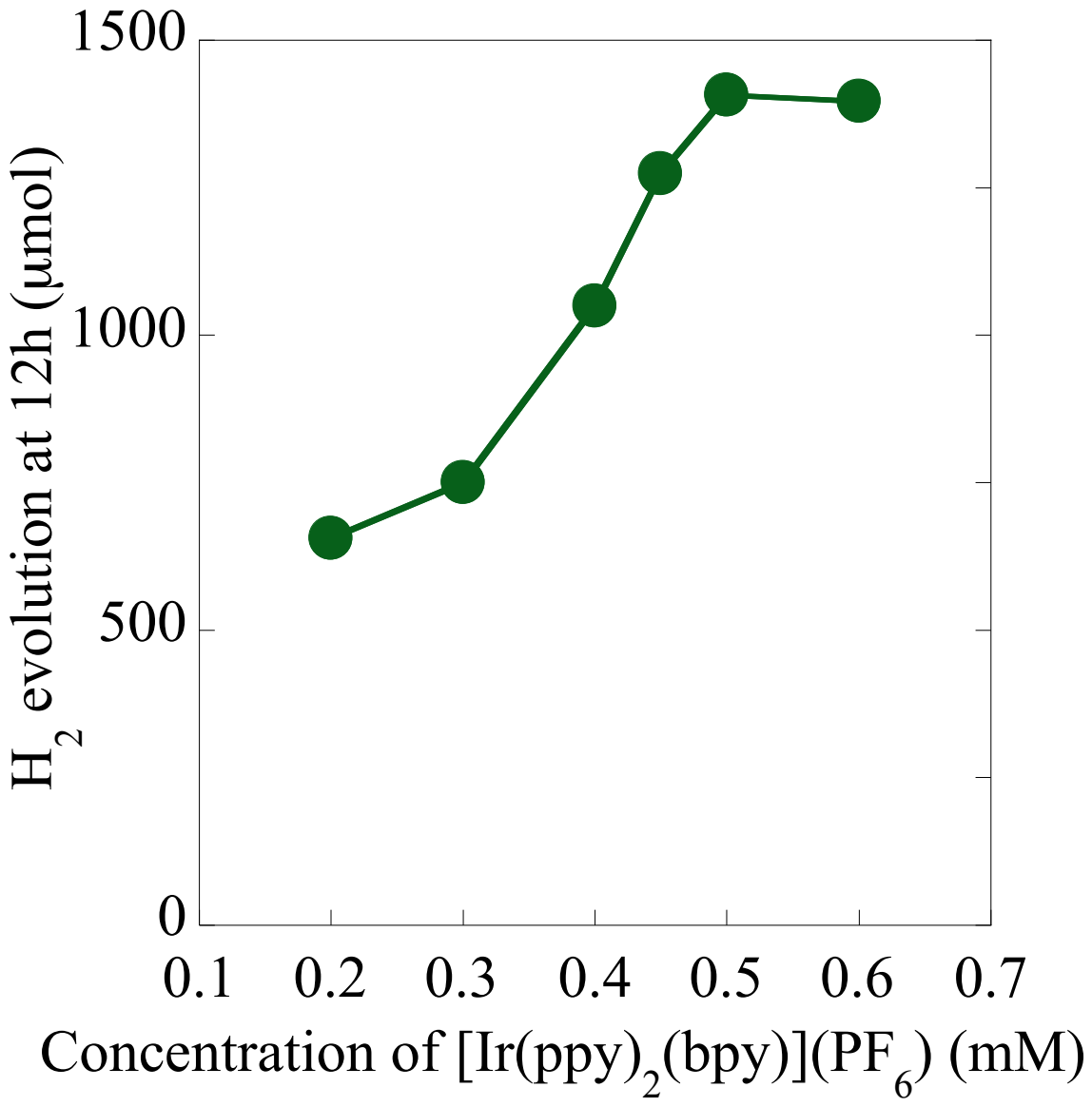

Figure S2. Total amounts of hydrogen evolution at 12 h of irradiation versus concentration of **[Ir-PS-1]** in the AP system. Here, the AP systems comprise 0.10 – 0.60 mM **[Ir-PS-1]**, 50.0 μM **[1(H_2O)$_2$]**, 0.5 mL TEA, 3.0 mL H_2O, and 6.5 mL THF.

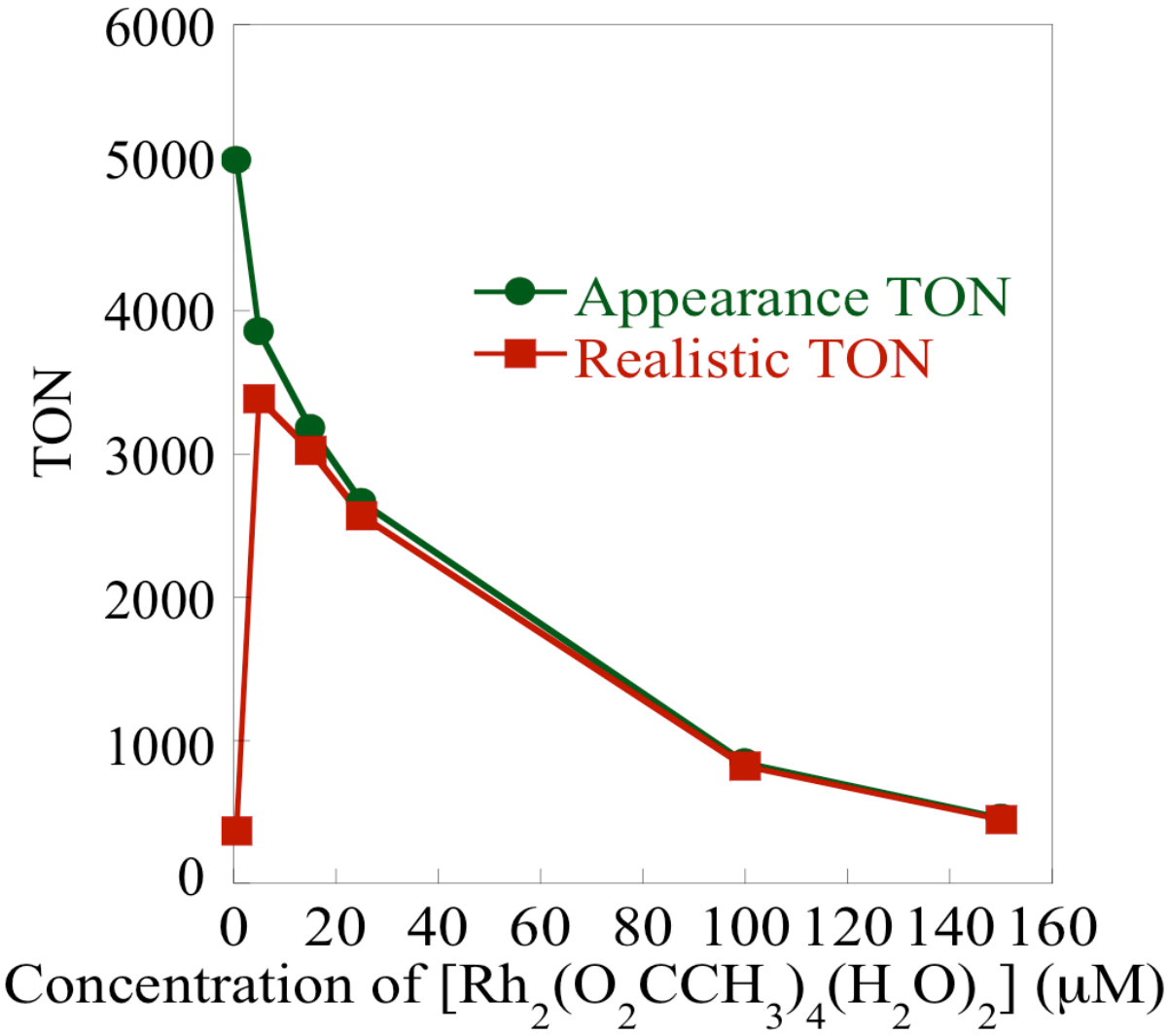

Figure S3. Total amount of H_2 evolution at 12 h of irradiation versus concentration of **[1-(H_2O)$_2$]**. The AP systems comprise 0.50 mM **[Ir-PS-1]**, 5 - 150 μM **[1(H_2O)$_2$]**, 0.5 mL TEA, 3.0 mL H_2O, and 6.5 mL THF. Here, we denoted "Appearance TON" (●) and "Realistic TON" (■). The former is total amount of hydrogen evolution (raw data) catalyzed by **[1(H_2O)$_2$]** with the AP system, and the later is the calculated amount of hydrogen evolution, which is subtracted total amount of hydrogen evolution catalyzed by the AP system without **[1(H_2O)$_2$]** from observed amount of hydrogen evolution catalyzed by **[1(H_2O)$_2$]** with AP system (raw data).

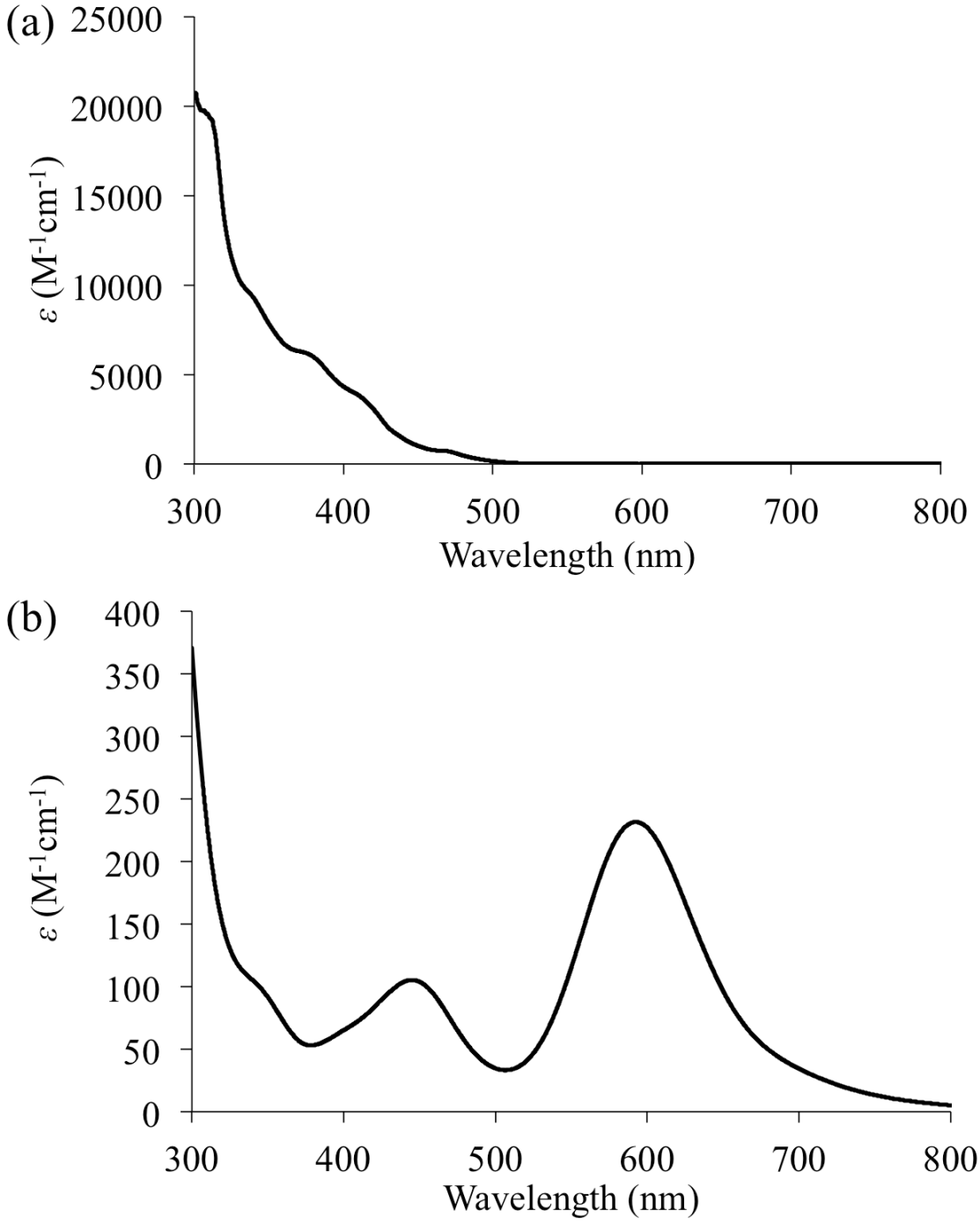

Figure S4. Absorption spectra of (a) **[Ir-PS-1]** and (b) **[1(H_2O)$_2$]** in THF/H_2O (7:3).

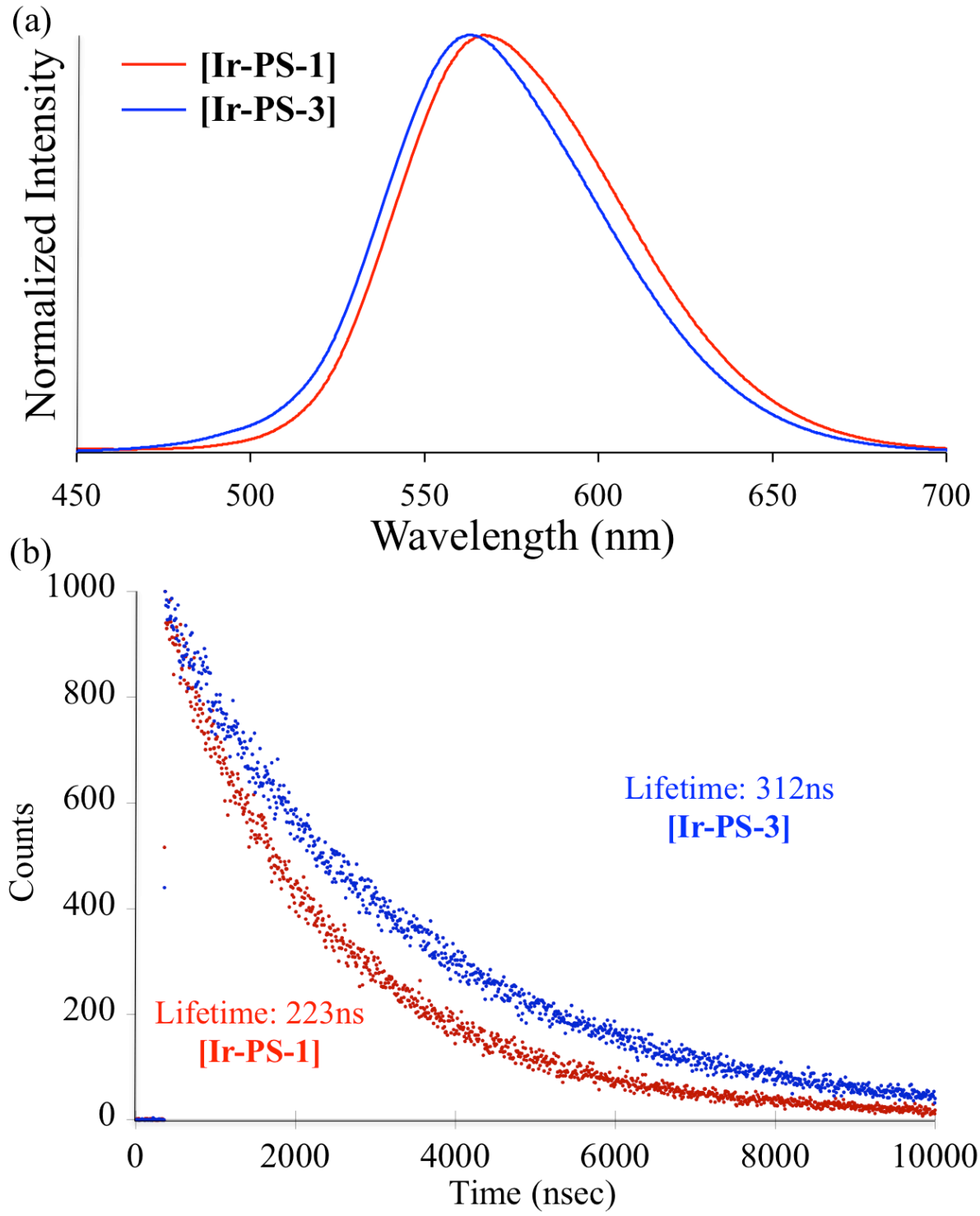

Figure S5. (a) Emission spectra and (b) decays of **[Ir-PS-1]** and **[Ir-PS-3]** in THF/H_2O (7:3).

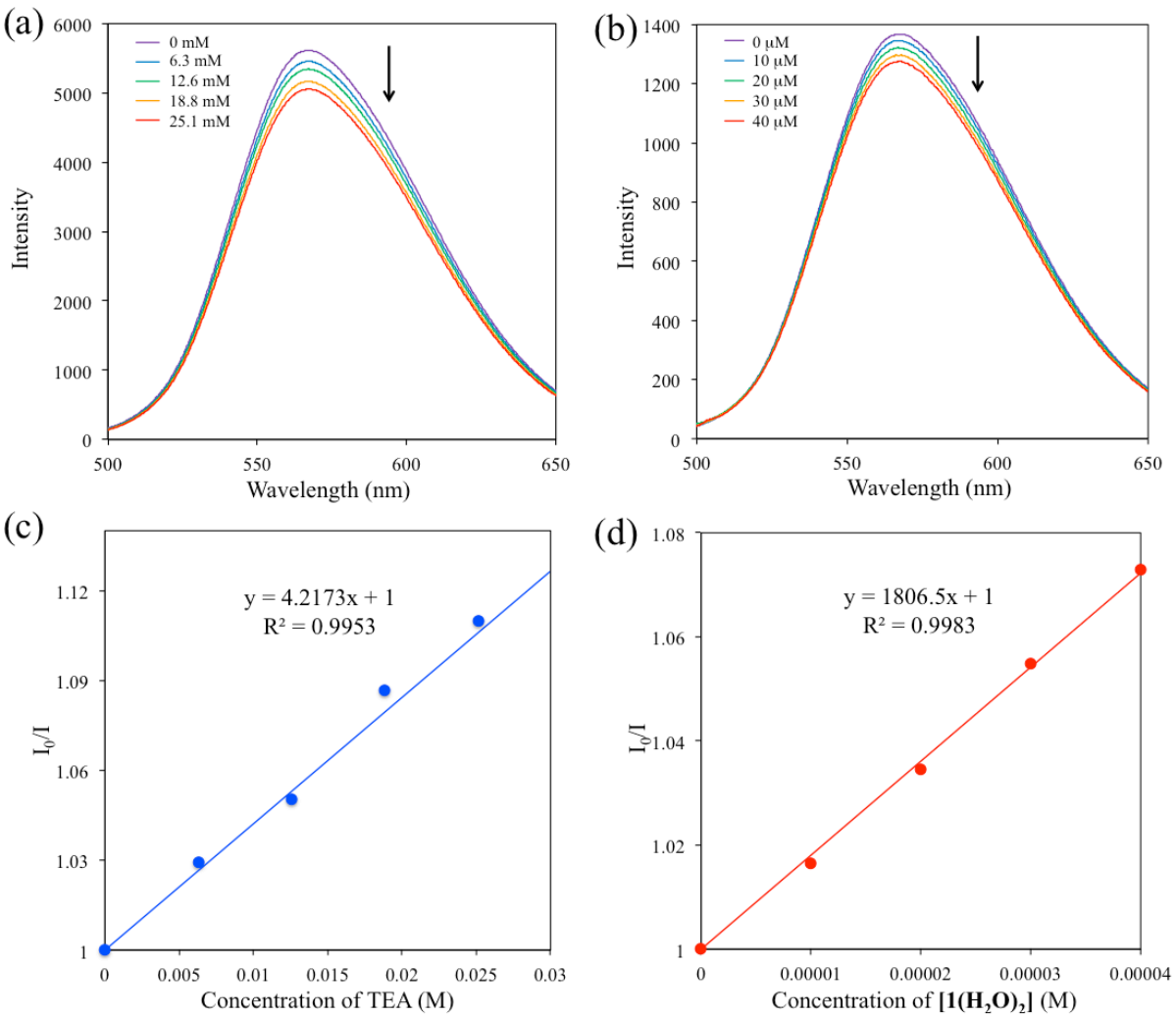

Figure S6. Emission spectra and Stern-Volmer plots of **[Ir-PS-1]** quenched by TEA ((a) and (c)) and **[1(H$_2$O)$_2$]** ((b) and (d)), respectively, in the THF/H$_2$O (7:3) solution.

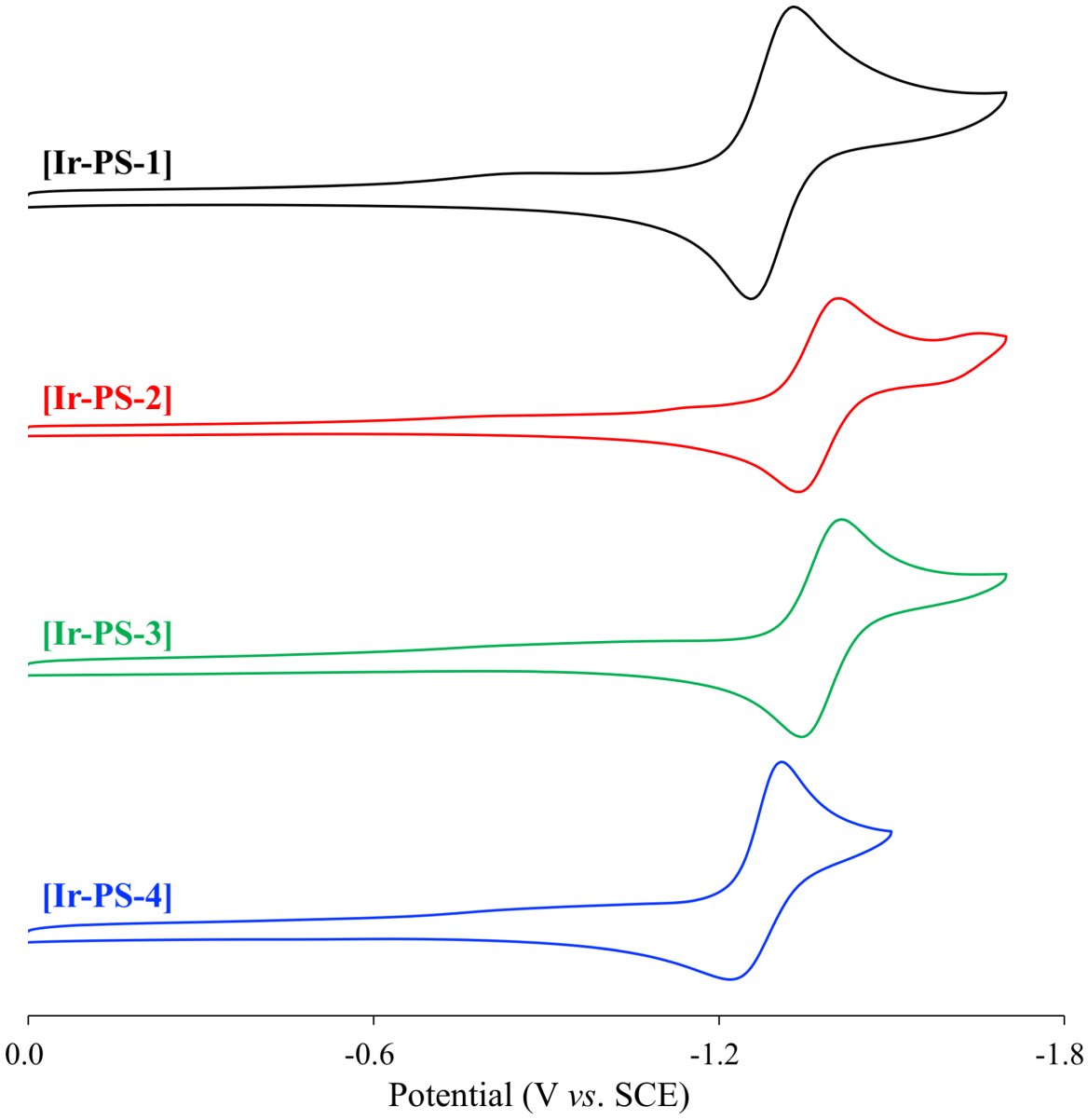

Figure S7. CV of **[Ir-PS-n]** (1.0 mM) in DMF containing the $TBAPF_6$ as a supporting electrolyte.

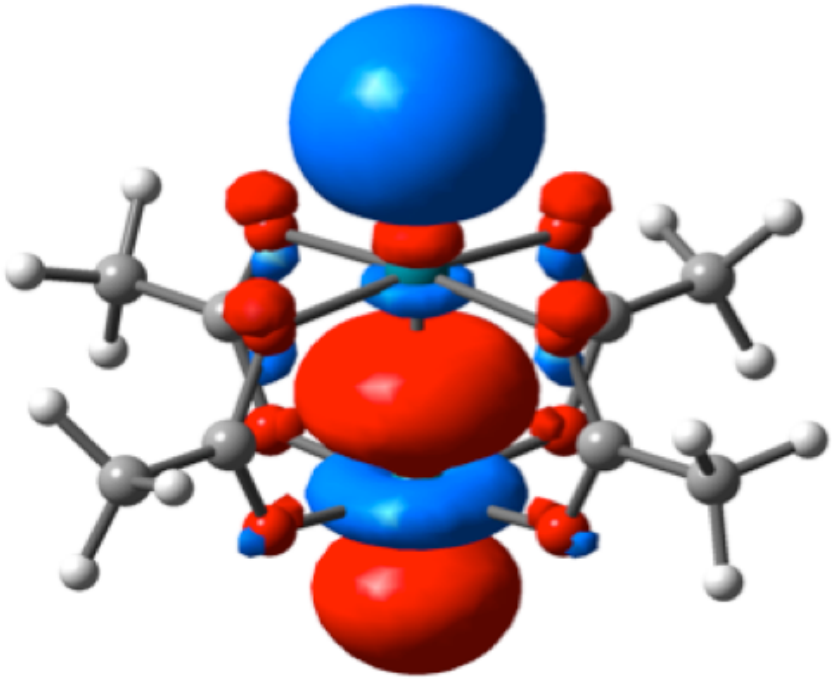

Figure S8. LUMO of the **[H-1]**.

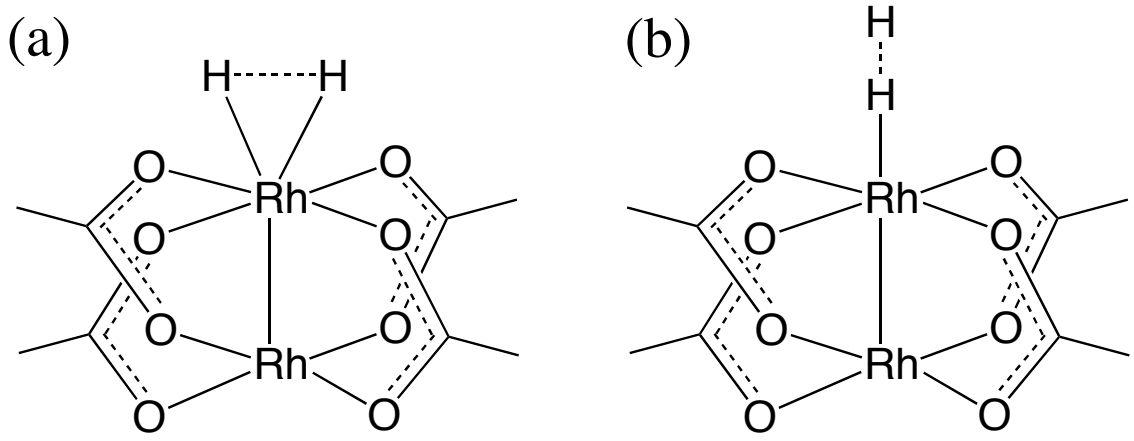

Figure S9. Molecular structures of possible **[2H-1]** intermediates. (a) Side-on structure and (b) top-on structure.

Table. S1. Total amount of H_2 evolution and TON of catalysis using AP system containing **[Ir-PS-1]** (0.50 mM), **[1(H_2O)$_2$]** (5.0 μM), and 1:6:13 (v/v/v) of the TEA/H_2O/organic solution (10.0 mL) after 12 h photo-irradiation.

Solvents	H_2 evolution (μmol)	TON (per Rh ion)
THF	385.7	3857
DMF	344.3	3443
Acetone	356.9	3569
DMSO	16.6	166
Acetonitrile	23.8	238