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$_2$O ($n$ mL) in the AP system. Here, the AP systems comprise 0.50 mM [Ir-PS-1], 50.0 µM [I(H$_2$O)$_3$], 0.5 mL TEA, $n$ mL H$_2$O, 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(H2O)₂], 0.5 mL TEA, 3.0 mL H2O, and 6.5 mL THF.
Figure S3. Total amount of H₂ evolution at 12 h of irradiation versus concentration of [1-(H₂O)₂].

The AP systems comprise 0.50 mM [Ir-PS-1], 5 - 150 µM [1(H₂O)₂], 0.5 mL TEA, 3.0 mL H₂O, 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(H₂O)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(H₂O)₂] from observed amount of hydrogen evolution catalyzed by [1(H₂O)₂] with AP system (raw data).
Figure S4. Absorption spectra of (a) [Ir-PS-1] and (b) [1(H2O)2] in THF/H2O (7:3).
Figure S5. (a) Emission spectra and (b) decays of [Ir-PS-1] and [Ir-PS-3] in THF/H₂O (7:3).
Figure S6. Emission spectra and Stern-Volmer plots of [Ir-PS-1] quenched by TEA ((a) and (c)) and [1(H₂O)₂] ((b) and (d)), respectively, in the THF/H₂O (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$_2$O)$_2$] (5.0 µM), and 1:6:13 (v/v/v) of the TEA/H$_2$O/organic solution (10.0 mL) after 12 h photo-irradiation.

<table>
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<tr>
<th>Solvents</th>
<th>H$_2$ evolution (µmol)</th>
<th>TON (per Rh ion)</th>
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<tr>
<td>THF</td>
<td>385.7</td>
<td>3857</td>
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<tr>
<td>DMF</td>
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<tr>
<td>Acetone</td>
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<tr>
<td>DMSO</td>
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<tr>
<td>Acetonitrile</td>
<td>23.8</td>
<td>238</td>
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