Supporting information

For

Large Improvement in Catalytic Activity due to Small Changes in Diimine ligands: New Mechanistic Insight into the Dirhodium(II, II) Complex-based Photocatalytic H₂ Production

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Figure S1. The absorption spectrum changes of Rh$_2$phen$_2$ and Rh$_2$bpy$_2$ in THF/water (8:2, v/v) solutions upon addition and then removal of Hg.
Figure S2. Stern-Volmer plots for the luminescence lifetime quenching of the Ir-based photosensitizer by (a) Rh2phen2, (b) Rh2bpy2, and (c) TEA.
Figure S3. Transient absorption spectra of the multi-component systems based on Rh$_2$phen$_2$ and Rh$_2$bpy$_2$, respectively, that had underwent 20 h of irradiation for photocatalytic H$_2$ production. The spectra were recorded 1 µs after the laser irradiation at 420 nm. [Ir] = 0.05 mM, [TEA] = 0.6 M, [Rh-based catalyst] = 0.05 mM.
**Figure S4.** Absorption spectrum changes of the THF/water (8:2, v/v) solutions of 0.05 mM Rh<sub>2</sub>phen<sub>2</sub> (a) and 0.05 mM Rh<sub>2</sub>bpy<sub>2</sub> (b) during 9 h of irradiation.