

Supporting Information

Homogeneous photocatalytic production of hydrogen from water by a bioinspired [Fe₂S₂] catalyst with high turnover numbers

Pan Zhang,^a Mei Wang,^{*a} Yong Na,^a Xueqiang Li,^a Yi Jiang^a and Licheng Sun^{*a,b}

^a State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian, 116012, China, Fax: +86 411 83702185; Tel: +86 411 88993886; E-mail: symbuono@dlut.edu.cn

^b Department of Chemistry, Royal Institute of Technology (KTH), 10044, Stockholm, Sweden

Experimental Section

Materials

All reactions were carried out under N₂ atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. 2,2'-bipyridyl (bpy) and 2-phenylpyridine (ppy) were purchased from Aldrich and used as received. Photosensitizers [Ir(ppy)₂(bpy)]PF₆ and [Ru(bpy)₃](PF₆)₂ were synthesized according to the literature procedures.^{1,2} Complex [{(μ-SCH₂)₂NCH₂C₆H₅}{Fe(CO)₃}{Fe(CO)₂P(Pyr)₃}] (**1**) was synthesized as in the previous report.³

Methods and instruments

In a typical experiment, [Ir(ppy)₂(bpy)]PF₆ (0.5 mL, 2 × 10⁻⁴ M), complex **1** (0.5 mL, 1 × 10⁻³ M) and CH₃COCH₃ (8 mL) were added to a Schlenk bottle. The mixture

was magnetically stirred under N₂ atmosphere for 5 min before water (1 mL) and TEA (0.2 mL) were added. The solution was freeze-pump-thaw degassed for three times and then warmed to room temperature prior to irradiation. The gas phase volume in the bottle is 59 mL and the total amount of hydrogen gas evolved in the photocatalytic reaction is no more than 1 mL. The reaction solution was irradiated at 25 °C using a Xe lamp (500 W) with a filter ($\lambda > \text{ca. } 400 \text{ nm}$). The gas phase of the reaction system was analyzed on a GC 7890T instrument with a 5 Å molecular sieve column, a thermal conductivity detector, and with N₂ as carrying gas. The amount of hydrogen generated was determined by the external standard method. Hydrogen in the resulting solution was not measured and the slight effect of the hydrogen gas generated on the pressure of the Schlenk bottle was neglected for calculation of the volume of hydrogen gas.

Steady-state absorption measurements were carried out on a Jasco-V-530 spectrophotometer. Samples of the iridium and ruthenium chromophores were purged with Ar gas for 15 min. Photoluminescence spectra were recorded using a Spex Fluorolog fluorimeter by exciting at 420 nm.

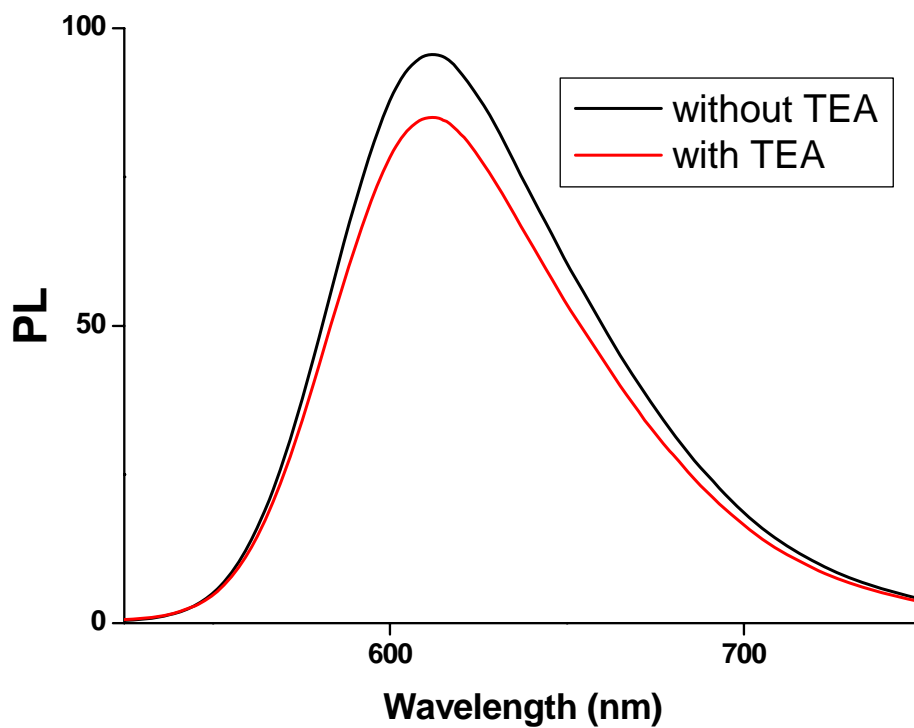


Fig. S1 Photoluminescence spectra of [Ru(bpy)₃]²⁺ (2×10^{-5} M) in acetone with (red) or without (black) TEA (0.3 M).

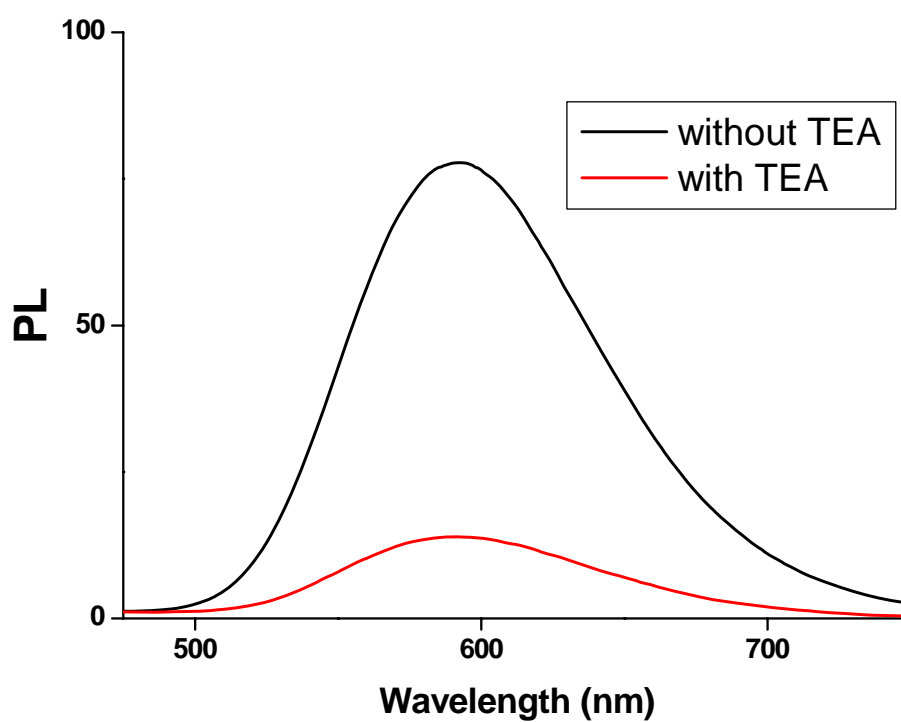


Fig. S2 Photoluminescence spectra of [Ir(ppy)₂(bpy)]⁺ (2×10^{-5} M) in acetone with (red) or without (black) TEA (0.3 M).

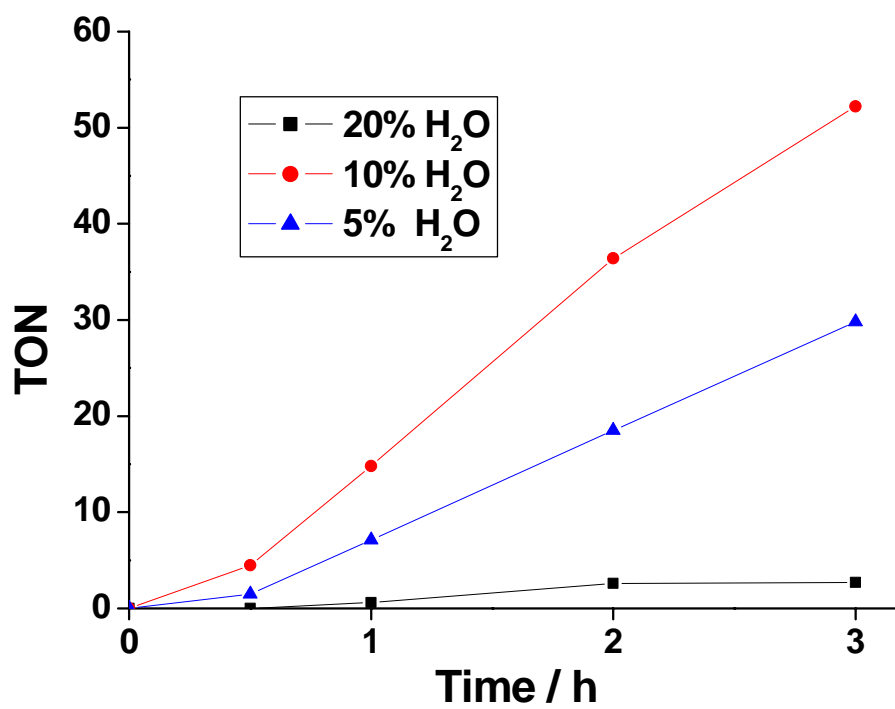


Fig. S3 Evolution of H₂ generated by the system at different acetone/water ratio during 3 h irradiation experiment.

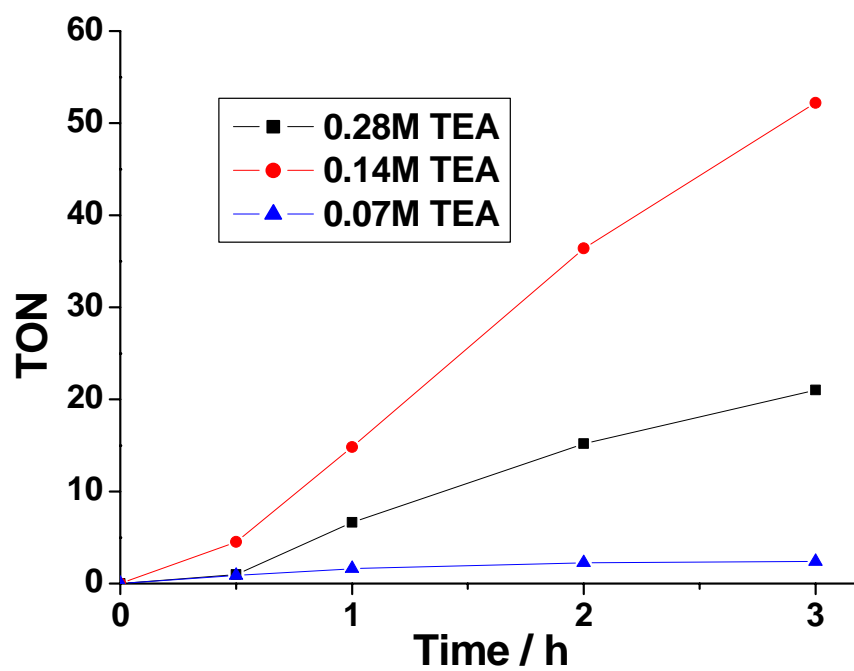


Fig. S4 Evolution of H₂ generated by the system at the different concentration of TEA during a 3 h irradiation in acetone/water (9:1 v/v).

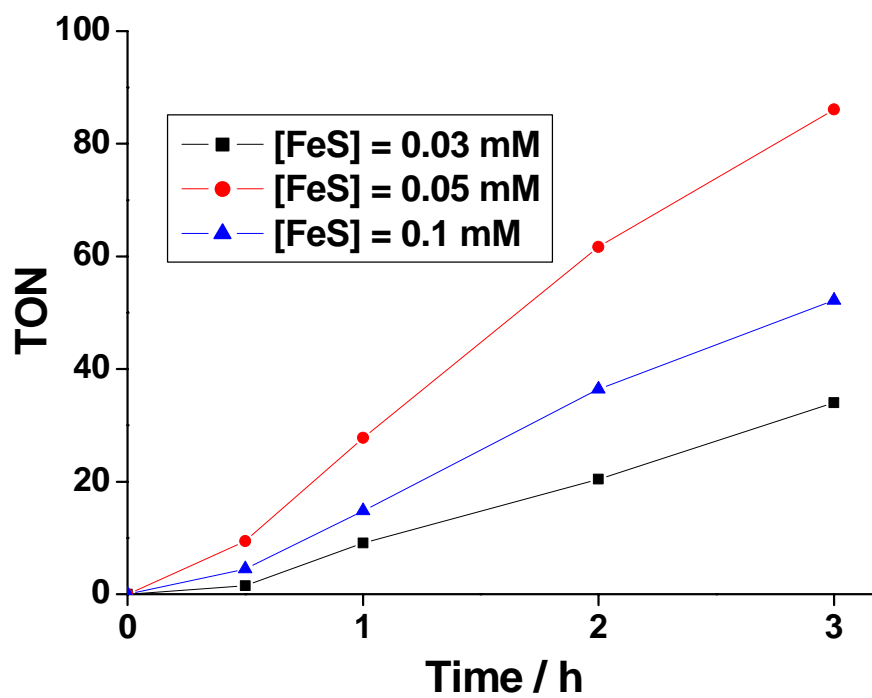


Fig. S5 Evolution of H_2 generated by the system at the different concentration of $[2Fe_2S]$ catalyst during a 3 h irradiation experiment in acetone/water solution.

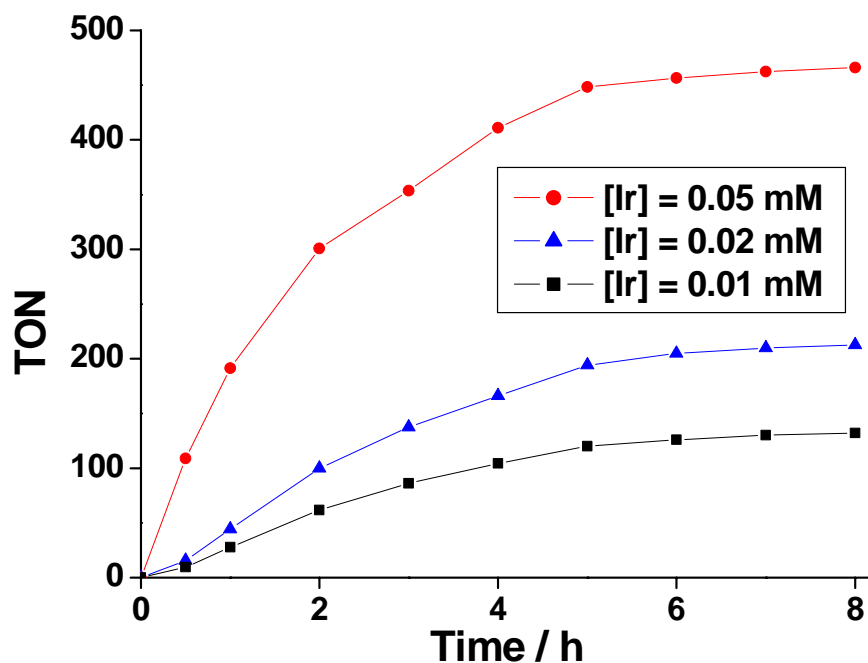


Fig. S6 Evolution of H₂ generated by the system at the different concentration of [Ir(ppy)₂(bpy)]⁺ during a 8 h irradiation experiment in acetone/water solution.

References:

- [1] Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.
- [2] Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334–3341.
- [3] Na, Y.; Wang, M.; Pan, J.; Zhang, P.; Åkermark, B.; Sun, L. *Inorg. Chem.* **2008**, *47*, 2805–2810.