Supporting Information

Efficient Photo-driven Hydrogen Evolution by Binuclear Nickel Catalysts of Different Coordination in Noble-metal-free Systems

Hong-hua Cui, Jin-yun Wang, Ming-qiang Hu, Cheng-bing Ma, Hui-min Wen, Xiao-wei Song, Chang-neng Chen*

* Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian, China, E-mail: <u>ccn@fjirsm.ac.cn</u>; Fax: 35002



Fig. S1 Time dependence of H₂ evolution from the systems containing **C1** (0.2 mM) and TEA (5% v/v) in CH₃CN-H₂O (v/v 1:1) solution (pH = 11) upon irradiation (>400 nm) with EB (2 mM), RB (2 mM), EY (2 mM) and Fl (2 mM).



Fig. S2 Time dependence of H_2 evolution from the systems containing C2 (0.2 mM) and TEOA (5% v/v) in CH₃CN-H₂O (v/v 1:1) solution upon irradiation (>400 nm) with EB (2 mM) and EY (2 mM).



Fig. S3 Absorption spect ra of the system containing $Fl(1.0 \times 10^{-6} \text{ M})$ and TEOA (0.5% v/v) in CH₃CN-H₂O (v/v 1:1) solution upon irradiation (>400 nm).



Fig. S4 Absorption spectra of the system with $Fl(1.0 \times 10^{-6} \text{ M})$ containing **C2** ($1.0 \times 10^{-6} \text{ mM}$) and TEOA (0.5% v/v) in CH₃CN-H₂O (v/v 1:1) solution upon irradiation (>400 nm).



Fig. S5 Absorption spectra of system with EY $(2.0 \times 10^{-6} \text{ M})$ containing TEOA (0.5% v/v) in CH₃CN-H₂O (v/v 1:1) solution upon irradiation (>400 nm).



Fig. S6 (a) Cyclic voltmmogram of the complex **C2** (1 mM) was obtained at the scan rate of 0.1 V s⁻¹ in the CH₂Cl₂ solution, which indicated that there were no redox reactions of **C2** in the range of the electrochemical reaction of ferrocene. (b) Cyclic voltmmograms of the first reduction process of **C2** using the equivalent ferrocene (0.5 mM) as the internal standard with the integral areas (Ah) of 9.587e-6 C for the reduction process of **C2** and 9.473e-6 C for the one of ferrocene, respectively.



Fig. S7 Cyclic voltammograms of MBT (1 mM) (black) and MBD (1 mM) (red) at a scan rate of 100 mV s^{-1} .



Fig. S8 Cyclic voltammograms of **C1** (1 mM) with the initial scanning voltage of -1.73 V (vs. Fc^{+}/Fc) at a scan rate of 100 mV s⁻¹.



Fig. S9 Absorption spectra of C1 and C2 $(2.0 \times 10^{-6} \text{ mM})$ with the addition of HOAc in CH₃CN-H₂O (v/v 1:1) solution upon irradiation (>400 nm).