Supporting Information

Light-driven Hydrogen Evolution with A Nickel Thiosemicarbazone Redox Catalyst Featuring Ni····H interactions under Basic Conditions

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Figure S1 Photocatalytic H₂ evolution in 1:1 EtOH/H₂O of the systems containing Co-thiop (10.0 μM), Fl (2.0 mM), TEA (10% v/v) at different pH values (left picture) and of the systems containing Co-thiop (10.0 μM), Fl (2.0 mM) at pH 12.5 with various TEA concentration (right one).

Figure S2 Initial rates of H₂ production in EtOH/H₂O (1:1) at pH 12.5 with 10% of TEA of systems containing Co−thiop (10.0 μM) with the concentration of Fl was 1.0 mM, 1.5 mM, 2.0 mM, 3.0 mM and 4.0 mM, respectively (left picture); and of the systems containing Fl (2.0 mM) with the concentration of Co−thiop was 5.0μM, 10.0μM, 15.0μM and 20.0μM, respectively (right one).
Figure S3  Family of the emission spectra of fluorescein solution (10 μM) in 1:1 EtOH/H₂O solution upon addition of TEA with various concentration at pH 12.51 (left picture) and The best-fit equation of the Stern-Volmer plot (right one).

Figure S4  UV/vis absorption spectra of aliquots taken during the course of the photolysis, Left picture: containing Co−thiop (10.0 μM), Fl (2.0 mM), with 10% of TEA in EtOH/H₂O. The right one: containing Co−thiop (50.0 μM), Fl (2.0 mM), with 1% of TEA in EtOH/H₂O.
Figure S5 UV/vis absorption spectra of aliquots taken during the course of the photolysis, Left picture containing Ni\textsuperscript{-}thiop (10.0 μM), Fl (2.0 mM), with 5% of TEA in EtOH/H\textsubscript{2}O. The right one containing Ni\textsuperscript{-}thiop (50.0 μM), Fl (2.0 mM), with 2% of TEA in EtOH/H\textsubscript{2}O.

Figure S6 Family of the emission spectra of fluorescein solution (10 μM) in 1:1 EtOH/H\textsubscript{2}O solution upon addition of Ni\textsuperscript{-}thiop with various concentration at pH 12.51 (left picture) and The best-fit equation of the Stern-Volmer plot (right one).
Figure S7. Family of Uv-vis absorption spectra of Ni-thiop (20.0 µM) at different pH values in 1:1 EtOH/H2O solution (left picture) and the best-fitting of the titration plot indicating a pKa of 12.58 (right one).

Figure S8 The volumes and Initial rates of H2 production in EtOH/H2O (1:1) at pH 12.5 with 5% of TEA of systems containing Ni-thiop (10.0 µM) with the different concentration of Fl
Figure S9 Spin density of reduced Ni–thioP: isovalue is 0.002 a.u. for spin density.

Figure S10 Potential structure of the proton reduction intermediate of the reduced Ni–thioP