Supporting Information

Title: Incorporation of Iron Hydrogenase Active Site into Highly Stable Metal–Organic for Photocatalytic Hydrogen Generation

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Chemicals and Instrumentation:

Pyrrole, elemental sulfur, propionic acid, N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), benzoic acid, acetone, iron pentacarbonyl and zinc (II) chloride, zirconyl chloride octahydrate and ect have been purchased from Sigma-Aldrich.

Powder X-ray diffraction data (XRD) were collected using a Bruker D8-Advance powder diffractometer operating at 40kV, 40mA for Cu Kα radiation (λ=1.5406 Å). The scanning electron microscopy (SEM) images were obtained on Philips XL30 FEG with the accelerating voltage at 10 kv. The sorption isotherms of N2 were measured by using a Micromeritics ASAP 2020 surface-area and pore-size analyzer.Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. Thermogravimetry analysis (TGA) was conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer.The fluorecence epxeriment performed at excitation wavelength of 550nm by Spex Fluorolog Tau-3 fluorescence spectrophotometer.The FTIR specroscopy data were collected using a Nicolet 6700 FT-IR Spectromete.

Synthesis of complex $Fe_2S_2(CO)_6$:

$Fe_2S_2(CO)_6$ was prepared as described b by Hieber and Gruber. A three neck, 5-liter round-bottomed flask was fitted with a good mechanical stirrer and a nitrogen inlet tube was flushed with nitrogen for 15 min and charged with 200 mL of methanol and 35 mL (250 mmol) of iron pentacarbonyl. The solution was cooled to 0 °C with an ice bath before 80 mL of 50% aqueous KOH (w/v) were added dropwise to the reaction over the course of 30 min. To this mixture ($HFe(CO)_{4-}$) was added 83 g (2.7 mol) of elemental sulfur, delivered in two portions over 10 min. ***Caution: this step is extremely vigorous with formation of CO***. The black mixture was stirred for 30 min at 0 °C, then a degassed solution of 400 ml of 50% HCl (200 mL of 37% HCl and 200 mL of distilled H_20) were added to the reaction flask. ***Cautious: acidification of the reaction mixture resulted in the evolution of H_2S.*** The ice bath was then removed, and the reaction mixture was stirred at room temperature for 2 h. The brown solid was collected on air, washed with 500 mL of distilled H_20, and dried under vacuum overnight. The reaction mixture was extracted with pentane until the extracts were no longer red and this pentane extract was passed through the Celit. This solution was washed with 1000 ml of water (three washes) then dried over Mg SO_4.The solvent was removed on a rotary evaporator, leaving a red-brown solid which was dried on the vacuum overnight. The red-brown solid was chromatographed on an 8 x 25-cm silica column eluting with solution of pentanes: dichloromethane (9:1). The Solvent was removed, and the solid was briefly dried on the vacuum line. Sublimation of solid at 40 °C (0.1 mm) for 20 h yielded 24% red product of $Fe_2S_2(CO)_6$.[1] IR (pentanes):2084 (s), 2044 (m), 2008 (m) in the terminal CO region. Mass spectrum, m/z 344 (M^+), 316 (M^+ - 5CO), 176 (S_2Fe_2).*we highly recommend sublimation as a method of purification.*

Synthesis of complex $[(i\text{-}SCH_2)_2NH]Fe_2(CO)_6]$:

A red solution of $S_2Fe_2(CO)_6$ 0.344 g,(1.0 mmol) in THF (20 mL) was cooled to - 78 ^{0}C and then treated dropwise with Et_3BHLi 2.0 mL (2.0 mmol) to give a green solution containing $(\mu\text{ -LiS})_2Fe_2(CO)_6$. After stirring for 45 min, 0.32 mL of CF_3CO_2H (2.0 mmol) was added to cause an immediate color change from green to red, indicating the complete conversion of $(\mu\text{ -LiS})_2Fe_2(CO)_6$ to $(\mu\text{ -HS})_2Fe_2(CO)_6$. A mixture of 1.2 g (0.04 mol) of paraformaldehyde, 1.14 g (0.0118 mol) of $(NH_4)_2CO_3$ and 40 mL of THF was stirred for 6 h then add to a cold solution of $(\mu\text{ -HS})_2Fe_2(CO)_6$.The solution allowed to warm up to room temperature after 2 hours .THF was removed under vacuum, solid was chromatographed on silica gel eluting with dichloromethane : hexane (1:8).[2] Yield 35%. ^{1}H NMR (CD_3CN), 3.71 (d, 4H, NCH_2S), 2.22(bm,1H,NH) ppm. IR (hexane) 2076, 2036, 2008, 1989, 1979 cm^{-1}.

Synthesis of Complex 1[(í-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]-Fe$_2$(CO)$_6$]:

A solution of complex [(í-SCH$_2$)$_2$NH]Fe$_2$(CO)$_6$] 0.464 g (1.2 mmol), 4-pyridin-ecarboxylic acid chloride 0.510g (3.60 mmol), and Et_3N 0.80 mL (5.8mmol) in CH_2Cl_2 10 ml was stirred at room temperature for 6 h. The solution was filtrated and concentrated 1 mL under vacuum and then subjected to chromatography on silica gel eluting with petroleum ether/acetone (5/2).[3] 60% yield, IR 2078, 2039, 2002, 1680 (s) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): 4.07, 4.30 (2s, 4H,), 7.34 (d, 2H), 8.77 (d, 2H).

Synthesis of tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCPP) :

A solution of TPP-COOMe 1.69 g (2.0 mmol) and $ZnCl_2$ 3.5 g (25.6 mmol) in 150 mL of DMF was refluxed for overnight. After the mixture was cooled to room temperature, 250 mL of H_2O was added. The resultant precipitate was filtered and washed with 100 mL of H_2O for three times. The obtained solid was dissolved in Chloromethane, followed by washing two times with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative violet crystals. The obtained ester (1.50) was stirred in THF (60 mL) and MeOH (60 mL) mixed solvent, to which a solution of KOH 5.26g (93.90 mmol) in H_2O (50 mL) was introduced. This mixture was refluxed overnight. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved, then the solution was acidified with 1M HCl. The violet solid was collected by filtration, washed with water and dried in vacuum.[4] Yield 45%. H^1 NMR 8.80 (m, 12H), 8.39 (m, 8H), 7.81 (t, 4H) ppm.

Synthesis of ZrPF:

A mixture of zirconyl chloride octahydrate (20.0 mg), ZnTCPP, (8.0 mg), N,N-diethylformamide (DEF) (5.0 mL) and benzoic acid (200 mg) was capped in a 20 mL scintillation vials and heated at 130 °C for 3 days. Needle shaped crystals were harvested by filtration.[4] (40% yield).

The adsorption of N$_2$ experiment:

N_2 adsorption isotherm of ZrPF and [FeFe]@ZrPF were collected on the surface area analyzer ASAP-2020 using a liquid nitrogen bath. Before the measurements, the freshly prepared sample was solvent-exchanged with CH_2Cl_2 and activated under dynamic vacuum at room temperature 23 ˚C for 24 hours. ~200 mg activated sample was employed for the gas sorption measurement.

Fourier-transformed Infrared (FTIR) Spectroscopy:

Approximately 10 mg of samples were dried under vacuum prior to FTIR analysis. FTIR data were collected at ambient temperature on a Nicolet 6700 FT-IR Spectromete from 4000 cm^{-1} and 450 cm^{-1}.

Fluorecence experiment :

The ZrPF and [FeFe]@ZrPF samples were dried under vacuum. The fluorescence emission spectra were measured for the 550 nm excitation wavelength.[5] The fluorecence epxeriment performed by Spex Fluorolog Tau-3 fluorescence spectrophotometer. Solid samples for fluorescence spectra were prepared according to published procedure.[6,7]

Photocatalytic experiment:

Photocatalytic H_2 production experiments were conducted in a sealed circulation system. In a typical run, 2 µM of [FeFe]@ZrPF (based on the catalytic di-iron subsite) suspended on buffer solution pH 5 at presence of ascorbic acid (20 mM). After degassing the system for one hour, a 300 W Xe lamp with a 420 nm cut-on filter (Newport Corp.) was applied to execute the photocatalytic reaction. The products were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD).

Figures:

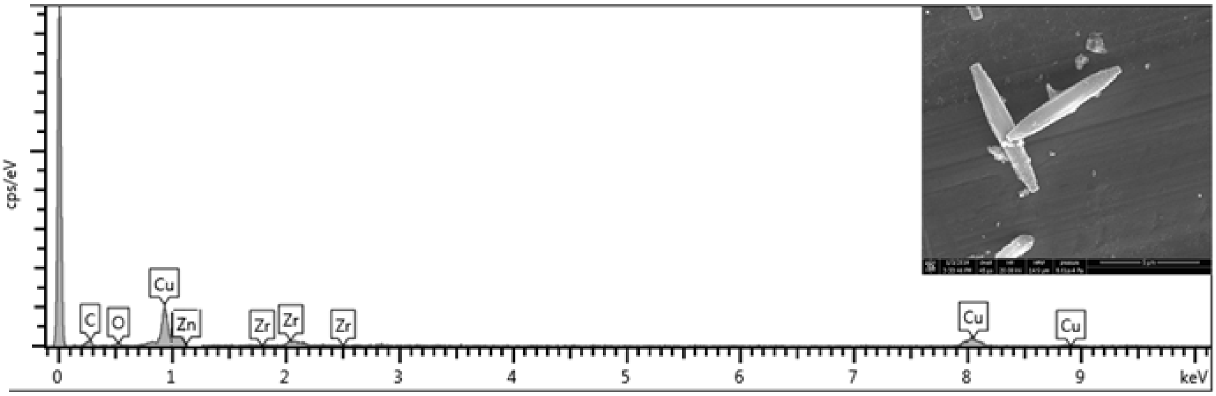

Figure S1. SEM and EDX analysis of ZrPF.

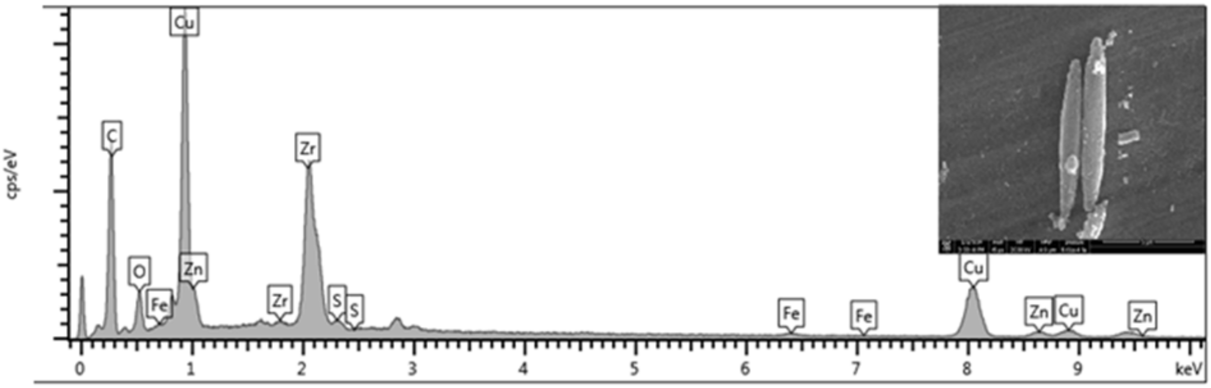

Figure S2. SEM and EDX analysis of [FeFe]@ZrPF.

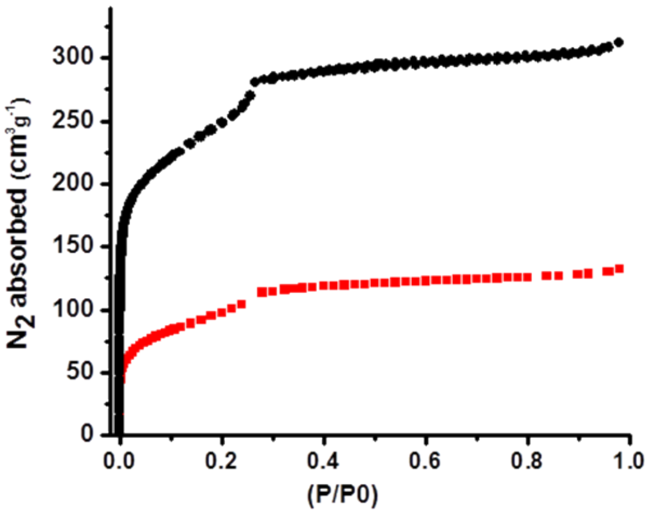

Figure S3. N2 absorption and desorption isotherms for ZrPF (black) and [FeFe]@ZrPF (red).

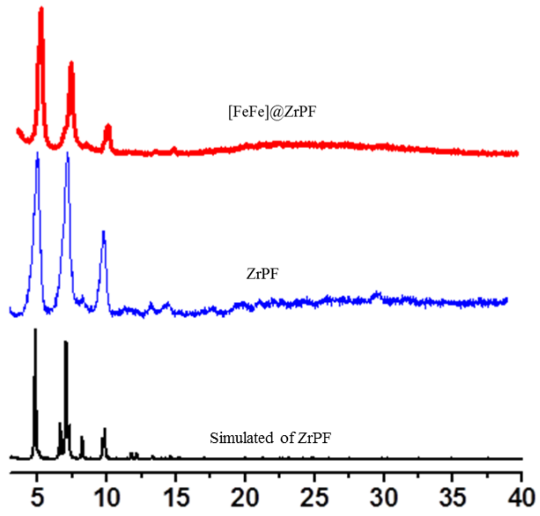

Figure S4. PXRD of Simulated of ZrPF (Black), ZrPF (blue) and [FeFe]@ZrPF (red).

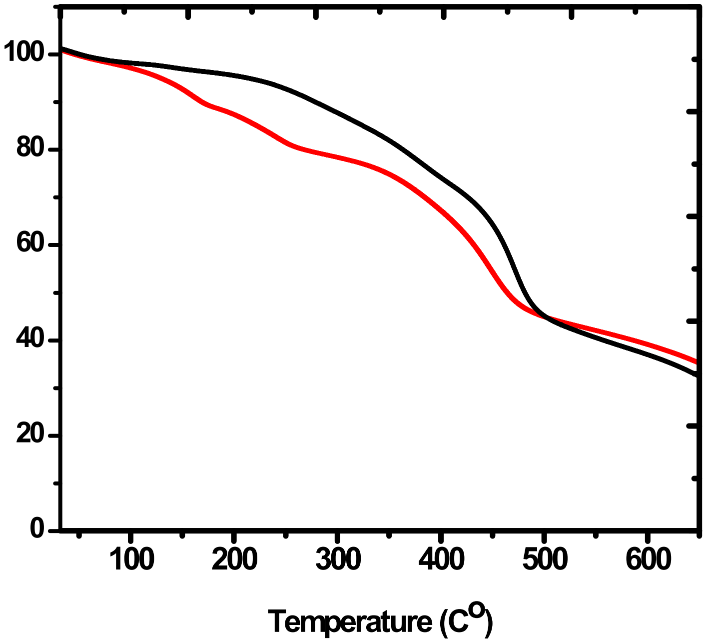

Figure S5. TGA of ZrPF (black) and [FeFe]@ZrPF (red).

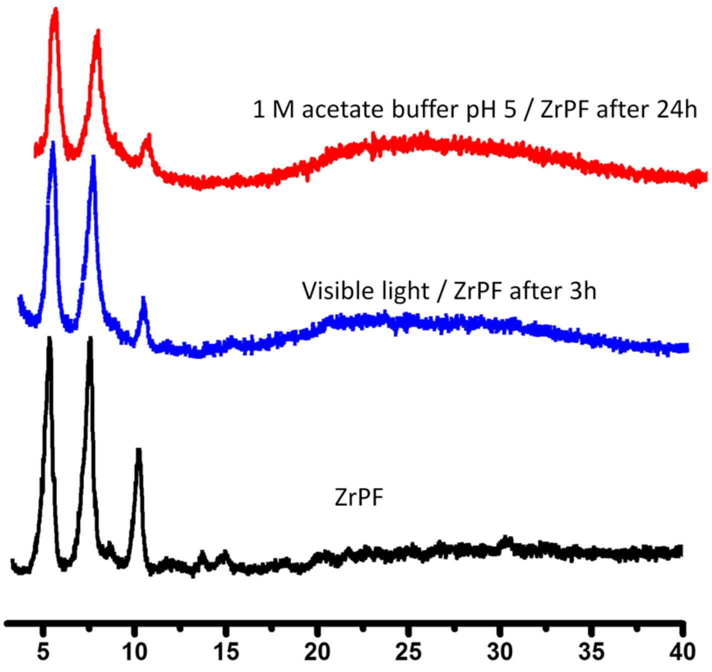

Figure S6. PXRD of ZrPF in acidic solutions (pH = 5 for 24 h) and exposure to visible light (>420 nm).

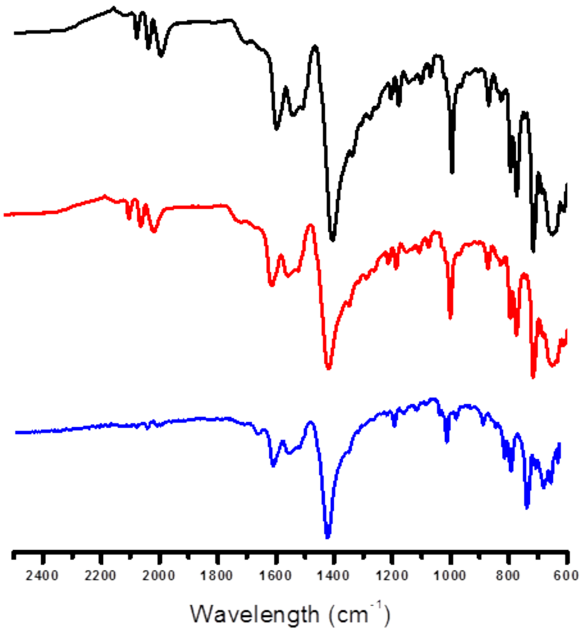

Figure S7. FTIR spectrum of heterogeneous catalyst [FeFe]@ZrPF upon exposure to visible light. Catalyst before exposure to visible light (Black) and after exposure to visible light for 40 mins (red), after exposure visible light 120 min (blue) .The characteristic IR absorption of the CO ligands around 2000 cm^{-1} have been disappear after 120 min exposure on visible light

References :

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