Supporting Information for

A Triad [FeFe] Hydrogenase System for Light-driven Hydrogen Evolution

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Scheme 1. The schematic representation of the complexes studied in this work
**Instrumentation and Methods** Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrophotometer. $^1$H NMR spectra were run on a Bruker-400 spectrometer with tetramethylsilane ($^1$H) as an internal standard. HR-ESI-MS was performed on a Bruker APEX III 7.0 Tesla FTICR Mass spectrometer combined with Apollo ESI source. Elemental analyses were determined on a FLASH EA1112 elemental analyzer. Electrochemical investigation was studied on a Princeton Applied Research Potentionstat-gravanostat model 283. The experiment for H$_2$ production in a Pyrex tube was performed by irradiation with a 500 W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 400 nm and thus guarantee the irradiation by visible light. Hydrogen detection was carried out on a Shimadzu GC-14B with methane as an internal standard. The response factor for H$_2$/CH$_4$ determined by calibration with known amounts of H$_2$ and CH$_4$ was 3.4 under the experimental conditions. The UV-vis absorption spectra were recorded using a Shimadzu 1601 PC spectrophotometer. The emission spectra were determined on a Hitachi 4500 spectrophotometer. The time-resolved emission and transient absorption spectroscopy were carried out on Edinburgh LP 920. A three-electrode system, a 3 mm glass carbon working electrode, a platinum wire counter electrode, and a non-aqueous Ag/Ag$^+$ reference electrode, was used to measure the cyclic voltammograms. The working electrode was polished with a 0.05 $\mu$m alumina paste and sonicated for 15 min before use. The electrolyte solution, 0.1 M of $n$-Bu$_4$NPF$_6$ used as electrolyte, was degassed with argon for 30 min before measurement.

**Materials** All reactions and operations were carried out under a dry argon atmosphere with standard Schlenk technique. All solvents were dried and distilled prior to use.$^{S1}$ Re(CO)$_5$Br, AgCF$_3$SO$_3$, 4-ethynylpyridine, and dichlorobis[(triphenyl)phosphine]palladium were purchased from Aldrich and used as received. Complexes $^3$,$^{S2}$ $^4$,$^{S2}$ $^6$,$^{S3}$ and $^7$,$^{S4}$ were synthesized according to procedures reported in the literature. Sonogashira reaction, the palladium-catalyzed cross-coupling reaction of terminal alkynes with aryl halides, was carried out according to the modified procedures.$^{S5}$
Synthesis of the active site of adt [FeFe]-H$_2$ase 5: 5 was synthesized according to the literature. Complex 4 (58.9 mg, 0.10 mmol) was treated with 4-ethynylpyridine (15.5 mg, 0.10 mmol) in an argon saturated THF/NEt$_3$ (5/1) by adding Pd(PPh$_3$)$_2$Cl$_2$(15 mg) and Cul (5 mg) as the catalysts. The mixture was then concentrated in vacuo and filtered after stirring under argon atmosphere at 40-50°C for 3 h. The resulting black residue was further purified by column chromatography on silica gel (ethyl acetate/CH$_2$Cl$_2$) to afford complex 5 as red solids. Yield: (85%). HR-ESI-MS ($m/z$): Anal. calcd for [C$_{21}$H$_{12}$Fe$_2$N$_2$O$_6$S$_2$+H$^+$]: 564.8914 (M+H)$^+$; Found: 564.8910. $^1$H NMR (CD$_3$COCD$_3$, 400 MHz, $\delta$ ppm): 8.57 (d, $J = 4.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 4.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 4.62 (s, 4H). Anal. calcd for C$_{21}$H$_{12}$Fe$_2$N$_2$O$_6$S$_2$: C, 44.71; H,
Synthesis of triad 1: Complex 6 (0.04 mmol, 32.1 mg) and AgCF$_3$SO$_3$ (0.06 mmol, 15.4 mg) was refluxing in an argon saturated THF for 7 h. After removal of AgBr solids, complex 5 (0.06 mmol, 32.0 mg) was added and the reaction mixture was further refluxing in THF overnight. Triad 1 was purified by flash chromatography on silica gel with CH$_3$COOCH$_2$CH$_3$/CH$_2$Cl$_2$/CH$_3$OH = 3:1:0.2 (V/V/V) as gradient eluents to produce the desired triad 1 as red solids. Yield: 70%. MS (MALDI-TOF): Cacld for C$_{48}$H$_{28}$F$_3$Fe$_3$N$_6$O$_{12}$ReS$_3$: 1387.7; Found: 983 (M-CF$_3$SO$_3$--9CO). $^1$H NMR (400 MHz, CD$_3$CN): 11.75 (s, 1H), 9.52 (t, $J$ = 18.8 Hz, 2H), 9.23 (d, $J$ = 7.4 Hz, 1H), 9.08 (d, $J$ = 8.6 Hz, 1H), 8.21 (d, $J$ = 6.7 Hz, 2H), 8.17- 8.13 (m, 2H), 7.40 (d, $J$ = 8.9 Hz, 2H), 7.18 (d, $J$ = 6.7 Hz, 2H); 6.78 (d, $J$ = 9.0 Hz, 2H), 5.12 (s, 2H), 4.57 (s, 2H), 4.37 (s, 4H), 4.16 (s, 5H). Anal. Cacld for C$_{48}$H$_{28}$F$_3$Fe$_3$N$_6$O$_{12}$ReS$_3$: C 41.54, H 2.03, N 6.06; found: C 41.28, H 2.33, N 5.85; IR (KBr, $\nu$ cm$^{-1}$): v(CO): 2076.1, 2032.7, 1997.1, 1920.9; v(C≡C): 2216.8; v(CF$_3$SO$_3$): 1203.4, 1145.5.

Complex 2: Complex 2 was synthesized by the procedure similar to that for 1 except that 7 was used in place of 5. ESI-MS (m/z): Cacld for C$_{40}$H$_{25}$ReF$_3$SO$_6$N$_5$Fe: 1003.0; Found: 853.7 (M-CF$_3$SO$_3$). $^1$H NMR (CD$_3$COCD$_3$, 400MHz, $\delta$ ppm) 9.78 (d, $J$ = 3.8 Hz, 2H), 9.37 (s, 2H), 8.64-8.62 (m, 2H), 8.32 (s, 2H), 7.48-7.37 (m, 7H), 5.21 (m, 2H), 4.55 (m, 2H), 4.17 (s, 5H). Anal. cacld for C$_{40}$H$_{25}$ReF$_3$SO$_6$N$_5$Fe·1.5CH$_2$Cl$_2$: C 44.10, H 2.05, N 6.20; Found: C 44.49, H 2.09, N 6.55. IR (KBr, $\nu$ cm$^{-1}$): v(CO): 2032.9, 1923.0; v(C≡C): 2222.2; v(CF$_3$SO$_3$): 1259.5, 1157.3.
**X-ray crystallography** The dark red crystal of 3-pyridyl-substituted [FeFe]-H\_2ase mimic was obtained by immersion of hexane into CH\(_2\)Cl\(_2\) solution at room temperature. The active site of [FeFe]-H\_2ase unit keeps the butterfly conformation, in which the metal atoms are connected to each other through a Fe-Fe single bond and the aryl group on the N(1)-bridged atom slants to one Fe site as a result of the two fused six-membered rings: N1C7S1Fe2S2C8 and N1C7S1Fe1S2C8 (Figure S1). The bond length of Fe-Fe is 2.5018 Å. The N atom at the adt bridge was sp\(^2\) hybridization (the sum of the angles C9-N1-C7, C9-N1-C8, C7-N1-C8, is 353.54') which shows the electronic communication between N atom and the conjugated reducible π-electron system (Table S1). Two types of hydrogen bonds exist in the crystal. One is C-H--N chains of organic tether: the donor is C-H from the benzyl connecting with the Fe\(_2\)(CO)\(_6\)(μ-adt), and the acceptor is N atom of the pyridine. Each molecule serves as either a donor or an accepter, so that guide the organic tether towards b axes to form a zonal structure. The data of the hydrogen bond are C13A-H13A: 0.950 Å; H13A--N2B: 2.551 Å; C13A-H13A--N2B: 170.1'. The others are C-H--O chains between the above zonal structures. The donor is C-H at the adt-bridge and the acceptor is the O atom at the CO zonal structure. The concrete data list are C8A-H8AA: 0.990 Å; H8AA--O2C: 2.444 Å; C8A-H8AA--O2C: 140.8’, respectively (Figure S2). Crystallographic data for 3-pyridyl-substituted [FeFe]-H\_2ase mimic have been depositeed with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 823956.

![Figure S1. The crystal structure of 3-pyridyl-substituted [FeFe]-H\_2ase mimic](#)
Table S1. Selected bond angle and bond length of 3-pyridyl-substituted [FeFe]-H₆ase mimic

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Bond angle</th>
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<tr>
<td>[Å]</td>
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<tr>
<td>Fe₁-Fe₂</td>
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<tr>
<td>Fe₁-S₂</td>
<td>2.2559(7)</td>
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<tr>
<td>Fe₂-S₁</td>
<td>2.2529(7)</td>
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<td>Fe₁-C₁</td>
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<tr>
<td>Fe₂-C₄</td>
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<td>C₁₅-C₁₆</td>
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Figure S2. Crystal stack structure of 3-pyridyl-substituted [FeFe]-H₆ase mimic
Figure S3. Electrochemistry of triad 1, 2, 3 (1.0 mM) and 8 (0.05 mM) in CH₃CN with 0.1 M n-Bu₄NPF₆ as electrolyte at a scan rate of 100 mVs⁻¹ under Ar atmosphere.
Table S2. The electrochemical data of triad 1, 2, 3 and 8 in CH$_3$CN with 0.1 M n-Bu$_4$NPF$_6$ as electrolyte

<table>
<thead>
<tr>
<th>Complex</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Fe$^{I}$/Fe$^{I}$/Fe$^{II}$, Fe$^{IV}$/Fe$^{III}$/Fe$^{II}$</td>
<td>Re$^{I}$/0, Phen$^{0}$/0, Fe$^{II}$/Fe$^{I}$/Fe$^{III}$/Fe$^{II}$</td>
</tr>
<tr>
<td>1</td>
<td>—, -1.49</td>
<td>-2.11, -1.81</td>
</tr>
<tr>
<td>2</td>
<td>—, —</td>
<td>-2.02, -1.78</td>
</tr>
<tr>
<td>3</td>
<td>—, -1.57</td>
<td>—, —</td>
</tr>
<tr>
<td>8</td>
<td>—, —</td>
<td>—, -1.79</td>
</tr>
</tbody>
</table>

[a] The reported values for Re (I) analogues is 1.46-1.2 V vs. SCE ($E_{1/2}$ vs. SCE),$^{56}$ which can be calculated to 1.07-0.81 V vs. Fe$^{+}$/Fc (Fc$^{+}$ is 0.39 vs. SCE).
Figure S4. Infrared spectra of triad 1, and its model complexes 2 and 3.
Driving force for the PET process: The assembly of the electron donor, the chromophore and the active site of adt [FeFe]-H₂ase provides a more powerful driving force for the PET process than those reported for dyads (J. Am. Chem. Soc. 2010, 132, 8813–8815. Chem. Asian. J. 2010, 8, 1796–1803). On the other hand, triad 1 displays a quasi-reversible reduction process at −1.49 V and an oxidation process at 0.17 V in CH₃CN, while complex 3 is at −1.57 V for the one-electron reduction of [Fe¹Fe¹]⁺ e⁻ → [Fe¹Fe⁰] process and complex 2 is at 0.19 V for the redox process of Fe⁺⁻ on the ferrocene subunit. Therefore, the driving force for the PET process was subsequently determined as −0.90 eV for intramolecular triad 1 and −0.80 eV for the combined intermolecular 2 and 3.

$$\Delta G_0 = E(D)_{\text{ox}} - E(A)_{\text{red}} - \Delta E_{0-0}$$

$E(D)_{\text{ox}}$: the oxidation potential of electron donor (Fc⁺/Fc)

$E(A)_{\text{red}}$: the reduction potential of electron acceptor (Fe⁺Fe¹/Fe⁺Fe⁰)

$\Delta E_{0-0}$: the excited state energy $E_{0-0}$ of the Re(I) chromophore, which was read from the cross-point (485 nm, 2.56 eV) of the excitation spectrum and the revived emission of complex 2 by Fe(ClO₄)₃ oxidant. The use of the cross point is reliable and generally accepted for the determination of $E_{0-0}$ (Principles of Molecular Photochemistry, N. J. Turro, V. Ramamurthy and J. C. Scaiano, Eds. University Science Books, 2009, Chapter 4).

![Emission and Excitation Spectra](image)

Figure S5. The emission and excitation spectra of the revived complex 2 by Fe(ClO₄)₃ oxidant

$\Delta G_0$ for triad 1: $\Delta G_0 = E(D)_{\text{ox}} - E(A)_{\text{red}} - \Delta E_{0-0} = 0.17 - (-1.49) - 2.56 = -0.90$ eV

$\Delta G_0$ for 2 and 3: $\Delta G_0 = E(D)_{\text{ox}} - E(A)_{\text{red}} - \Delta E_{0-0} = 0.19 - (-1.57) - 2.11 = -0.80$ eV
On the basis of the steady-state and time-resolved investigations, it could be speculated that the initial step is oxidative quenching of the excited Re(I) complex by the electron acceptor [FeFe] H$_2$ases mimic. The formed Re(II)$^+$ is subsequently regenerated by electron transfer from the ferrocene (Fc) electron donor, while the long-lived Fe(I)Fe(0) species is reacted with proton for H$_2$ evolution.

Figure S6. The multistep PET from the ferrocene electron donor to the active site of [FeFe]-H$_2$ase mimic in triad 1
Figure S7. Time-dependence of H₂ evolution from triad 1 (0.2 mM) or the combined 2 and 3 (2: 0.2 mM, 3: 0.2 mM) in CH₃CN/H₂O solution (V/V = 9:1, 10 mL) in the presence of H₂A (0.1 M). Control experiments were carried out under the same condition, the mixture of 2 (0.2 mM) and H₂A (0.1 M) and 3 (0.2 mM) and H₂A (0.1 M), respectively, as well as the mixture of triad 1 (0.2 mM) and H₂A (0.1 M) in the dark.

As compared with that recently reported for dyad systems (Chem. Asian. J. 2010, 8, 1796-1803), this triad system is capable of evolving H₂ in organic solution at higher amounts. Moreover, we found that the photochemical H₂ evolution is very dependent on the solvent used. When we used different solvent as did in our previous work (Chem. Asian. J. 2010, 8, 1796-1803), the amount of H₂ reached 10 uL after 1.5 h irradiation under the same condition.

Notes and references


S3. K. Feng, the Ph. D thesis of Technical Institute of Physics and Chemistry, the Chinese Academy of Sciences, 2007

