Supporting Information for

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

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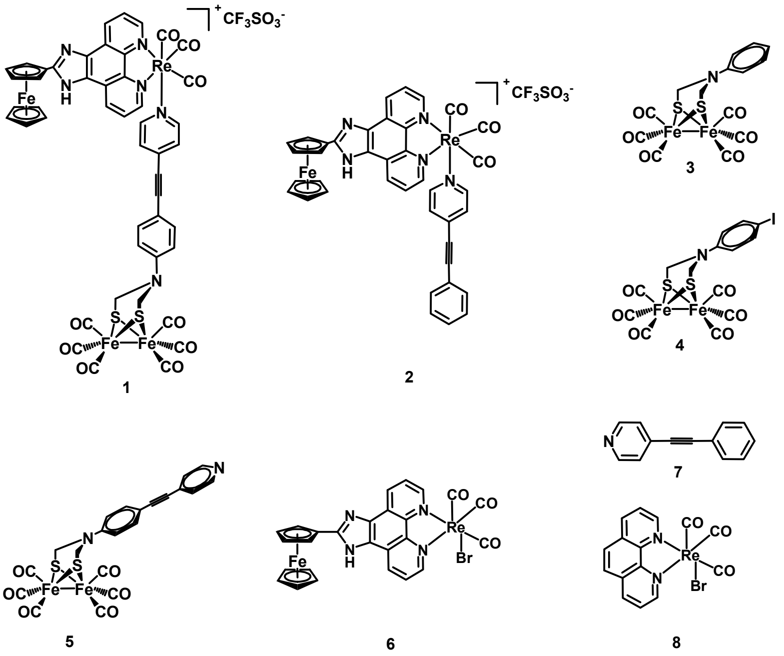
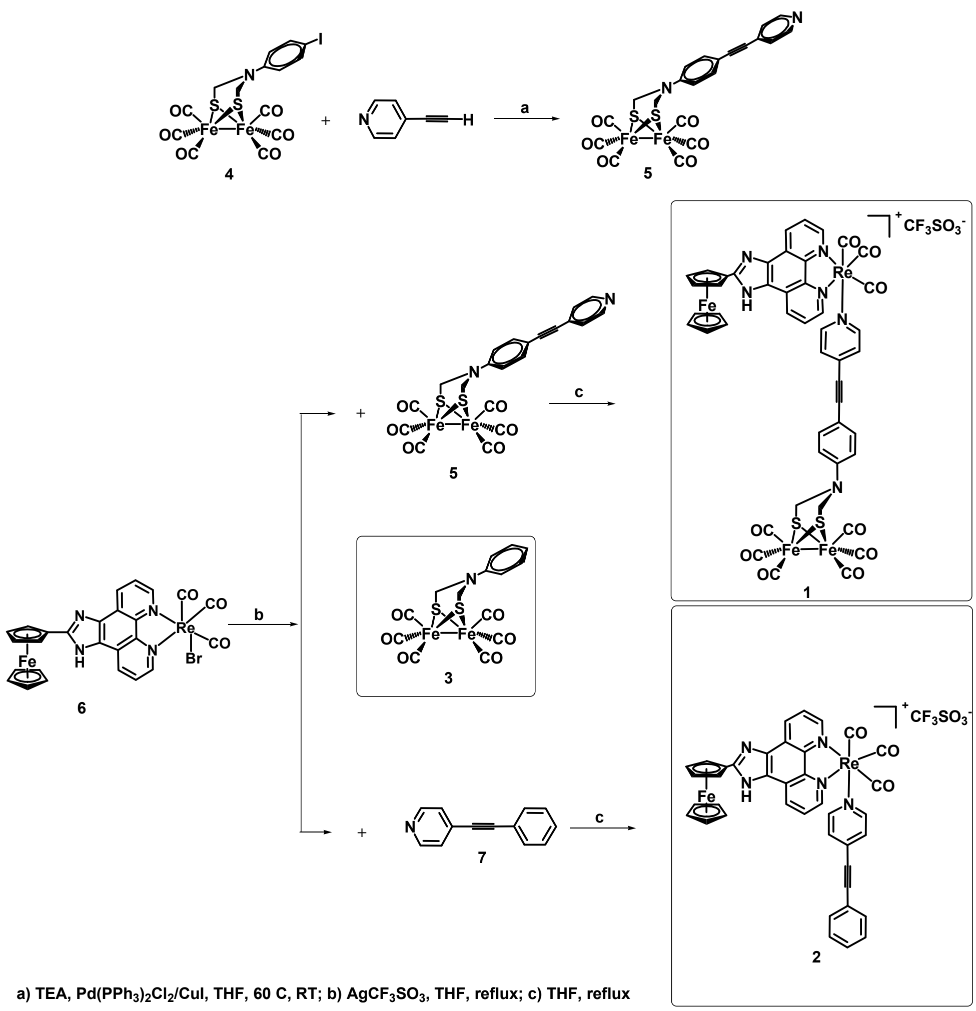


Scheme 1. The schematic representation of the complexes studied in this work

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 μm alumina paste and sonicated for 15 min before use. The electrolyte solution, 0.1 M of n-Bu_4NPF_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] $Re(CO)_5Br$, $AgCF_3SO_3$, 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]



a) TEA, $Pd(PPh_3)_2Cl_2$/CuI, THF, 60 C, RT; b) $AgCF_3SO_3$, THF, reflux; c) THF, reflux

Scheme S2. The synthetic routes to triad **1** and its models **2** and **3**

Synthesis of the active site of adt [FeFe]-H$_2$ase 5: **5** was synthesized according to the literature.[S5] 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 $Pd(PPh_3)_2Cl_2$(15 mg) and CuI (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_2Cl_2) to afford complex **5** as red solids. Yield: (85%). HR-ESI-MS (*m/z*): Anal. calcd for [$C_{21}H_{12}Fe_2N_2O_6S_2+H^+$]: 564.8914 $(M+H)^+$; Found: 564.8910. ^1H NMR (CD_3COCD_3, 400 MHz, δ 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 $C_{21}H_{12}Fe_2N_2O_6S_2$: C, 44.71; H, 2.14; N, 4.97; Found: C, 44.90; H, 2.37; N, 5.31. IR (KBr, ν cm^{-1}): ν(CO): 2076.81, 2032.75, 2001.82, 1964.14; ν(C≡C): 2215.9.

Synthesis of triad 1: Complex **6** (0.04 mmol, 32.1 mg) and $AgCF_3SO_3$ (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 $CH_3COOCH_2CH_3/CH_2Cl_2/CH_3OH$ = 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 $C_{48}H_{28}F_3Fe_3N_6O_{12}ReS_3$: 1387.7; Found: 983 ($M-CF_3SO_3^{-}$-9CO). ^1H NMR (400 MHz, CD_3CN): 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 $C_{48}H_{28}F_3Fe_3N_6O_{12}ReS_3$: C 41.54, H 2.03, N 6.06; found: C 41.28, H 2.33, N 5.85; IR (KBr, ν cm^{-1}): ν(CO): 2076.1, 2032.7, 1997.1, 1920.9; ν(C≡C): 2216.8; ν($CF_3SO_3^{-}$): 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 $C_{40}H_{25}ReF_3SO_6N_5Fe$: 1003.0; Found: 853.7 ($M-CF_3SO_3^{-}$). ^1H NMR (CD_3COCD_3, 400MHz, δ 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 $C_{40}H_{25}ReF_3SO_6N_5Fe\cdot 1.5CH_2Cl_2$: C 44.10, H 2.50, N 6.20; Found: C 44.49, H 2.09, N 6.55. IR (KBr, ν cm^{-1}): ν(CO): 2032.9, 1923.0; ν(C≡C): 2222.2; ν($CF_3SO_3^{-}$): 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_2Cl_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 *N1*-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 accepter 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 deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 823956.

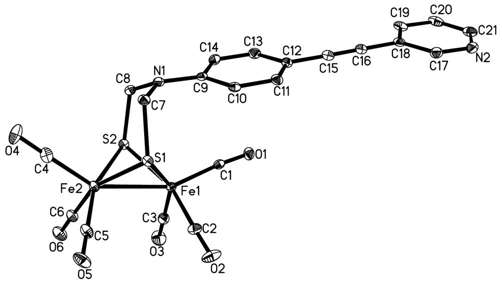


Figure S1. The crystal structure of 3-pyridyl-substituted [FeFe]-H_2ase mimic

Table S1. Selected bond angle and bond length of 3-pyridyl-substituted [FeFe]-H_2ase mimic

Bond length	[Å]	Bond angle	[˚]
Fe1-Fe2	2.5018(5)	C9-N1-C7	119.59(19)
Fe1-S2	2.2559(7)	C7-N1-C8	112.38(19)
Fe2-S1	2.2529(7)	C4-Fe2-Fe1	147.85(8)
Fe1-C1	1.804(2)	C9-N1-C8	121.57(19)
Fe2-C4	1.794(3)	C1-Fe1-Fe2	155.61(7)
Fe2-C6	1.806(2)	N1-C7-S1	114.88(15)
Fe1-S1	2.2673(6)	N1-C8-S2	116.90(16)
Fe2-S2	2.2618(7)	S2-Fe1-Fe2-S1	108.12(3)
Fe1-C3	1.789(2)		
Fe1-C2	1.781(3)		
Fe2-C(5)	1.798(3)		
C15-C16	1.196(3)		

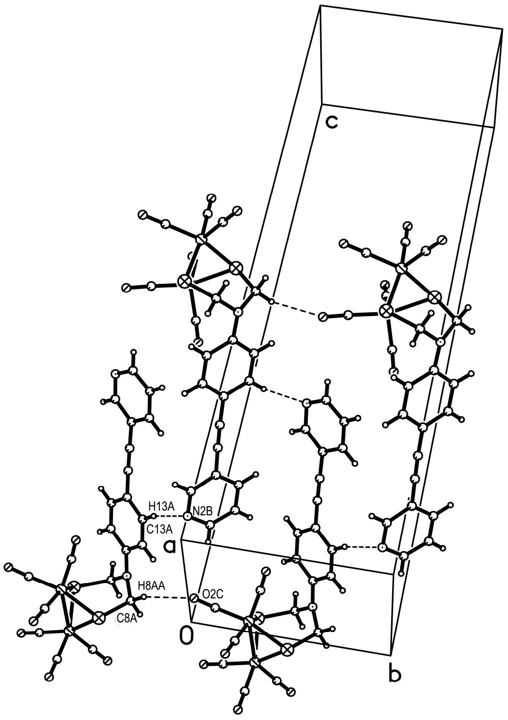
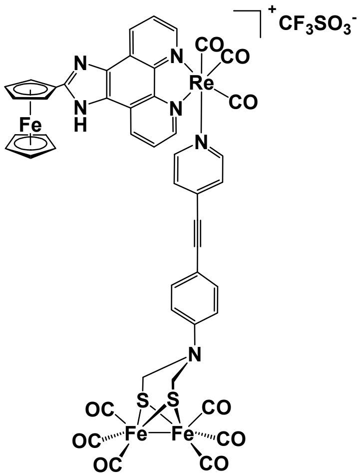


Figure S2. Crystal stack structure of 3-pyridyl-substituted [FeFe]-H_2ase mimic



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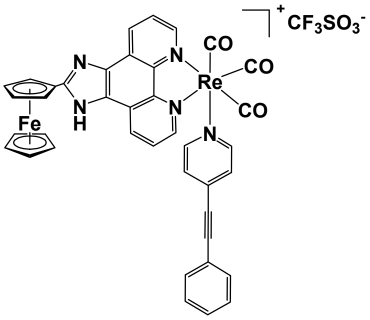

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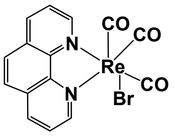

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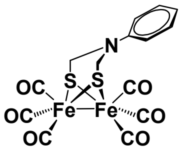

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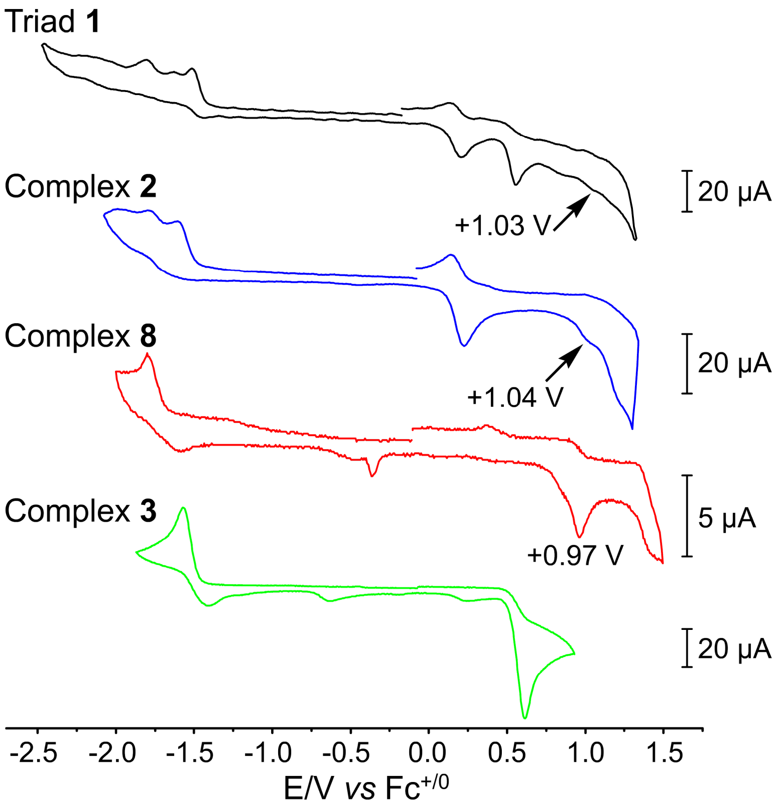

Figure S3. Electrochemistry of triad **1**, **2**, **3** (1.0 mM) and **8** (0.05 mM) in CH_3CN with 0.1 M *n*-Bu_4NPF_6 as electrolyte at a scan rate of 100 mVs^{-1} under Ar atmosphere

Table S2. The electrochemical data of triad **1**, **2**, **3** and **8** in CH_3CN with 0.1 M *n*-Bu_4NPF_6 as electrolyte

Complex	E_p versus Fc/Fc$^+$ (V)			
	Reduction		*Oxidation*	
	$Fe^{I}Fe^{0}/Fe^{0}Fe^{0}$, $Fe^{I}Fe^{I}/Fe^{I}Fe^{0}$	$Re^{I/0}$, $Phen^{0/-}$	Fc/Fc$^+$, $Fe^{I}Fe^{I}/Fe^{I}Fe^{II}$	[a]$Re^{I/II}$
1	—, -1.49	-2.11, -1.81	+0.17, +0.54,	+1.03
2	—, —	-2.02, -1.78	+0.19, —,	+1.04
3	—, -1.57	—, —	—, +0.61	—
8	—, —	—, -1.79	—, —,	+0.97

[a] The reported values for Re (I) analogues is 1.46-1.2 V *vs.* SCE ($E_{1/2}$ *vs.* SCE),[S6] which can be calculated to 1.07-0.81 V *vs.* Fc$^+$/Fc (Fc$^+$ is 0.39 *vs.* SCE).

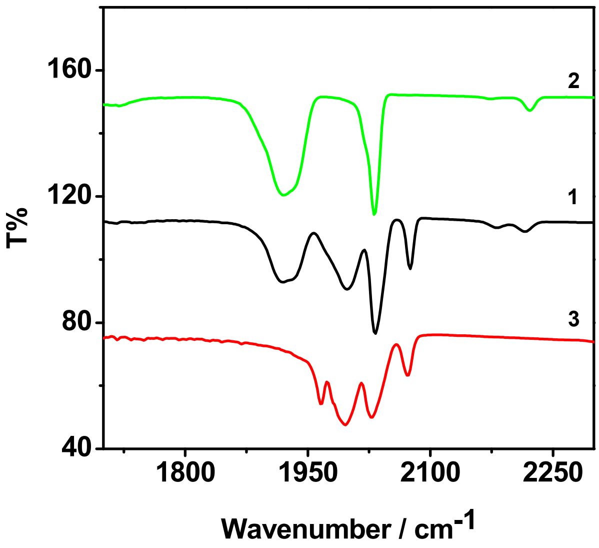

Figure S4. Infrared spectra of triad **1**, and its model complexes **2** and **3**

Driving force for the PET process: The assembly of the electron donor, the chromophore and the active site of adt [FeFe]-H_2ase 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 CH_3CN, while complex **3** is at −1.57 V for the one-electron reduction of $[Fe^IFe^I] + e^- \rightarrow [Fe^IFe^0]$ process and complex **2** is at 0.19 V for the redox process of $Fc^{+/0}$ 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**.

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

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

$E(\mathrm{A})_{\mathrm{red}}$: the reduction potential of electron acceptor (Fe^IFe^I/Fe^IFe^0)

$\Delta E_{0\text{-}0}$: the excited state energy $E_{0\text{-}0}$ 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 $Fe(ClO_4)_3$ oxidant. The use of the cross point is reliable and generally accepted for the determination of $E_{0\text{-}0}$ (*Principles of Molecular Photochemistry*, N. J. Turro, V. Ramamurthy and J. C. Scaiano, Eds. University Science Books, 2009, Chapter 4).

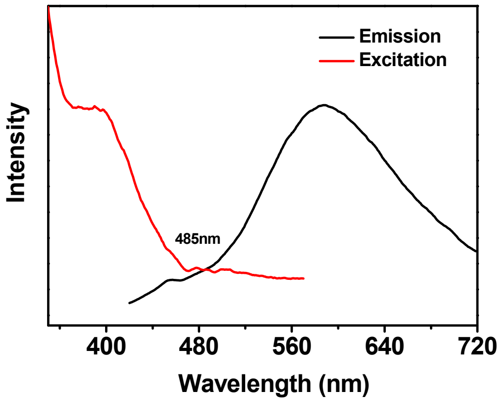

Figure S5. The emission and excitation spectra of the revived complex **2** by $Fe(ClO_4)_3$ oxidant

ΔG_0 for triad **1**: $\Delta G_0 = E(\mathrm{D})_{\mathrm{ox}} - E(\mathrm{A})_{\mathrm{red}} - \Delta E_{0\text{-}0} = 0.17 - (-1.49) - 2.56 = -0.90$ eV

ΔG_0 for **2** and **3**: $\Delta G_0 = E(\mathrm{D})_{\mathrm{ox}} - E(\mathrm{A})_{\mathrm{red}} - \Delta E_{0\text{-}0} = 0.19 - (-1.57) - 2.11 = -0.80$ 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_2ases 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.

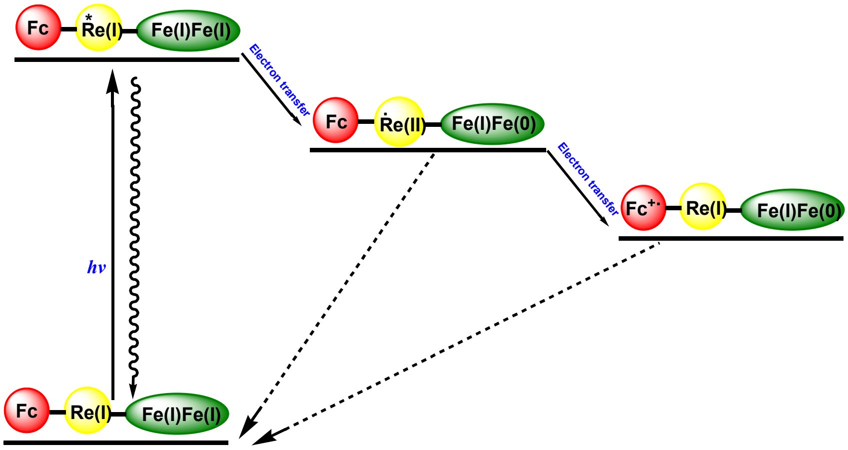

Figure S6. The multistep PET from the ferrocene electron donor to the active site of [FeFe]-H_2ase mimic in triad **1**

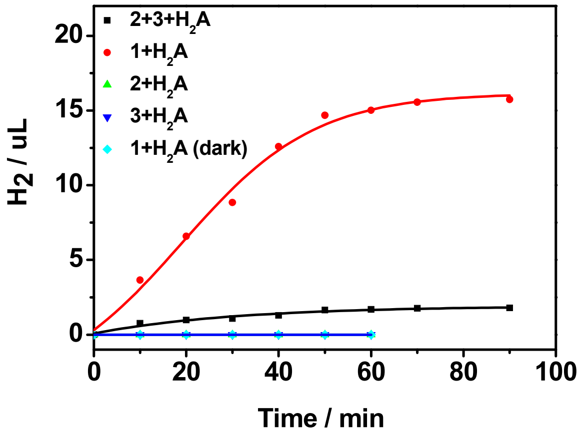

Figure S7. Time-dependence of H_2 evolution from triad **1** (0.2 mM) or the combined **2** and **3** (2: 0.2 mM, 3: 0.2 mM) in CH_3CN/H_2O solution (V/V = 9:1, 10 mL) in the presence of H_2A (0.1 M). Control experiments were carried out under the same condition, the mixture of **2** (0.2 mM) and H_2A (0.1 M) and **3** (0.2 mM) and H_2A (0.1 M), respectively, as well as the mixture of triad **1** (0.2 mM) and H_2A (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 H_2 in organic solution at higher amounts. Moreover, we found that the photochemical H_2 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 H_2 reached 10 uL after 1.5 h irradiation under the same condition.

Notes and references

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