

Supporting Information

Diiron Dithiolate Complex-Induced Helical Structure of Histone and Application in Photochemical Hydrogen Generation

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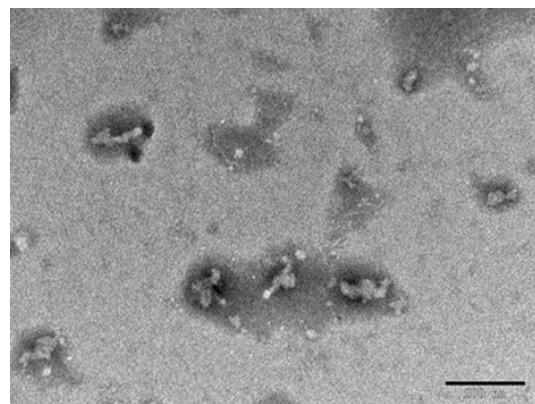


Figure S1. TEM image of histone H1 (1 mg mL^{-1}). Scale bar, 200 nm.

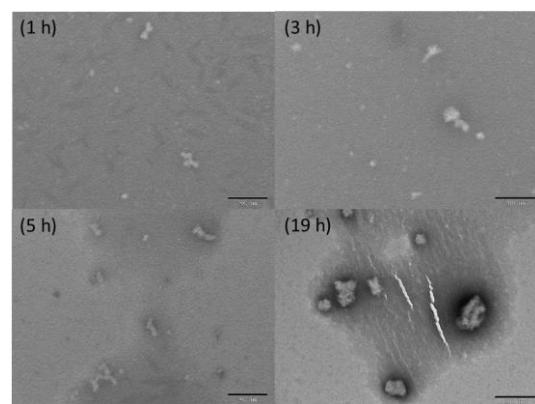


Figure S2. TEM images of H-Fe-1 after varying reaction time. Scale bar, 200 nm.

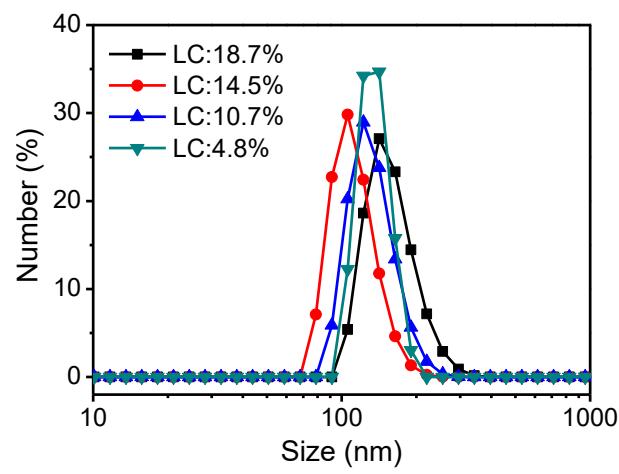


Figure S3. DLS analysis of H-Fe nanoparticles with varied LC in water (pH 5.0).

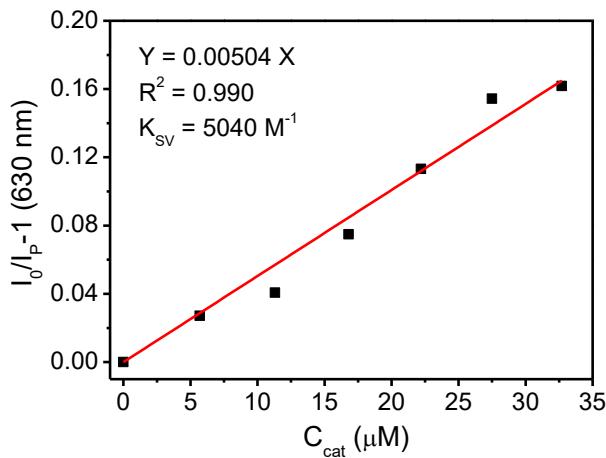


Figure S4. The Stern-Volmer plots of (I_0/I_p-1) values as a function of C_{cat} by successive addition of H-Fe-1 into a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (5 μM) and sodium ascorbate (10 mM). $\text{Ru}(\text{bpy})_3^{2+}$ was excited at 456 nm and luminesced at 630 nm.

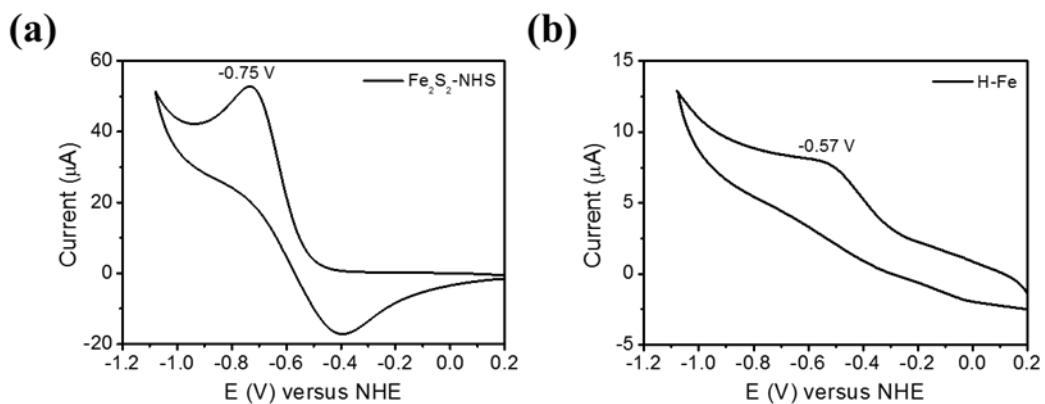


Figure S5. Cyclic voltammograms of (a) $\text{Fe}_2\text{S}_2\text{-NHS}$ (45 μM) in CH_3CN in the presence of 0.1 M $(\text{n-Bu}_4\text{N})\text{PF}_6$ and (b) H-Fe-1 (45 μM incorporated catalyst) in 0.1 M aq. Na_2SO_4 solution. Scan rate, 50 mV s^{-1} .

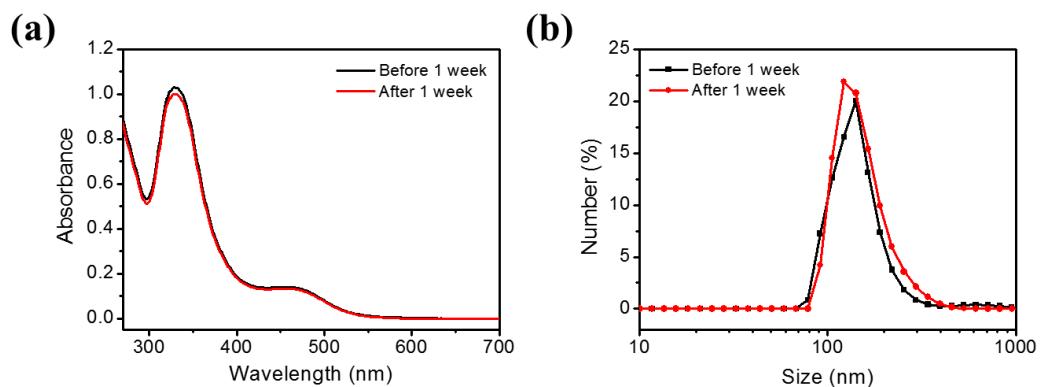


Figure S6. The UV-vis absorption spectra (a) and DLS analysis (b) of H-Fe-1 (120 μM incorporated catalyst) before and after 1-week storage protected from light at 4 $^{\circ}\text{C}$.

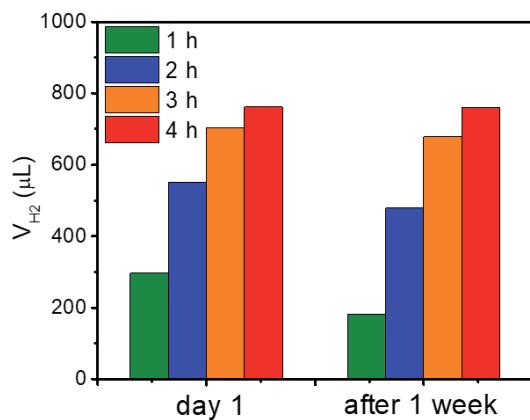


Figure S7. Photocatalytic H_2 production from H-Fe-1 before and after 1-week storage at 4 $^{\circ}\text{C}$. The reaction mixture (pH 5.0) contained incorporated catalyst (4 μM), $\text{Ru}(\text{bpy})_3^{2+}$ (400 μM), and ascorbic acid (160 mM).

Table S1. Comparison of reported photochemical systems based on peptides and proteins

Protein	PS	Catalyst	Electron donor	Light Source	TON ^[a]	Enhancement	TOF ^[a]	Time	Ref.
Flavodoxin	[Ru(4-CH ₂ Br-4'-bpy)(bpy) ₂]·2PF ₆ (5 μM)	NiC([Ni-(P ₂ ^{Ph} N ₂ ^{Ph}) ₂] (BF ₄) ₂ (5 μM)	Sodium ascorbate (0.1 M)	λ > 375 nm	620 ± 80	N.A.	410 ± 30 h ⁻¹ or ~6.8 min ⁻¹	N.A.	1
Cytochrome <i>b</i> ₅₆₂	Ru(bpy) ₃ ²⁺ (1 mM)	CoPP(IX) (10.8 μM)	Sodium ascorbate (0.1 M)	110 mW cm ⁻² , λ > 410 nm	310	~ 2.5	N.A.	8 h	2
Ferredoxin	[Ru(4-CH ₂ Br-4'-bpy)(bpy) ₂]·2PF ₆	[Co(dmgH) ₂ pyridyl]Cl	Sodium ascorbate (0.1 M)	λ > 375 nm	650 ± 150 (PS-based) or ~271	N.A.	170 ± 10 h ⁻¹ (PS-based) or 1.2 min ⁻¹	N.A.	3
Ferredoxin	[Ru(4-CH ₂ Br-4'-CH ₃ -2,2'-bpy)(bpy) ₂]·2PF ₆	Co(dmgBF ₂) ₂ ·2H ₂ O	Sodium ascorbate (0.1 M)	λ > 375 nm	210 ± 60 (PS-based) or ~76	N.A.	50 ± 10 h ⁻¹ (PS-based) or 0.3 min ⁻¹	8 h	4
Nitrobindin	Ru(bpy) ₃ ²⁺ (140 μM)	(μ-S-Cys) ₂ Fe ₂ (CO) ₆ core (7.8 μM)	Sodium ascorbate (0.1 M)	λ > 410 nm	130	~ 1	2.3 min ⁻¹	3 h	5
Myoglobin	Ru(bpy) ₃ ²⁺ (1 mM)	CoPP(IX) (5 μM)	Sodium ascorbate (0.1 M)	110 mW cm ⁻² , λ > 400 nm	518	4.32	1.47 min ⁻¹	8 h	6
Flavodoxin	PSI monomer (80 nM)	[Ni(P ₂ ^{Ph} N ₂ ^{Ph}) ₂] (BF ₄) ₂ 2.4 uM	Sodium ascorbate (0.1 M)	λ > 400 nm	2825 (PS-based)	2	1.25 s ⁻¹ (PS-based)	4 h	7
A β ₁₆₋₂₂ peptide	Eosin Y	Pt (10 wt%)	TEOA (10 vol%)	λ > 420 nm	92.9	5	0.39 min ⁻¹	20 h	8
Cytochrome <i>c</i> ₅₅₆	[Ru(tpy)(bpy)(im)](PF ₆) ₂ (140 μM)	[FeFe]Pep-18 (H10A) (140 μM)	Sodium ascorbate (0.1 M)	λ > 410 nm	9	N.A.	0.19 min ⁻¹	3 h	9
Helical peptide	Ru(bpy) ₃ ²⁺ (150 μM)	(μ-S-(CH ₂) ₃ -S) [Fe ₂ (CO) ₆] (9.33 μM)	Sodium ascorbate (0.1 M)	110 mW cm ⁻² , λ > 410 nm	84	N.A.	N.A.	2.3 h	10
Cytochrome <i>c</i>	Ru(bpy) ₃ ²⁺ (140 μM)	(μ-S-Cys) ₂ [Fe ₂ (CO) ₆] (14 μM)	Sodium ascorbate (0.1 M)	189 mW cm ⁻² , λ > 410 nm	82	6.83	0.21 min ⁻¹	3 h	11
Apo ferritin	Ru(bpy) ₃ ²⁺ (1 mM)	FeFe-COOH (51 μM)	Ascorbic acid (0.05 M)	200 mW cm ⁻² , λ > 400 nm	31 or 1.58 (PS-based)	8.5	N.A.	3 h	12
Histone H1	Ru(bpy) ₃ ²⁺ (400 μM)	Fe ₂ S ₂ -lip (4 μM)	Ascorbic acid (0.16 M)	200 mW cm ⁻² , λ > 400 nm	359 Or 3.59 (PS-based)	6	1.8 min ⁻¹	6 h	This work

^[a] TON and TOF were calculated based on the amount of catalyst unless otherwise stated.

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