Electronic Supplementary Information

Enhanced photocatalytic hydrogen production from a MCM-41-immobilized photosensitizer—[Fe-Fe] hydrogenase mimic dyad

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Synthesis and characterization of the photosensitizer—[Fe-Fe]-hydrogenase mimic dyad Ps-Hy and the model compounds



Fig. S1 Synthesis of compounds 3 and Ps-Hy.

Compound 1. A mixture of the 4-hydroxybenzyl alcohol (2.5 g, 20 mmol), 3-bromopropyne (3.57 g, 30 mmol), dried potassium carbonate (5.52 g, 40 mmol), and 18-crown-6 (1.1 g, 4 mmol) in 100 mL dry acetone was stirred vigorously at reflux under nitrogen for 21 h. After removal of solvent under vacuum, the residue was partitioned between water and dichloromethane (CH_2Cl_2) and the aqueous layer was extracted with CH_2Cl_2 3 times. The combined organic layers were then dried over anhydrous magnesium sulfate and evaporated to dryness. The crude product was purified by column chromatography eluting with 1/10 (v/v) ethyl acetate/CH₂Cl₂ to give as a colorless oil (2.6 g, 80%). ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.28 (s, 2H, ArH), 6.97 (s, 2H, ArH), 4.69 (s, 2H, -CH₂OAr), 4.59 (s, 2H, -OCH₂Ar), 2.52 (s, 1H, -CCH), 1.96 (s, 1H, -OH).

Compound 2. Compound **1** (1.6 g, 10 mmol) and $SOCl_2$ (2 mL, 28 mmol) was dissolved in THF (15 mL) and stirred vigorously at reflux under nitrogen for 1 h. After removal of solvent under reduced pressure, the residue was partitioned between water and ethyl acetate and the aqueous layer was extracted with ethyl acetate 3 times. The combined organic layers were then dried over anhydrous magnesium sulfate and evaporated to dryness to give the product as colorless oil: 1.7 g.

Compound 3. A solution of {(μ -S)₂Fe₂(CO)₆} (667.7 mg, 2 mmol) in dry THF (10 mL) was precooled to-78 °C, and then treated with LiBHEt ₃ (4.4 mL, 1 M in THF). After stirring the mixture for 20 min, compound **2** (726.1 mg, 4 mmol) was added and the mixture was warmed to room temperature for additional 18 h. A crude product was obtained by removal of the solvent, which was purified by using column chromatography (petroleum ether/CH₂Cl₂, v/v, from 2/1 to 1/1) to give as a red solid (600 mg, 48%). IR (KBr) ν (cm⁻¹): 2072 (CO), 2031 (CO), 1984 (CO), 3303, 1245, 636 (C=C - H). ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.32 (s, 2H, ArH, *e,e*-isomer), 7.02 (s, 6H, ArH, *a,e*-isomer,), 4.66 (s, 4H, -CH₂OAr, *e,e*-isomer and *a,e*-isomer), 3.67–3.09 (m, 4H, -SCH₂Ar, *e,e*-isomer and ae-isomer), 2.51 (s, 2H, -CCH, *e,e*-isomer and ae-isomer, *a,e/e,e* = 3:1). HR-MS (ESI-TOF) *m/z*: found 393.2080 (M-Fe₂(CO)₆+K⁺), calcd. m/z 393.0385 (M-Fe₂(CO)₆+K⁺).

Compound 4. A mixture of 4-bromomethyl-4-methyl-2,2'-bipyridine (5 g, 0.019 mol) and NaN₃ (6.2 g, 0.095 mol) were dissolved in a solvent mixture of dimethyl formamide (DMF) and water (55 mL, v/v, 10/1), the solution was stirred at 70 °C overnight. After removal of solvents under vacuum, the crude product was extracted with CH₂Cl₂, and the organic layer was washed with brine, dried over anhydrous magnesium sulfate. 4-Azidomethyl-4-methyl-2,2'-bipyridine was obtained as a white solid (4.0 g, 87.0%) by removal of the solvent. m.p. 39-41 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.68 (d, 1H, bpy-H^{3'}), 8.54 (d, 1H, bpy-H³), 8.35 (s, 1H, bpy-H^{6'}), 8.25 (s, 1H, bpy-H⁶), 7.32 – 7.26 (m, 1H, bpy-H^{5'}), 7.15 (d, 1H, bpy-H⁵), 4.48 (s, 2H, -CH₂bpy), 2.44 (s, 3H, -bpyCH₃).

Tetrakis(2-phenylpyridine-C2,N') (μ -dich1oro)diiridium ([Ir(ppy)₂]Cl₂) (2.14 g, 2.0 mmol) and 4-azidomethyl-4-methyl-2,2'-bipyridine (1.1g, 4.4 mmol) were dissolved in a solvent mixture of CH₂Cl₂ and CH₃OH (48 mL, v/v, 3/1) under nitrogen. The mixture was stirred at 40 °C overnight. After removal of solvents under vacuum, the residue was dissolved in 30 mL CH₃OH. An aqueous solution of ammonium hexafluorophosphate (5.0 g in 10 mL of deionized water) was slowly added to the CH₃OH solution and yielding a yellow precipitate. The precipitate was collected and purified by column chromatography on silica gel (CH₂Cl₂/diethyl ether, v/v, 10/1) to give a yellow solid (1.5 g, 43%). ¹H NMR (400 MHz, *d*⁶-DMSO, ppm) δ 8.81 (s, 2H, bpy-H³', bpy-H³), 8.25 (s, 2H, bpy, pyridyl-H⁶', pyridyl-H⁶), 7.92 (s, 4H, ppy, pyridyl-H⁶, phenyl-H³), 7.82 (d, 1H, bpy-H⁵'), 7.70 (s, 1H, bpy-H⁵), 7.01 (s, 2H, ppy, pyridyl-H³, phenyl-H⁴), 7.15 (s, 2H, ppy, phenyl-H⁵), 7.01 (s, 2H, ppy), phenyl-H⁵), 7.01 (s, 2H, ppy), phe

phenyl-H⁶), 6.89 (s, 2H, ppy, pyridyl-H⁵), 6.19 (s, 2H, ppy, pyridyl-H⁴), 4.83 (s, 2H, -CH₂bpy), 2.54 (s, 3H, -bpyCH₃). HR-MS (ESI-TOF) m/z: found 726.1957 (M-PF₆⁻), calcd. m/z 726.1978 (M-PF₆⁻).

Ps-Hy. A mixture of the compound 3 (210 mg, 0.33 mmol), compound 4 (605.4 mg, 0.70 mmol), copper sulfate pentahydrate (16.6 g, 0.06 mmol) and sodium ascorbate (28.2 mg, 0.13 mmol) in a solvent mixture of water and THF (10 mL, v/v, 1/1) was stirred vigorously at room temperature (RT) under nitrogen for 27 h. The mixture was evaporated to dryness under reduced pressure. The residue was partitioned between brine and CH₂Cl₂. The organic layer was then dried and evaporated to dryness. The crude product was purified by column chromatography eluting with 1/30 (v/v) methanol/CH₂Cl₂ to give as an orange solid (320 mg, 41%). IR (KBr) v (cm⁻¹): 2069 (CO), 2035 (CO), 1990 (CO), 1630 (triazole). ¹H NMR (400 MHz, d^{6} -DMSO, ppm) δ 8.89 (s, 2H, bpy-H^{3'}), 8.71 (s, 2H, bpy-H³), 8.39 (d, 2H, $bpy-H^{6'}$), 8.25 (s, 4H, ppy, pyridyl-H⁶), 7.86 (m, 10H, ppy, pyridyl-H³, phenyl-H², bpy- H^{6}), 7.73 – 7.51 (m, 8H, ppy, phenyl- $H^{3,5}$), 7.35 (d, 4H, phenyl-H), 6.89-7.14 (m, 18H, phenyl-H, triazole-H, ppy, pyridyl-H⁴, phenyl-H⁴, bpy-H⁵), 6.17 (s, 4H, ppy, pyridyl- H^5), 5.85 (s, 4H, -CH₂bpy), 5.15 (d, 4H, -CH₂OAr, *e,e*-isomer and *a,e*-isomer), 3.23-3.70 (m, 4H, -SCH₂Ar, *e,e*-isomer and *a,e*-isomer, a,e/e,e = 3:1), 2.54 (s, 6H, -bpyCH₃). HR-MS (ESI-TOF) *m/z*: found 1043.1594 ([M-2PF₆⁻]/2), calcd. *m/z* 1043.1598 ([M-2PF₆⁻]/2).



Fig. S2 The synthesis of the model compound Ps.

Ps. The procedure was similar as that of Ps-Hy. A mixture of compound **1** (30.8 mg, 0.19 mmol), compound **4** (124.8 mg, 0.14 mmol), copper sulfate pentahydrate (7.5 g, 0.04 mmol) and sodium ascorbate (11.5 mg, 0.06 mmol) in a solvent mixture of water and THF (5 mL, v/v, 1/1) was stirred vigorously at RT under nitrogen for 48 h. The crude product was purified by column chromatography to give a yellow solid (64.2 mg, 44%). IR (KBr) ν (cm⁻¹): 1608 (triazole), 1228 (OH). ¹H NMR (400 MHz, d^6 -DMSO, ppm) δ 8.88 (s, 1H, bpy-H^{3'}), 8.71 (s, 1H, bpy-H³), 8.38 (s, 1H, bpy-H^{6'}), 8.25 (s, 2H, ppy, pyridyl-H⁶), 7.90 (s, 4H, ppy, pyridyl-H³, phenyl-H²), 7.83 (d, 1H, bpy-H⁶), 7.55-7.66 (m, 4H, ppy, phenyl-H^{3.5}), 7.37 (s, 1H, triazole-H), 7.21 (s, 2H, phenyl-H), 7.15 (s, 2H, ppy, pyridyl-H⁴), 6.98 (s, 4H, ppy, phenyl-H⁴), 6.89 (s, 2H, phenyl-H), 6.17 (s, 2H, ppy, pyridyl-H⁴), 5.86 (s, 2H, -CH₂bpy), 5.13 (s, 2H, -CH₂OAr), 4.40 (d, 2H, -OCH₂Ar), 2.54 (s, 3H, -bpyCH₃). HR-MS (ESI-TOF) *m/z*: found 888.2687 (M- PF₆⁻), calcd. *m/z* 888.2638 (M- PF₆⁻).

Estimation of the free energy change (ΔG) for different electron transfer routes¹ The ΔG_a of direct electron transfer from the excited photosensitizer *[Ir(ppy)₂(bpy)]⁺ to the [2Fe2S] core of Ps-Hy involved in an electron transfer process was estimated by the equation:

$$\Delta G_{\rm a} = E({\rm D}^{\bullet+}/{\rm D}) - E({\rm A}/{\rm A}^{\bullet-}) - E_{0,0} - e^2/r\varepsilon - e^2/2(1/r_+ + 1/r_-)(1/\varepsilon' - 1/\varepsilon)$$

 $E(D^{+}/D)$ and $E(A/A^{-})$ are the oxidation potential of electron donor $(Ir(ppy)_2(bpy)^{+}/Ir(ppy)_2(bpy)^{2+})$ and the reduction potential of electron acceptor $(Fe^{I}Fe^{I}/Fe^{I}Fe^{0})$, respectively. $E_{0,0}$ represents the excited state energy of $Ir(ppy)_2(bpy)PF_6$ here, which was read from the cross-point (509 nm, 2.44 eV, Fig. S11) of the excitation and the emission spectra. The $e^2/r\varepsilon$ represents the Coulombic energy associated with bringing separated radical ions at a distance r in a solvent of dielectric constant ε (37.5 for CH₃CN and 41.8 for Water). The distance between the donor and the acceptor (r) is about 8.1 Å. To estimate the Born correction to the solvation energy, we set r_+ and r_- equal to 5.6 and 6.5 Å, respectively, by assuming that both donor and acceptor are spherical.

The G_b of the electron transfer from the reduced photosensitizer [Ir(ppy)₂(bpy)] to the [2Fe2S] center of Ps-Hy involved in an electron transfer process was estimated by the following equation:

$$\Delta G_{\rm b} = E({\rm D}/{\rm D}^{\bullet}) - E({\rm A}/{\rm A}^{\bullet}) - e^2/r\varepsilon - e^2/2(1/r_+ + 1/r_-)(1/\varepsilon' - 1/\varepsilon)$$

 $E(D/D^{-})$ and $E(A/A^{-})$ are the reduction potential of electron donor $(Ir(ppy)_2(bpy)^+/Ir(ppy)_2(bpy))$ and the reduction potential of electron acceptor (Fe^IFe^I/Fe^IFe^0) , respectively.



Fig. S3 ¹H NMR spectrum of Ps-Hy (400 MHz, d^6 -DMSO).



Fig. S4 HR-MS (ESI-TOF) spectrum of Ps-Hy.



Fig. S5. DLS datum of suspension derived from 5.6 mg Ps-Hy@MCM-41 (loading: 77.8 μmol/g) in 10 mL CH₃CN/H₂O (9/1, v/v) with TEA (0.8 M) at pH value of 10.



Fig. S6 Diffuse reflectance spectra of K-MCM-41 (solid line), Ps-Hy (dash line) and Ps-Hy@MCM-41 (dot line). The loading of Ps-Hy@MCM-41 is 77.8 μ mol g⁻¹.



Fig. S7 TGA curve of Ps-Hy@MCM-41. The loading of Ps-Hy@MCM-41 is 77.8 μ mol g⁻¹.



Fig. S8 Photochemical production of hydrogen in 10 mL CH_3CN/H_2O binary solvent with various ratio of CH_3CN/H_2O . Ps-Hy@MCM-41: 5.5 mg with loading of 19.1 μ mol/g, [TEA] = 0.6 M.



Fig. S9 Photocatalytic hydrogen evolution in 10 mL CH₃CN/H₂O (9/1, v/v) at different pH values. Ps-Hy@MCM-41: 5.5 mg with loading of 19.1 μ mol/g, [TEA] = 0.6 M.



Fig. S10 Photochemical production of hydrogen in 10 mL CH_3CN/H_2O (9/1, v/v) as a function of

TEA concentrations, Ps-Hy@MCM-41: 5.5 mg with loading of 19.1 µmol/g, pH = 10.



Fig. S11. The FTIR (KBr) spectra of Ps-Hy (4×10^{-5} M) and 5.6 mg Ps-Hy@MCM-41 (loading 77.8 µmol/g) in 10 mL CH₃CN/H₂O (9/1, v/v) with TEA (0.8 M) at pH value of 10 before and after 2 h irradiation.



Fig. S12 Emission spectra of Ps-Hy@MCM-41 (3 mg with loading of 77.8 μ mol/g) in CH₃CN/H₂O (9/1, v/v) in the presence and in the absence of TEA (0.8 M).



Fig. S13 Emission (dash line) and excitation (solid line) spectra of Ps $(4 \times 10^{-5} \text{ M})$ in CH₃CN.



Fig. S14 Cyclic voltammogram of compound 3 (1.0 mM) (a) and Ps-Hy (0.5 mM) (b) in CH_3CN

with 0.1 M n-Bu₄NPF₆ as the electrolyte at a scan rate of 100 mV·s⁻¹ under Ar atmosphere.



Fig. S15 Transient absorption spectra of Ps $(1.2 \times 10^{-4} \text{ M})$ and Ps-Hy $(6 \times 10^{-5} \text{ M})$ in the presence of TEA (0.8 M) in deaerated CH₃CN/H₂O = 9/1 (v/v) at the pH value of 10 after laser excitation (420 nm) taken at 50 µs. Inset: Kinetic trace of Ps and Ps-Hy at 530 nm.



Fig. S16 Kinetic traces of Ps $(1.2 \times 10^{-4} \text{ M})$ (a), Ps@MCM-41 (3.0 mg, Ps: 60µmol g⁻¹) (b), Ps-Hy (6 × 10⁻⁵ M) (c) and Ps-Hy@MCM-41 (3.0 mg, Ps-Hy: 77.8 µmol g⁻¹) (d) at 530 nm in the presence of TEA (0.8 M) upon excitation with 420 nm light in 5 mL CH₃CN/H₂O = 9/1 (v/v); The purple solid line is the fitted curve and the bottom trace shows the residual distribution for the monoexponential (a and b) or double-exponential (c and d) fit.



Fig. S17 Kinetic traces of (a) Ps-Hy (6×10^{-5} M) and (b) Ps-Hy@MCM-41 (3.0 mg, Ps-Hy: 77.8 μ mol g⁻¹) at 530 nm in the presence of TEA (0.8 M) at pH value of 10 upon excitation with 420 nm light in 5 mL CH₃CN/H₂O = 9/1 (v/v) after 0, 30 and 60 min irradiation with visible light, respectively.

Commlayor	$E_{\rm pa}({\rm V})$	$E_{\rm pa}({ m V})$	$E_{\rm pc}({\rm V})$	$E_{\rm pc}({\rm V})$	$E_{\rm pc}({\rm V})$
Complexes	$\mathbf{Ir}^{\mathrm{III}}/\mathbf{Ir}^{\mathrm{IV}}$	$\mathbf{Fe}^{\mathrm{I}}\mathbf{Fe}^{\mathrm{I}}/\mathbf{Fe}^{\mathrm{I}}\mathbf{Fe}^{\mathrm{II}}$	Fe ¹ Fe ¹ /Fe ¹ Fe ⁰	Fe ¹ Fe ⁰ /Fe ⁰ Fe ⁰	L_{Ir}/L_{Ir}
$Ir(ppy)_2(bpy)PF_6$	0.87	—	—	—	-1.8
Ps	0.90				-1.79
3	_	0.53	-1.67	-2.27	_
Ps-Hy	0.86	0.52	-1.65	-2.38	-1.87

Table S1 Electrochemical data for PS, compound 3 and Ps-Hy^a.

a All potentials are vs. Fc/Fc⁺.

Table	S2.	Lifetimes	measured	at	530	nm	in	the	presence	and	absence	of	K-MCM-41	in
CH ₃ C	N/H_2	O = 9/1 (v)	/v).											

	A_1	$\tau_1 (\mu s)$	A ₂	τ_2 (ms)
Ps+TEA			1.0	14.5
Ps@MCM-41+TEA			1.0	19.0
Ps-Hy+TEA	0.06	61	0.94	2.9
Ps-Hy+TEA ^a	0.69	19	0.31	3.2
Ps-Hy+TEA ^b	0.77	14	0.23	3.6
Ps-Hy@MCM-41+TEA	0.06	91	0.94	4.4
Ps-Hy@MCM-41+TEA ^a	0.22	74	0.78	4.5
Ps-Hy@MCM-41+TEA ^b	0.58	40	0.42	5.0

a: after 30 minutes irradiation; b: after 60 minutes irradiation.

1. T. Yu, Y. Zeng, J. Chen, Y.-Y. Li, G. Yang and Y. Li, Exceptional dendrimer-based mimics of diiron hydrogenase for the photochemical production of hydrogen, *Angew. Chem.*, *Int. Ed.*, 2013, **52**, 5631-5635.