Supporting Information

Visible-Light-Driven Hydrogen Evolution on a Polyoxometalate-Based Copper Molecular Catalyst

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1. Supplementary Structural Figures

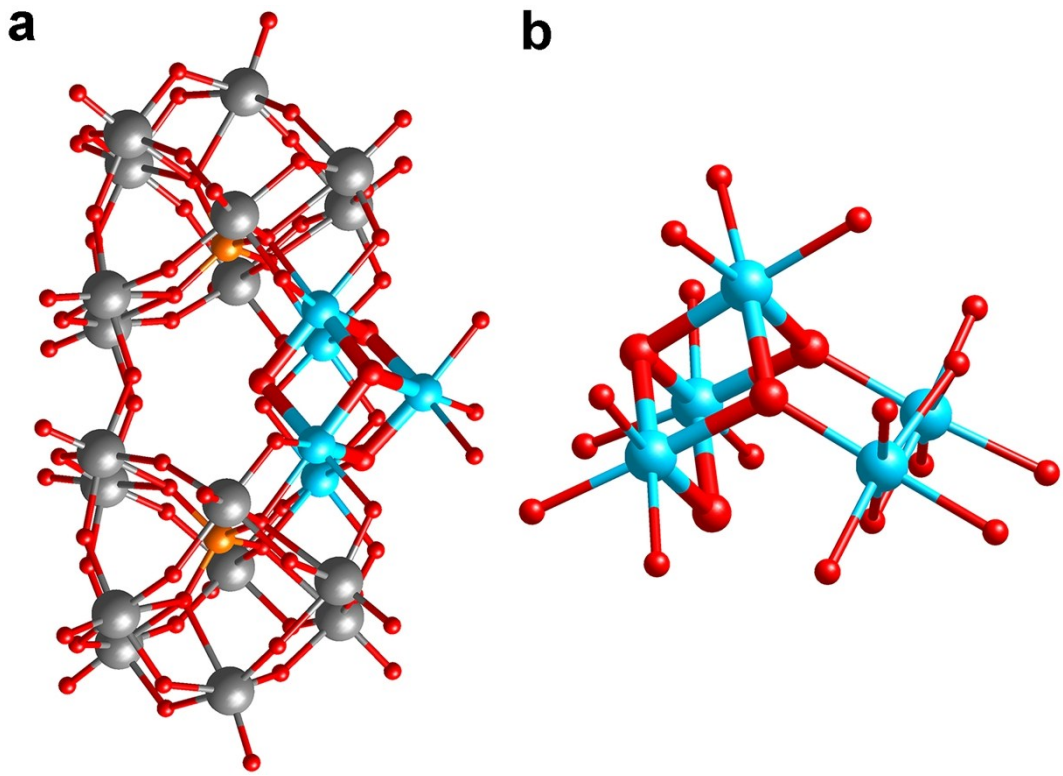


Fig. S1 Ball-and-stick representations of the structure of (a) compound **1** and (b) {Cu_5} core in **1**. W, gray sphere; Si, orange sphere; O, red sphere; Cu, blue sphere.

2. Visible-Light-Driven HER

Table S1. TON and TOF of visible light-driven HER catalyzed by different concentrations of catalysts[a].

Catalysts	Catalyst concentration (μM)	TON[b]	TOF[c] [h^{-1}]
1	2	718.9 ± 16.4	149.0 ± 14.4
1	5	401.7 ± 5.6	80.2 ± 5.3
1	10	234.1 ± 2.9	52.9 ± 1.6
1	15	182.1 ± 2.1	42.9 ± 1.8
1	20	156.7 ± 1.6	37.5 ± 1.4
2	2	582.7 ± 14.1	134.8 ± 11.0
2	5	301.3 ± 4.9	73.5 ± 4.2
2	10	187.4 ± 2.1	43.0 ± 2.3
2	15	151.3 ± 1.6	33.6 ± 1.6
2	20	131.6 ± 1.4	32.7 ± 3.8
3	20	87.0 ± 1.6	23.3 ± 1.3
$Cu(NO_3)_2$	20	25.3 ± 1.4	6.0 ± 0.9
$Cu(NO_3)_2$	100	9.2 ± 0.3	2.4 ± 0.2

[a] Conditions: 100 W white LED light; catalysts (2–100 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)]^+$ (0.2 mM) after 6 h of visible-light irradiation, vigorous stirring (1.0×10^3 rpm). [b] TON = mol of H_2/mol of catalyst. [c] $TOF_{initial}$ = mol of H_2/(mol of catalyst × 1.0 h), based on the amount of H_2 produced after 1.0 h of visible-light irradiation.

Table S2. Visible light-driven HER catalyzed by different POM-based photocatalysts.

Catalysts	Representative conditions	TON	TOF	Ref.
1	100 W white LED light, 0.2 mM $[Ir(ppy)_2(dtbbpy)]^+$, 2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O	718.9 ± 16.4	149.0 ± 14.4 h^{-1}	This work
2		582.7 ± 14.1	134.8 ± 11.0 h^{-1}	
3		87.0 ± 1.6	23.3 ± 1.3 h^{-1}	
$Cu(NO_3)_2$		9.2	2.4 ± 0.2 h^{-1}	
$[\alpha\text{-}Sn_4(SiW_9O_{34})_2]^{28-}$	300 W Xe lamp (400 nm cut-off filter), H_2PtCl_6 co-catalyst (0.5 g), and 270 mL MeOH (20 vol%) solution	1.4	0.025 h^{-1}	1
$[Mn_4(H_2O)_2(VW_9O_{34})_2]^{10-}$	LED light (20 mW, 455 nm), 0.67 mM $[Ru(bpy)_3]Cl_2$, TEOA (0.25 M), and 2 mL DMF/H_2O (1.86/1)	42	–	2
$[\{Ni_4(OH)_3AsO_4\}_4(B\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$	LED light (20 mW, 455 nm), $[Ir(ppy)_2(dtbbpy)]^+$ (0.2 mM), TEOA (0.25 M), H_2O (1.4 M), and 2 mL CH_3CN/DMF (1/3)	360	–	3
$[Ni(H_2O)PW_{11}O_{39}]^{5-}$	High power LED (λ = 470 nm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 0.12 M ascorbate buffer, pH 4	10.8	0.0097 s^{-1}	4
$[Ni(H_2O)SiW_{11}O_{39}]^{6-}$		inactive	–	
$[Ni(H_2O)GeW_{11}O_{39}]^{6-}$		36.8	0.009 s^{-1}	
$[\{Ni_4(OH)_3(PO_4)\}_4(A\text{-}PW_9O_{34})_4]^{28-}$	100 W white LED light, 0.2 mM $[Ir(ppy)_2(dtbbpy)][PF_6]$, 2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O	578.8	100.5 h^{-1}	5
$[\{Ni_4(OH)_3(PO_4)\}_4(A\text{-}PW_9O_{34})_2(B\text{-}PW_9O_{34})_2]^{28-}$		679.1	112.7 h^{-1}	
$[\{Ni_4(OH)_3(VO_4)\}_4(B\text{-}PW_9O_{34})_4]^{28-}$		931.1	185.5 h^{-1}	
$[Cu_4(H_2O)_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{10-}$	LED light (20 mW, 455 nm), 0.2 mM $[Ir(ppy)_2(dtbbpy)]^+$, TEOA (0.25 M), H_2O (1.4 M), and 2 mL CH_3CN/DMF (1/3)	1270	–	6
$[Ni_3(OH)_3(H_2O)_3P_2W_{15}O_{59}]^{9-}$	LED light (20 mW, 455 nm), 0.2 mM $[Ir(ppy)_2(dtbbpy)]^+$, TEOA (0.25 M), and 2 mL CH_3CN/DMF/H_2O	161	–	7
$[Ni_{14}(OH)_6(H_2O)_{10}(HPO_4)_4\text{-}(P_2W_{15}O_{56})_4]^{34-}$		260	–	
$[Ni_2(P_2W_{15}O_{56})_2]^{20-}$		1	–	
$[Cu^{II}_{14}Te^{IV}_{10}O_{28}(B\text{-}\alpha\text{-}SiW_9O_{34})_4]^{28-}$	Xe light (100 W, 420 nm cut off), $[Ir(ppy)_2(dtbbpy)]^+$ (0.2 mM), 1 mL TEOA, 5.5 mL CH_3CN, 16.5 mL DMF, and 2 mL H_2O	343.6	116.7 h^{-1}	8

Solubility experiments of [Ir(ppy)$_2$(dtbbpy)][PF$_6$]. Firstly, 0.5 mg [Ir(ppy)$_2$(dtbbpy)][PF$_6$] was put into a 50 mL beaker with 10 mL distilled water. Then, the beaker was sonicated for 20 minutes. As shown in Fig. S2a, [Ir(ppy)$_2$(dtbbpy)][PF$_6$] is quite hard to be dissolved in water and it is just dispersed in water. When the water being poured out the beaker, the undissolved yellow [Ir(ppy)$_2$(dtbbpy)][PF$_6$] can be obviously seen on the inside of the beaker (Fig. S2b). Secondly, 0.5 mg [Ir(ppy)$_2$(dtbbpy)][PF$_6$] was put into 1 mL CH$_3$CN/DMF/H$_2$O (volume ratio, 33/11/4) mixed solution, [Ir(ppy)$_2$(dtbbpy)][PF$_6$] is dissolved immediately and a clear yellow solution was formed (Fig. S2c).

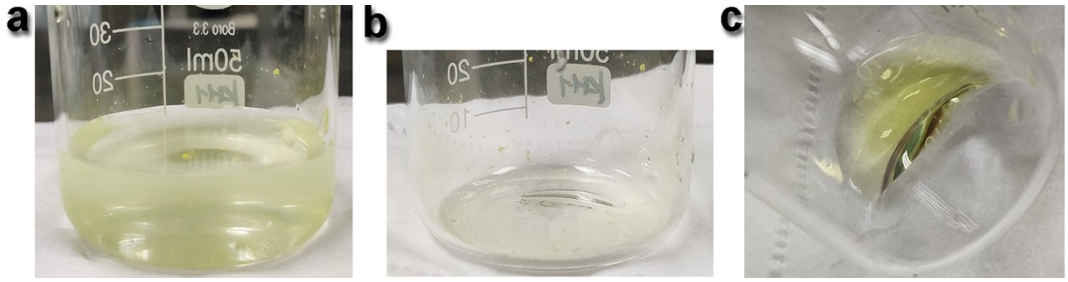


Fig. S2 Solubility experiments of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] in different solvents. (a) [Ir(ppy)$_2$(dtbbpy)][PF$_6$] was almost insoluble in water. (b) [Ir(ppy)$_2$(dtbbpy)][PF$_6$] is on the inside of the beaker after pouring out water. (c) [Ir(ppy)$_2$(dtbbpy)][PF$_6$] was dissolved in 1 mL CH$_3$CN/DMF/H$_2$O (volume ratio, 33/11/4) mixed solution.

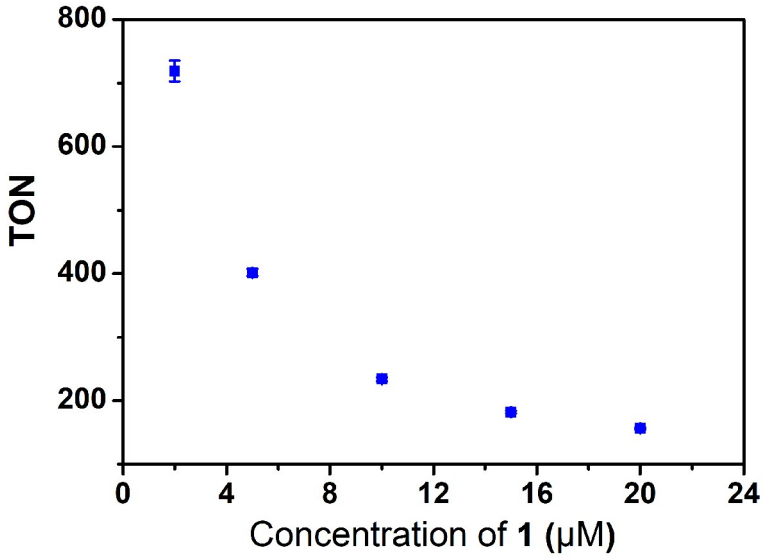


Fig. S3 TON *vs.* different concentrations of **1**. Conditions: 100 W white LED light, catalyst concentrations (2–20 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) after 6 hours of visible-light irradiation, vigorous stirring (1.0×10^3 rpm).

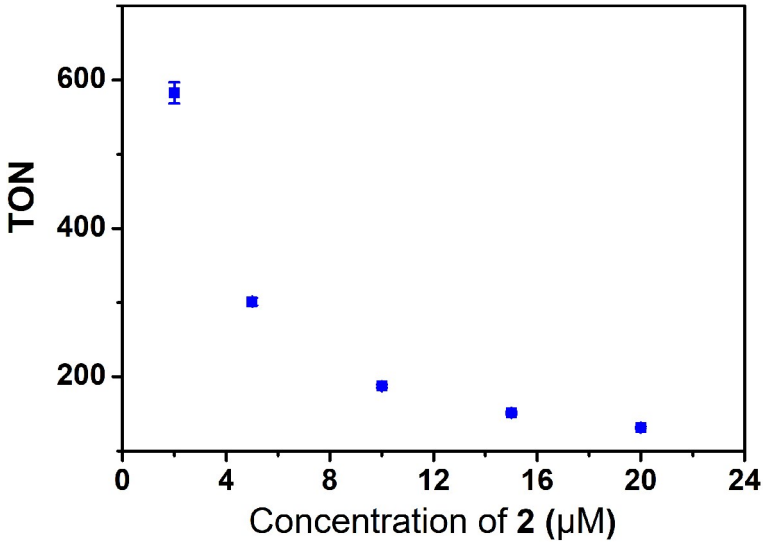


Fig. S4 TON *vs.* different concentrations of **2**. Conditions: 100 W white LED light, catalyst concentrations (2–20 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) after 6 hours of visible-light irradiation, vigorous stirring (1.0×10^3 rpm).

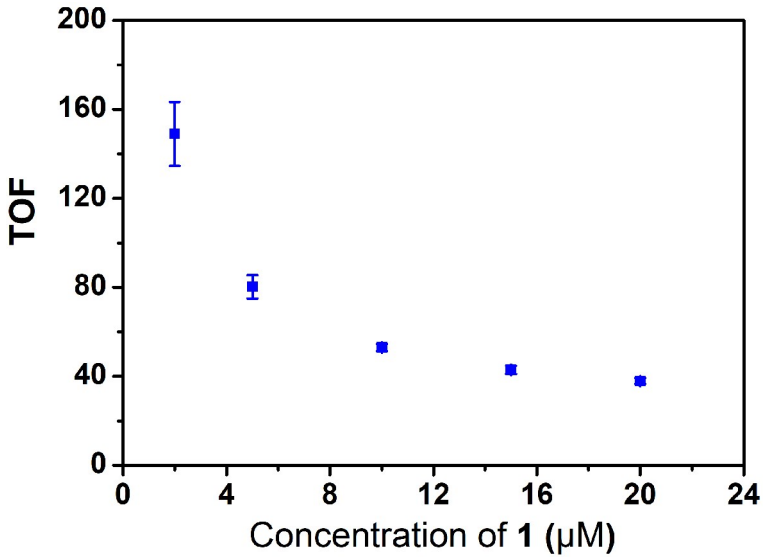


Fig. S5 TOF *vs.* different concentrations of **1**. Conditions: 100 W white LED light, catalyst concentrations (2–20 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) after 6 hours of visible-light irradiation, vigorous stirring (1.0×10^3 rpm).

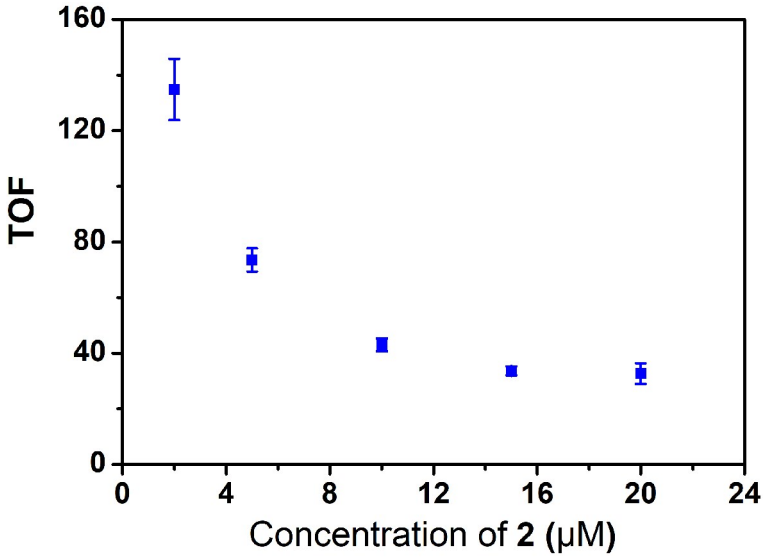


Fig. S6 TOF *vs.* different concentrations of **2**. Conditions: 100 W white LED light, catalyst concentrations (2–20 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) after 6 hours of visible-light irradiation, vigorous stirring (1.0×10^3 rpm).

Quantum yield calculation:

$$\Phi_{QY} = 2 \times \frac{n(evolved\ H_2)}{n(incident\ photons)} \times 100\%$$

Initial radius = 0.5 cm = 0.005 m

$$A_R = \pi R^2 = \pi \times (0.005m)^2 = 7.854 \times 10^{-5} m^2$$

$$P = \bar{E} \cdot A_R$$

$$n(incident\ photons) = \frac{Pt\bar{\lambda}}{hcN_A} = 3.23 \times 10^{-3}\ mol$$

where P is the illumination power (W), *t* is the illumination time (s, in our cases *t* = 21600s), A_R is the irradiation area, *h* is the Planck constant, *c* is the velocity of light and N_A is Avogadro's number.

For compound **1**:

H_2 formation rate = 7.30×10^{-9} mol/s

$$\Phi_{QY} = 2 \times \frac{7.30 \times 10^{-9} \times 3600 \times 6}{3.23 \times 10^{-3}} \times 100\% = 9.8\%$$

For compound **2**:

H_2 formation rate = 6.09×10^{-9} mol/s

$$\Phi_{QY} = 2 \times \frac{6.09 \times 10^{-9} \times 3600 \times 6}{3.23 \times 10^{-3}} \times 100\% = 8.2\%$$

For compound **3**:

H_2 formation rate = 4.03×10^{-9} mol/s

$$\Phi_{QY} = 2 \times \frac{4.03 \times 10^{-9} \times 3600 \times 6}{3.23 \times 10^{-3}} \times 100\% = 5.4\%$$

The high quantum yield of 9.6% for **1**, 8.2% for **2**, and 5.4% for **3** is achieved at a catalyst concentration of 20 μM (Table S2), respectively, which is comparable to many other visible-light-driven HER systems.[8–15]

Table S3. Quantum yield of visible light-driven HER catalyzed by different photocatalysts.

Catalysts	**Representative reaction conditions**	**Quantum yield**	**Ref.**
1	100 W white LED light, 20 μM catalysts, 0.2 mM $[Ir(ppy)_2(dtbbpy)][PF_6]$, 2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O	9.8%	This work
2		8.2%	
3		5.4%	
$[(CF_3PY_5Me_2)Co(H_2O)](CF_3SO_3)_2$	150 W Xe lamp (455 nm long-pass filter), 50 μM catalyst, 0.2 mM $[Ru(bpy)_3]Cl_2$ and 0.1 M ascorbic acid in 1.0 M phosphate buffer (pH 7)	0.23%	9
$[Ni^{II}_4(H_2O)_2(TiW_9O_{34})_2]^{12-}$	300 W Xe light (λ = 532 nm), 5 mL 6% TEA aqueous solution, 4 mM fluorescein, deaerated with N_2.	0.52%	10
$[Co(bpyPY_2Me)(CH_3CN)(CF_3SO_3)](CF_3SO_3)$	Blue LED light (452 ± 10 nm), 40 μM catalyst, 0.33 mM $[Ru(bpy)_3]^{2+}$ and 0.5 M H_2A/HA^- at pH 4	7.5 ± 0.8%	11
$(Et_4N)Ni(X\text{-}pyS)_3$ (X = 5-H)	LED (520 nm, 13 mW/cm^2), catalysts (4.0 μM), fluorescein (2.0 mM), and TEA (0.36 M) in EtOH/H_2O (1/1), pH 11.6, 15 °C.	4.5 ± 0.7%	12
$(Et_4N)Ni(X\text{-}pyS)_3$ (X = 6-CH_3)		6.0 ± 0.8%	
$[SiW_{11}O_{39}]^{8-}$	Hg lamp (400 W) with a cutoff filter (λ > 420 nm), $[SiW_{11}O_{39}]^{8-}$ (32 mM), EY (0.31 mM), 1.0 wt% Pt, pH 7.0.	11.4%	13
Ni-ME complex	300 W Xe lamp with a bandpass filter (centered at 460 nm), $Ni(OAc)_2$ (3 mM), 2-mercaptoethanol (30 mM), Erythrosine B (2.25 mM) in a 100 mL of aqueous solution containing 15 vol% of TEOA (pH 8.5).	24.5%	14
RuP-NiP system	RuP (0.3 μmol) and NiP (0.1 μmol) in AA (0.1 M, pH 4.5) was measured using an LED light source (λ 460 nm, 5 mW cm^{-2}).	10%	15

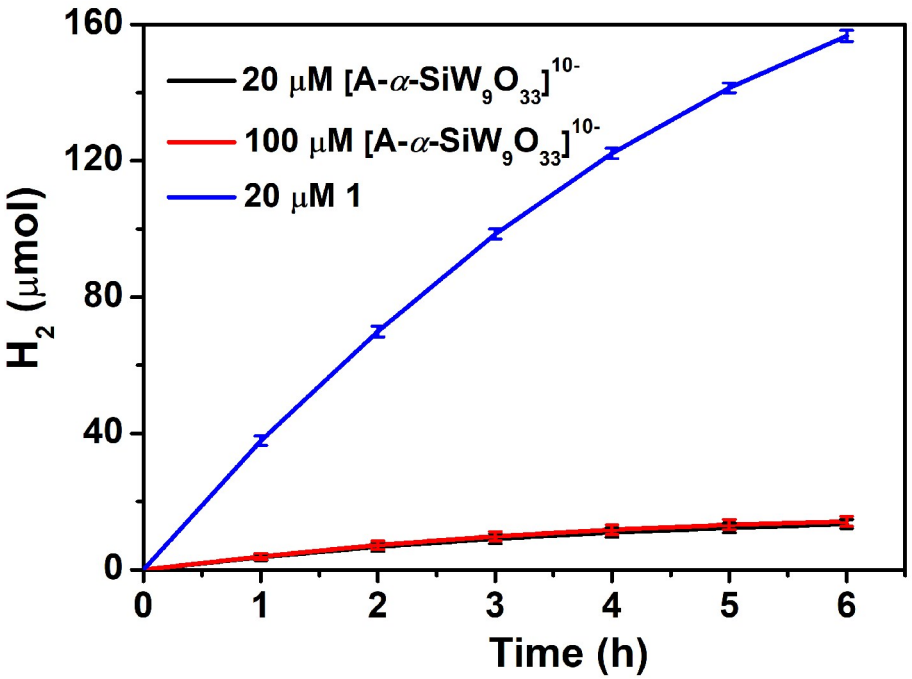


Fig. S7 Comparison of visible light-driven HER activity of different concentrations of $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ and 20 μM of **1**. Conditions: 100 W white LED light, 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), vigorous stirring (1.0×10^3 rpm).

3. Quenching Mechanism Studies

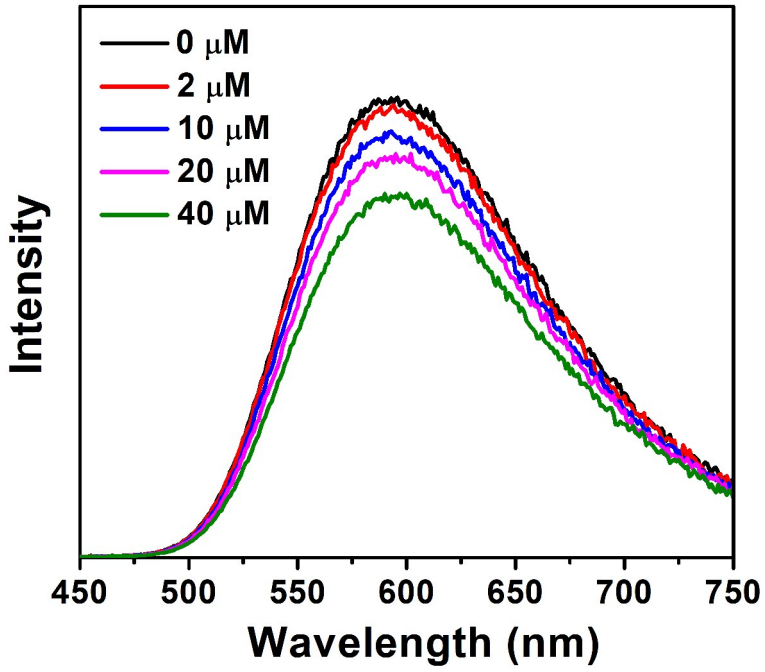


Fig. S8 Emission spectra of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) with different concentrations of **2** (0–40 μM).

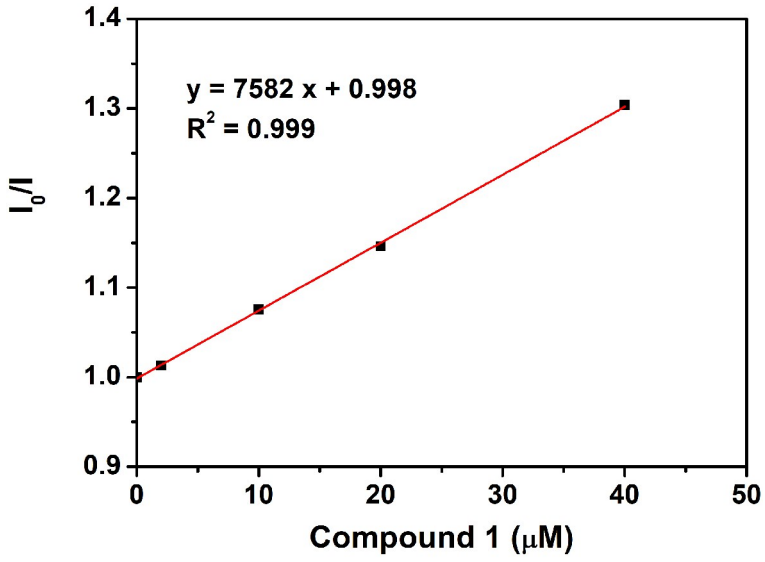


Fig. S9 Stern-Volmer plots for emission spectra of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) with different concentrations of **1** (0–40 μM).

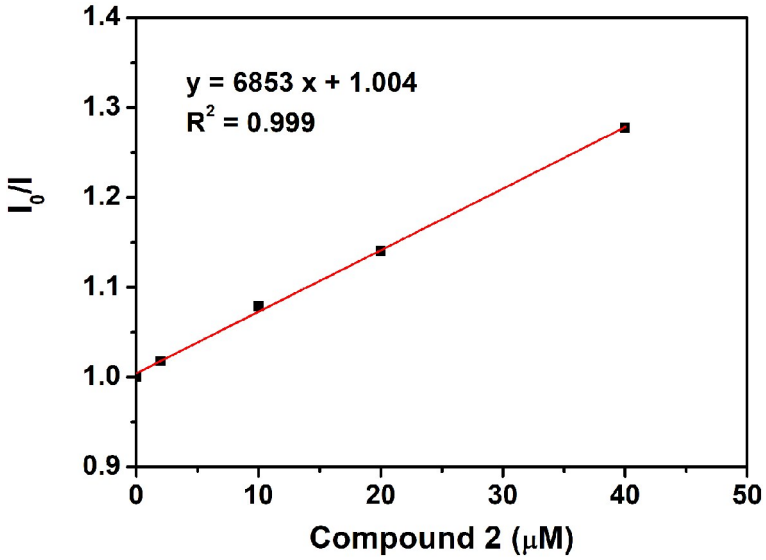


Fig. S10 Stern-Volmer plots for emission spectra of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) with different concentrations of **2** (0–40 μM).

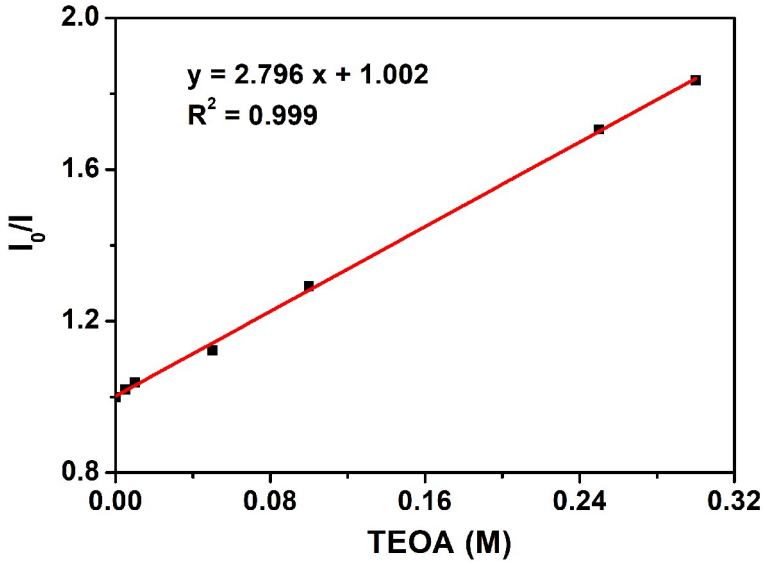


Fig. S11 Stern-Volmer plots for emission spectra of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM) with different concentrations of TEOA (0–0.3 M).

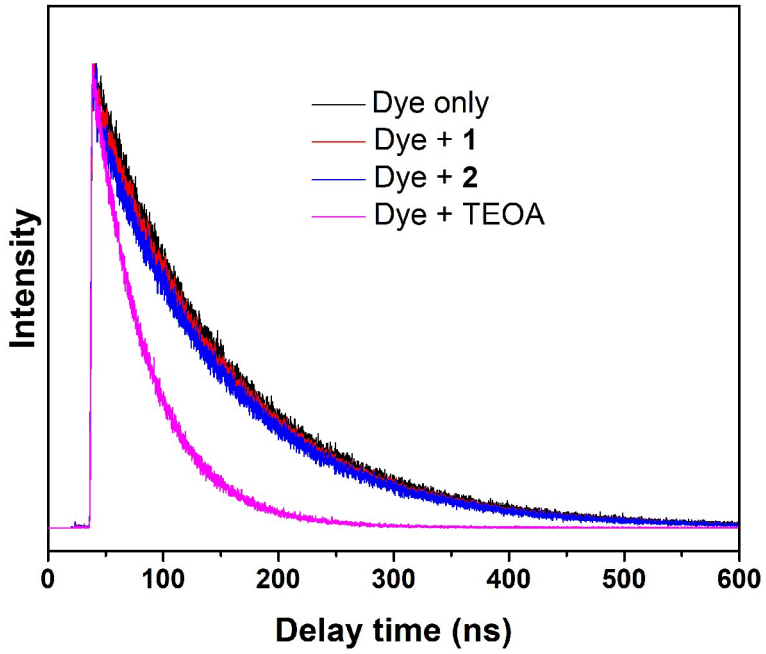
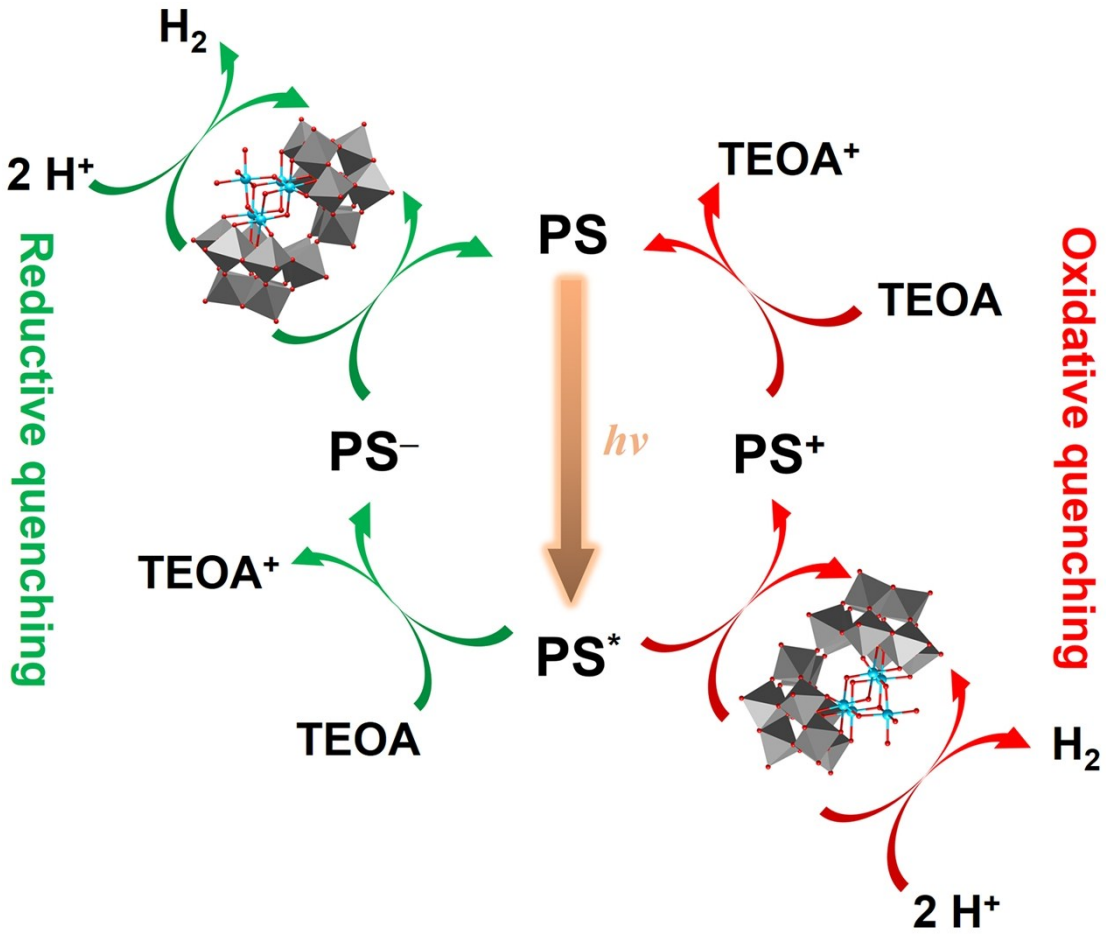


Fig. S12 Time-resolved fluorescence spectra of $[Ir(ppy)_2(dtbbpy)]^+$ dye only (black curve), $[Ir(ppy)_2(dtbbpy)]^+$ dye with **1** (red curve), $[Ir(ppy)_2(dtbbpy)]^+$ dye with **2** (blue curve) and $[Ir(ppy)_2(dtbbpy)]^+$ dye with TEOA (pink curve). Conditions: 400 nm excitation, 0.2 mM $[Ir(ppy)_2(dtbbpy)]^+$, 50 μM catalysts, 0.25 M TEOA and $CH_3CN/DMF/H_2O$ (volume ratio: 11/33/4).

Table S4. Comparison of lifetimes of excited state $[Ir(ppy)_2(dtbbpy)]^+$ dye.

Sample	Lifetime (ns)
$[Ir(ppy)_2(dtbbpy)]^+$ dye only	114.3 ± 0.5
$[Ir(ppy)_2(dtbbpy)]^+$ dye + **1**	107.9 ± 0.3
$[Ir(ppy)_2(dtbbpy)]^+$ dye + **2**	104.7 ± 0.3
$[Ir(ppy)_2(dtbbpy)]^+$ dye + TEOA	47.3 ± 1.0



Scheme S1. Proposed mechanism for the visible-light-driven HER system catalyzed by **1** with oxidative and reductive quenching mechanism, PS = $[Ir(ppy)_2(dtbbpy)]^+$.

4. Stability Studies

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 0.01501	Peak 1:	0.000	0.0	0.000
PdI: 0.043	Peak 2:	0.000	0.0	0.000
Intercept: 0.376	Peak 3:	0.000	0.0	0.000
Result quality : Refer to quality report				

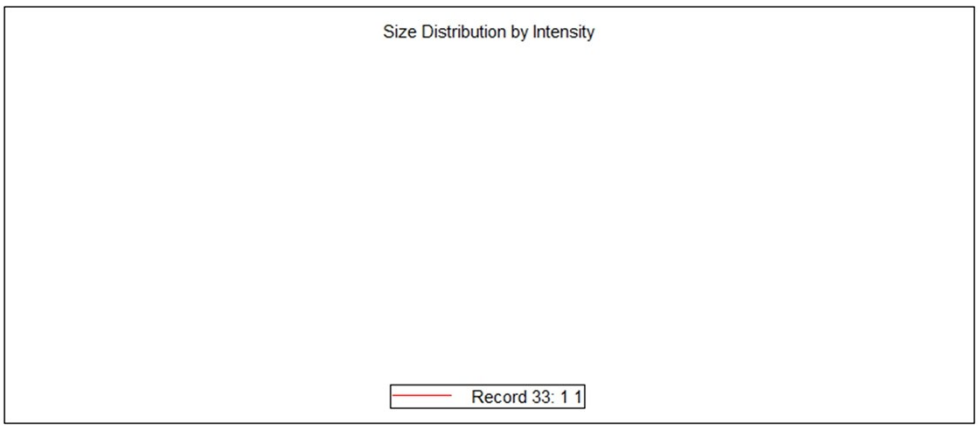


Fig. S13 DLS measurement of **1** (20 μM) solution after 6 hours of visible-light irradiation. Conditions: 100 W white LED light, 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), vigorous stirring (1.0×10^3 rpm).

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 2806	Peak 1:	100.3	54.2	6.992
PdI: 1.000	Peak 2:	12.73	45.8	0.9183
Intercept: 0.692	Peak 3:	0.000	0.0	0.000
Result quality : Refer to quality report				

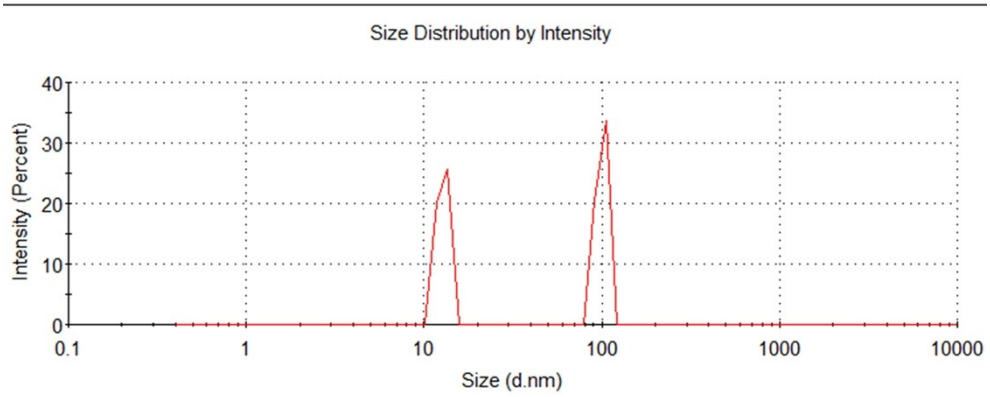


Fig. S14 DLS measurement of $Cu(NO_3)_2$ (10 μM) solution after 6 hours of visible-light irradiation. Conditions: 100 W white LED light, 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), vigorous stirring (1.0×10^3 rpm).

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 115.1	Peak 1:	145.8	100.0	63.03
PdI: 0.243	Peak 2:	0.000	0.0	0.000
Intercept: 0.869	Peak 3:	0.000	0.0	0.000
Result quality : Good				

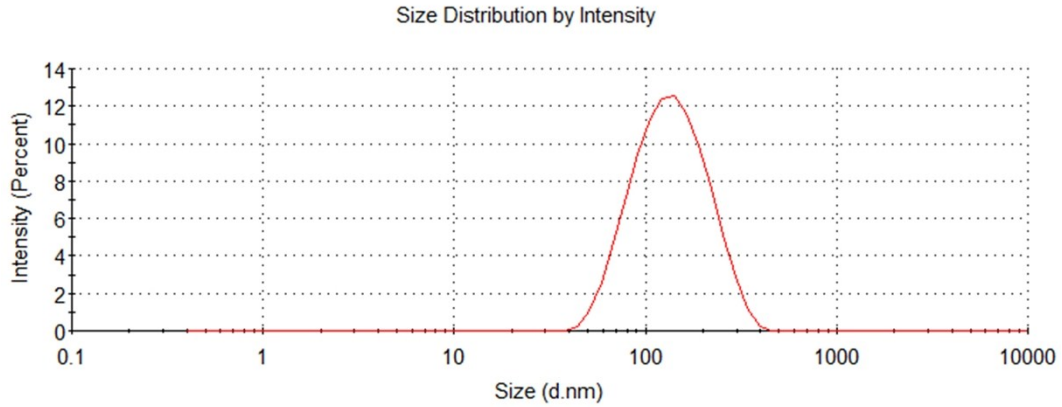


Fig. S15 DLS measurement of $Cu(NO_3)_2$ (20 μM) solution after 6 hours of visible-light irradiation. Conditions: 100 W white LED light, 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), vigorous stirring (1.0×10^3 rpm).

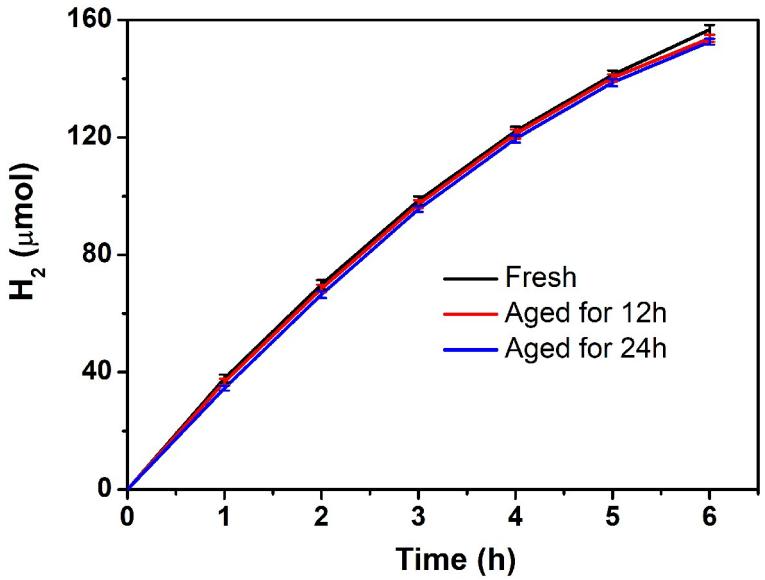


Fig. S16 Visible light-driven HER activity of **1** after being aged for 12 hours and 24 hours. Conditions: 100 W white LED light, catalyst (20 μM) in a 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O) with $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), vigorous stirring (1.0×10^3 rpm).

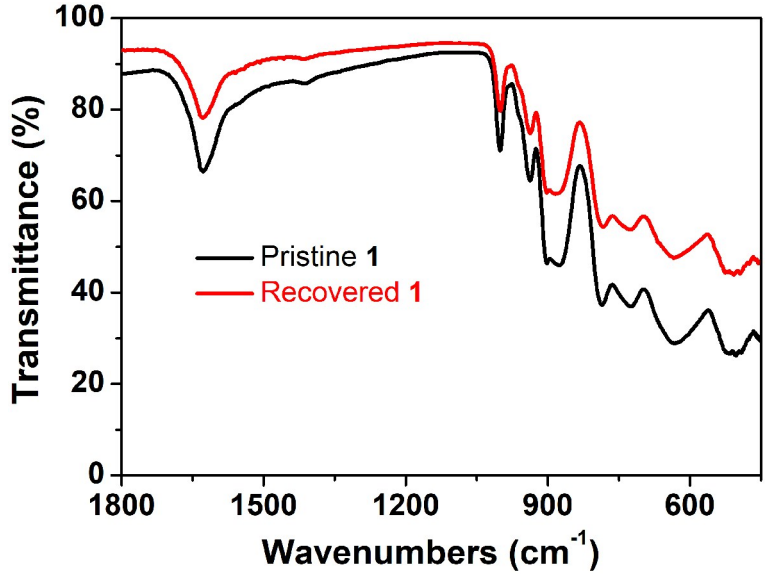


Fig. S17 FT-IR spectra of pristine **1** and recovered **1** after photocatalytic HER.

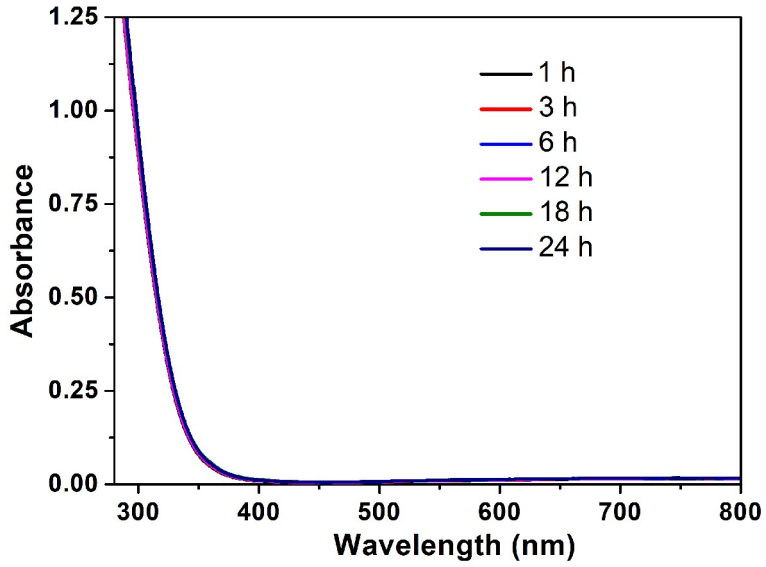


Fig. S18 Time-dependent UV-Vis spectra of **1** (1.0×10^{-4} M) in the DMF/CH_3CN/TEOA/H_2O solution (volume ratio, 33/11/2/4).

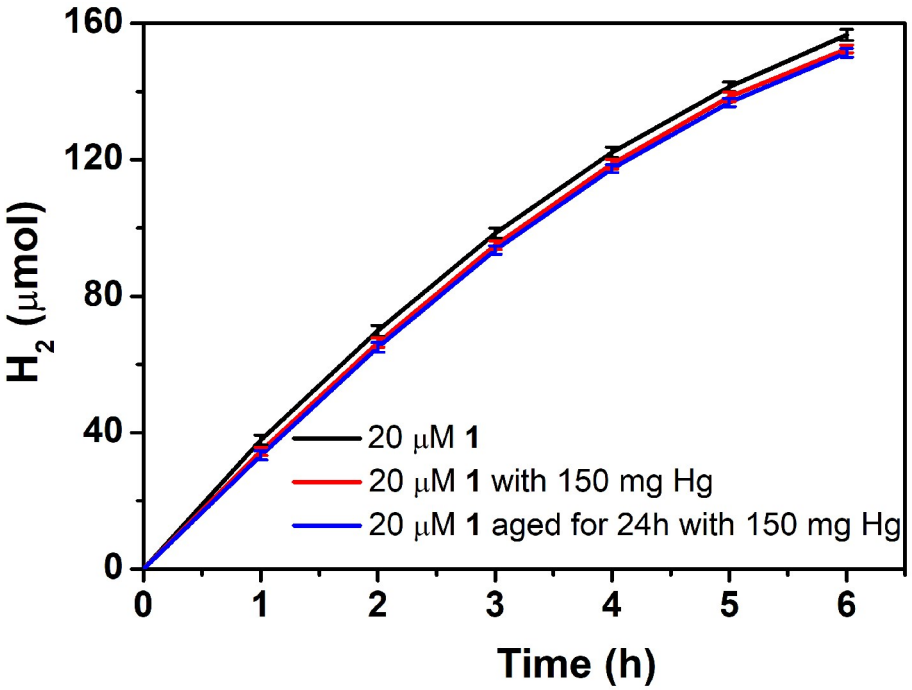


Fig. S19 Visible light-driven HER using 20 μM of **1** with 150 mg Hg and 20 μM of **1** with aged for 24h with 150 mg Hg. Conditions: 100 W white LED light, 20 μM of **1** with 150 mg Hg, $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O), vigorous stirring (1.0×10^3 rpm).

As can be seen in Table S5, the concentration of Cu is 0.36 μM after extraction. There are five Cu atoms in each molecular **1**. The total concentration of Cu is 100 μM as 20 μM of **1** was used for photocatalytic HER. As a result, catalyst extraction and ICP-MS analysis indicated that less than < 0.36% of **1** might have decomposed to other Cu species in the photocatalytic HER process.

Table S5. ICP-MS for compound **1** after 6 hours of visible-light irradiation.

Reaction time (h)	Concentration of **1** (μM)	Elements	Cu, W after extraction (μM)
6	20	Cu	0.36
		W	0.69

Conditions: 100 W white LED light, compound **1** (20 μM), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF, and 4 mL H_2O), vigorous stirring (1.0×10^3 rpm).

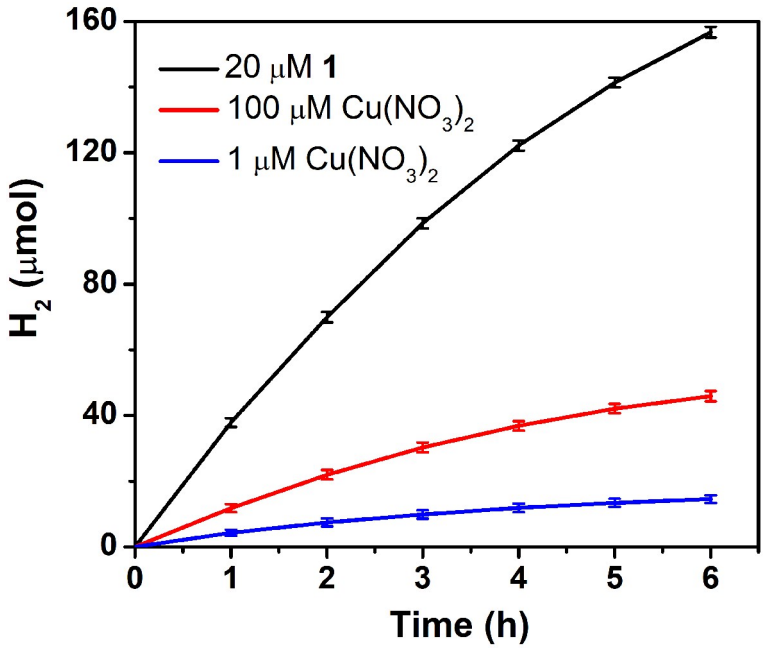


Figure S20. Kinetics of visible light-driven HER with 20 μM of **1**, 100 μM of $Cu(NO_3)_2$, and 1 μM of $Cu(NO_3)_2$. Conditions: 100 W white LED light, 50 mL solution (2 mL TEOA, 11 mL CH_3CN, 33 mL DMF and 4 mL H_2O), $[Ir(ppy)_2(dtbbpy)][PF_6]$ (0.2 mM), 6 hours of visible-light irradiation, vigorous stirring (1.0×10^3 rpm).

5. Supplementary Physical Characterizations

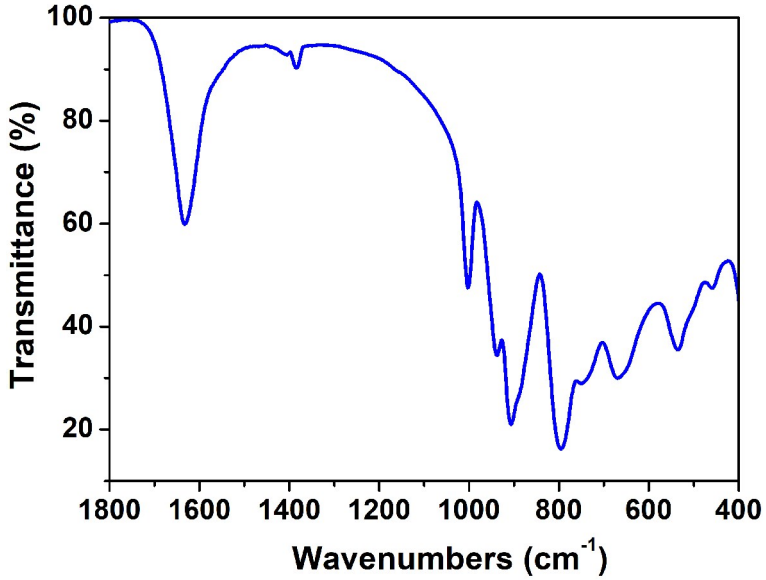


Fig. S21 FT-IR spectrum for compound **1**.

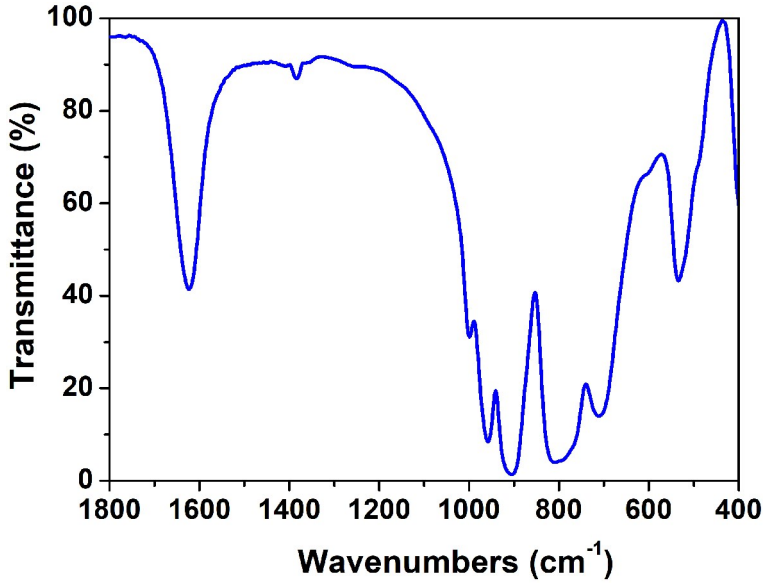


Fig. S22 FT-IR spectrum for compound **2**.

6. References

(1) Z. Y. Zhang, Q. P. Lin, S.-T. Zheng, X. H. Bu, P. Y. Feng, *Chem. Commun.,* **2011**, 47, 3918–3920.

(2) H. J. Lv, J. Song, H. M. Zhu, Y. V. Geletii, J. Bacsa, C. C. Zhao, T. Q. Lian, D. G. Musaev, C. L. Hill, *J. Catal.,* **2013**, 307, 48–54.

(3) H. J. Lv, Y. N. Chi, J. V. Leusen, P. Kögerler, Z. Y. Chen, J. Bacsa, Y. V. Geletti, W. W. Guo, T. Q. Lian, C. L. Hill, *Chem. - Eur. J.,* **2015**, 21, 17363–17370.

(4) K. V. Allmen, R. Moré, R. Müller, J. Soriano-López, A. Linden, G. R. Patzke, *ChemPlusChem,* **2015**, 80, 1389–1398.

(5) X.-B. Han, C. Qin, X.-L. Wang, Y.-Z. Tan, X.-J. Zhao, E.-B. Wang, *Appl. Catal. B-Environ.* **2017**, 211, 349–356.

(6) H. Lv, Y. Gao, W. Guo, S. M. Lauinger, Y. Chi, J. Bacsa, K. P. Sullivan, M. Wieliczko, D. G. Musaev, C. L. Hill, *Inorg. Chem.*, **2016**, 55, 6750–6758.

(7) W. Guo, H. Lv, J. Bacsa, Y. Gao, J. S. Lee and C. L. Hill, *Inorg. Chem.*, **2016**, 55, 461–466.

(8) W.-C. Chen, S.-T. Wu, C. Qin, X.-L. Wang, K.-Z. Shao, Z.-M. Su, E.-B. Wang, *Dalton Trans.,* **2018**, 47, 16403–16407.

(9) Y. Sun, J. Sun, J. R. Long, P. Yang and C. J. Chang, *Chem. Sci.*, 2013, **4**, 118–124.

(10) G.-H. Zhang, W.-B. Yang, W.-M. Wu, X.-Y. Wu, L. Zhang, X.-F. Kuang, S.-S. Wang, C.-Z. Lu, *J. Catal.*, 2019, **369**, 54–59.

(11) R. S. Khnayzer, V. S. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang and F. N. Castellano, *Energy Environ. Sci.*, 2014, **7**, 1477–1488.

(12) Z. Han, L. Shen, W. W. Brennessel, P. L. Holland, and R. Eisenberg, *J. Am. Chem. Soc.* 2013, **135**, 14659–14669.

(13) X. Liu, Y. Li, S. Peng, G. Lu, S. Li, *Int. J. Hydrogen Energy*, 2013, **38**, 11709–11719.

(14) W. Zhang, J. Hong, J. Zheng, Z. Huang, J. S. Zhou, and R. Xu, *J. Am. Chem. Soc.* 2011, **133**, 20680–20683.

(15) M. A. Gross, A. Reynal, J. R. Durrant, and E. Reisner, *J. Am. Chem. Soc.* 2014, **136**, 356–366.