Supporting Information for

Dual Non-Noble-Metals-Immobilized Covalent Organic Frameworks for Visible-Light-Driven Photocatalytic Hydrogen Evolution

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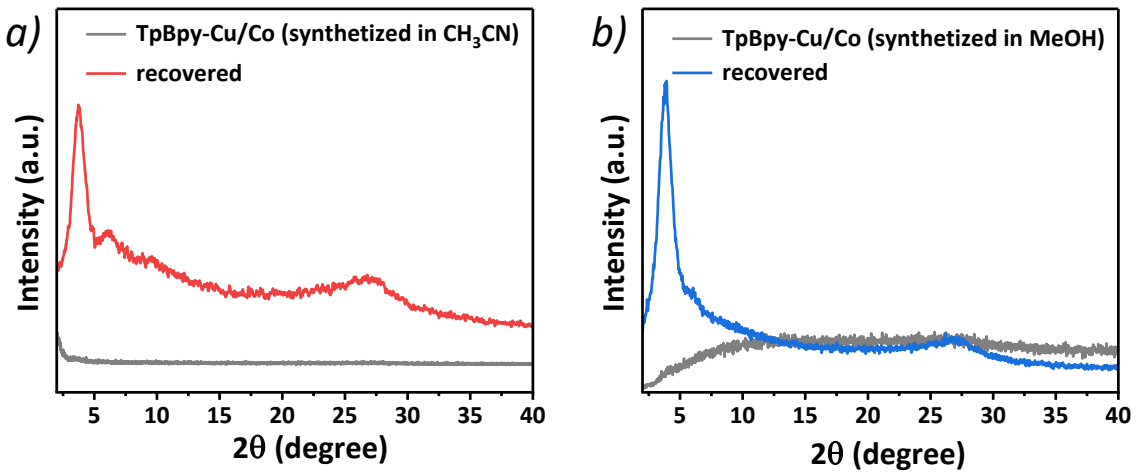

Figure S1. PXRD patterns of TpBpy-Cu/Co synthesized in a) CH_3CN and b) MeOH before and after recrystallization.

Table S1: ICP-MS data of TpBpy-Cu and TpBpy-Cu/Co.

Sample	Cu(wt%)	Co(wt%)	Cu/Co molar ratio
TpBpy-Cu	3.51	/	/
TpBpy-Cu/Co	3.45	1.77	1.8:1
TpBpy-Cu/Co-2	3.24	2.84	1.1:1
TpBpy-Cu/Co-3	5.92	1.93	2.8:1

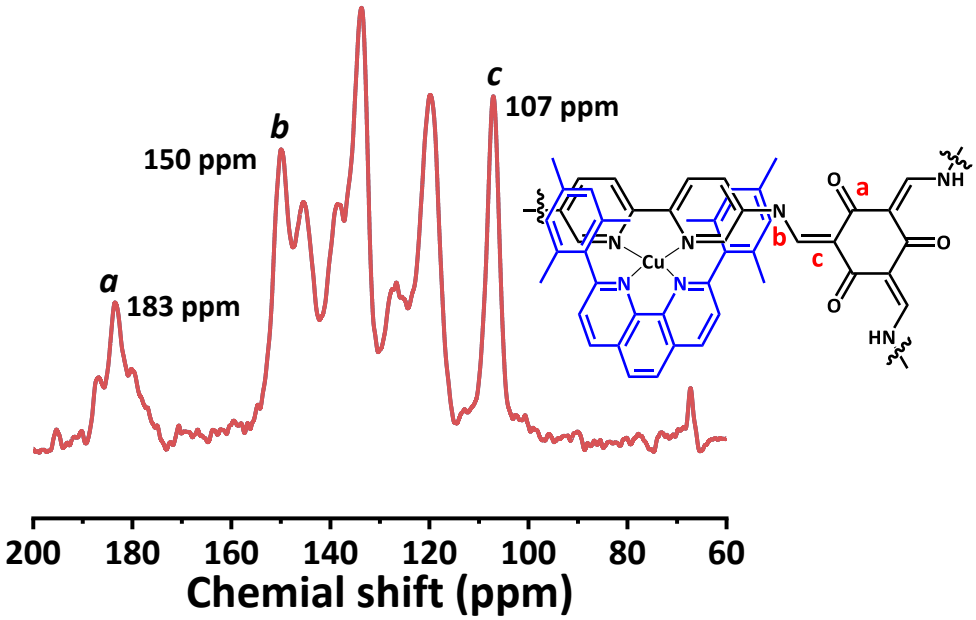

Figure S2. Solid-state ^{13}C NMR spectrum of TpBpy-Cu.

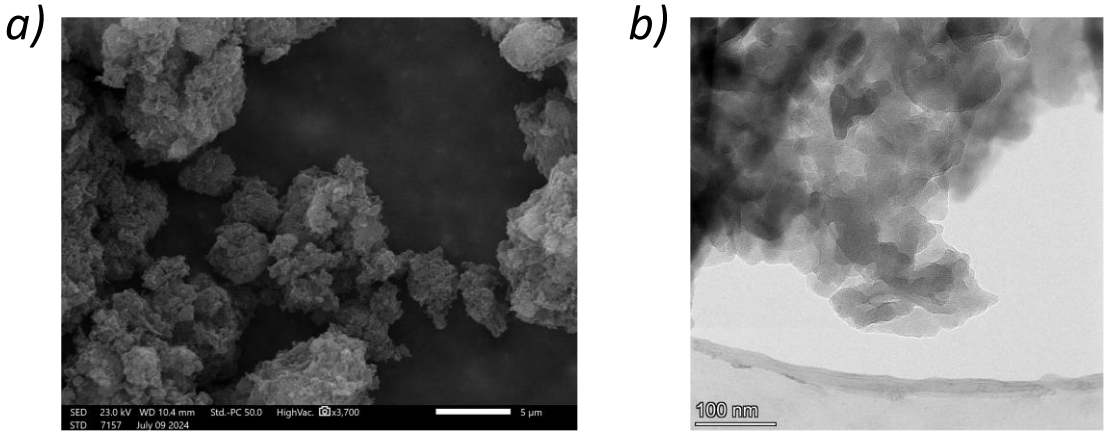

Figure S3. a) SEM image and b) TEM image of TpBpy.

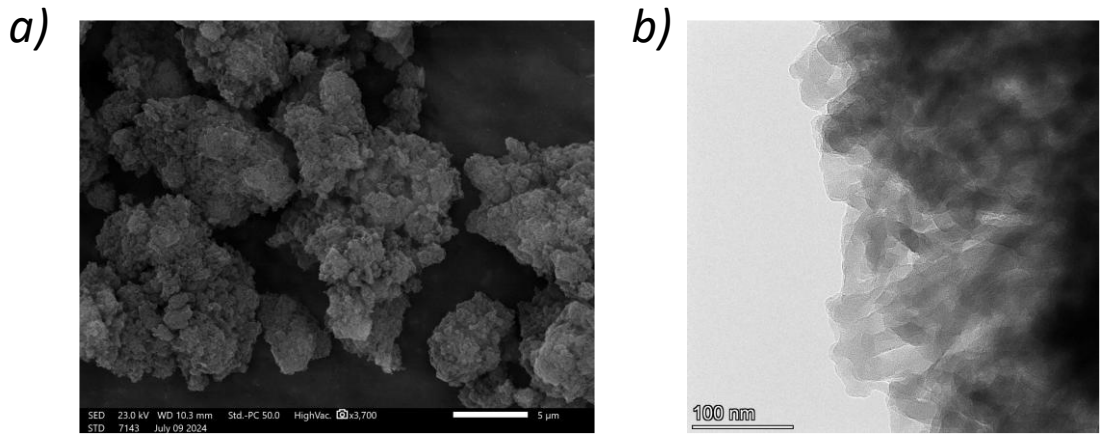

Figure S4. a) SEM image and b) TEM image of TpBpy-Cu.

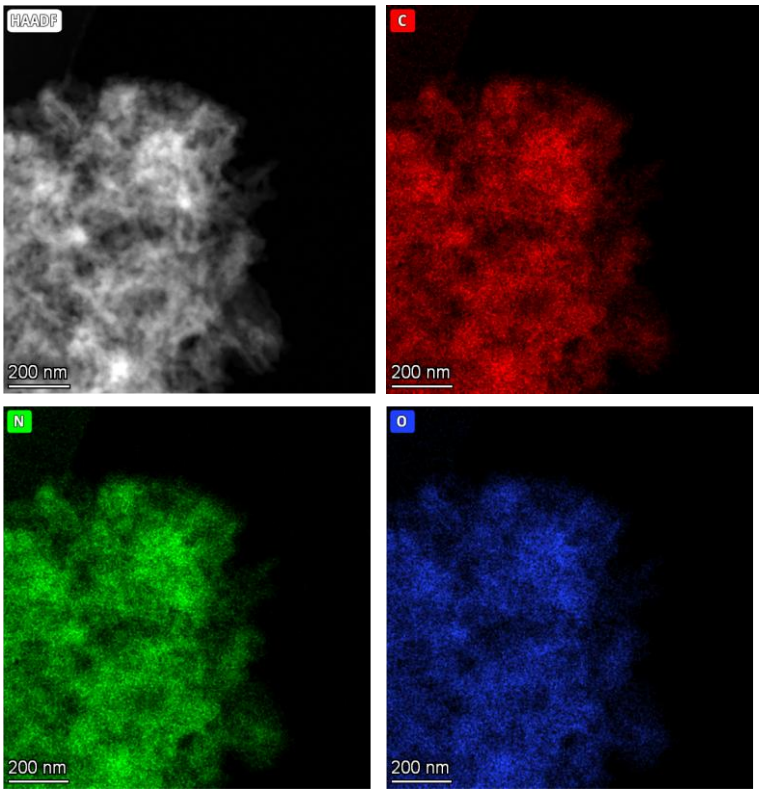

Figure S5. EDS mapping images for TpBpy.

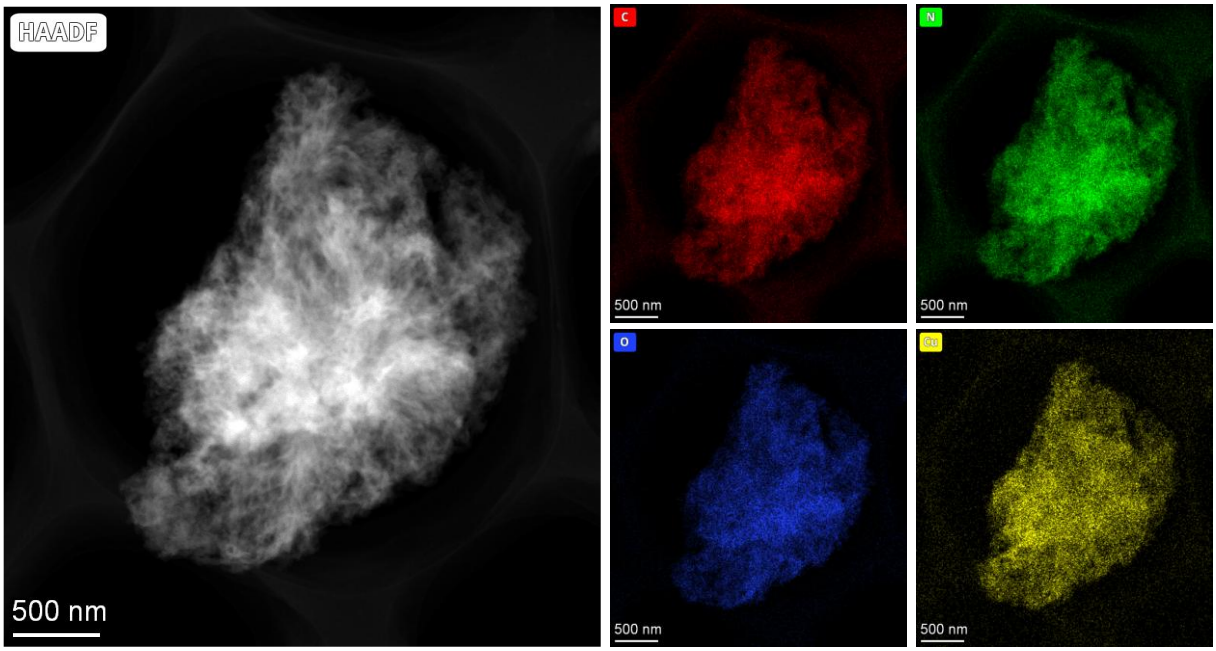

Figure S6. EDS mapping images for TpBpy-Cu.

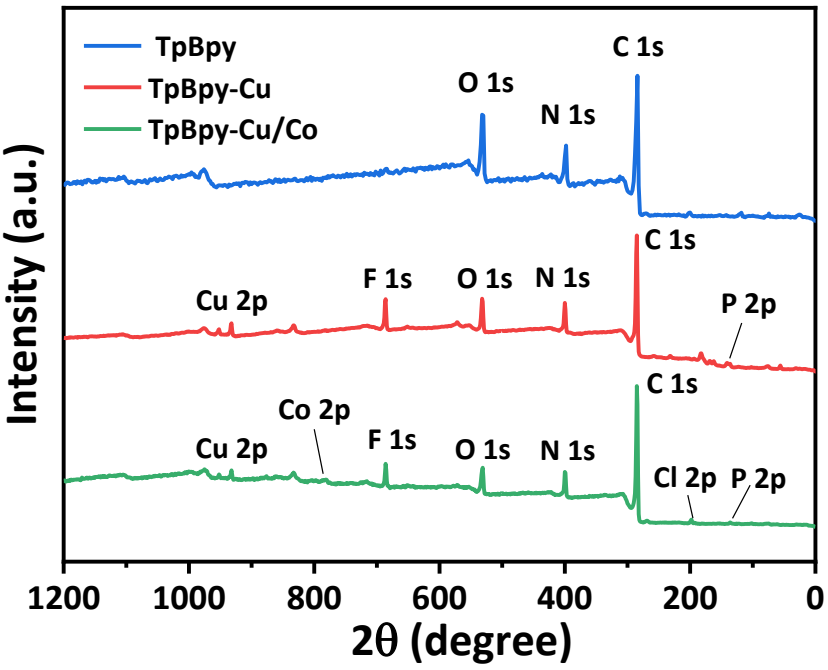

Figure S7. XPS survey of TpBpy, TpBpy−Cu and TpBpy−Cu/Co.

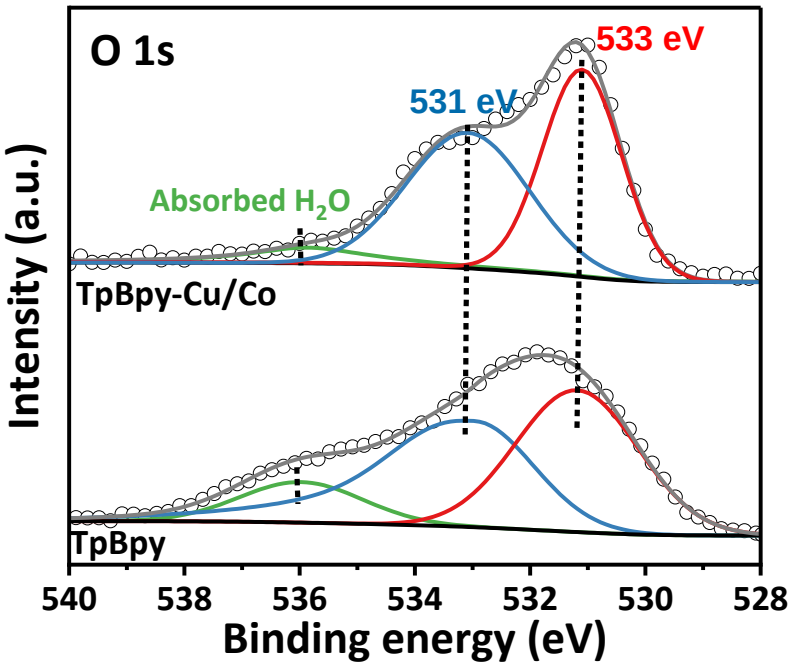

Figure S8. O 1s XPS spectrum of a) TpBpy and b) TpBpy−Cu/Co.

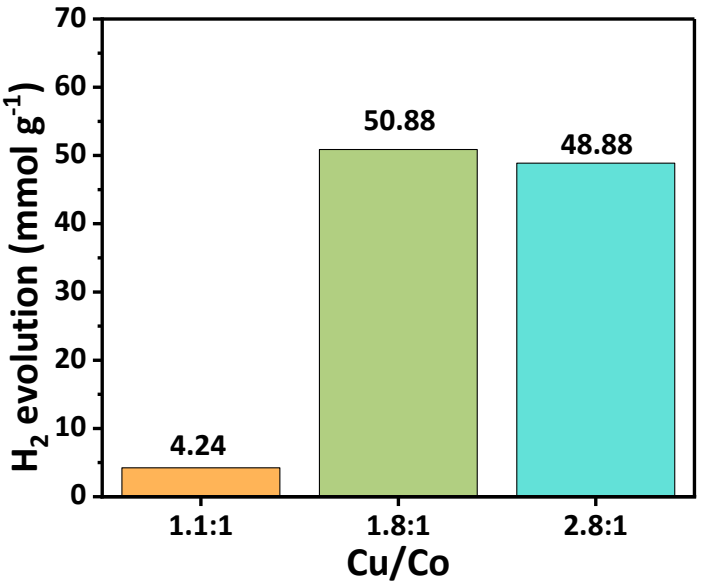

Figure S9. Photocatalytic H_2 evolution of TpBpy-Cu/Co with different content of Cu and Co under visible irradiation in 3 mL DMF/AcOH = 19/1. A 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as light source.

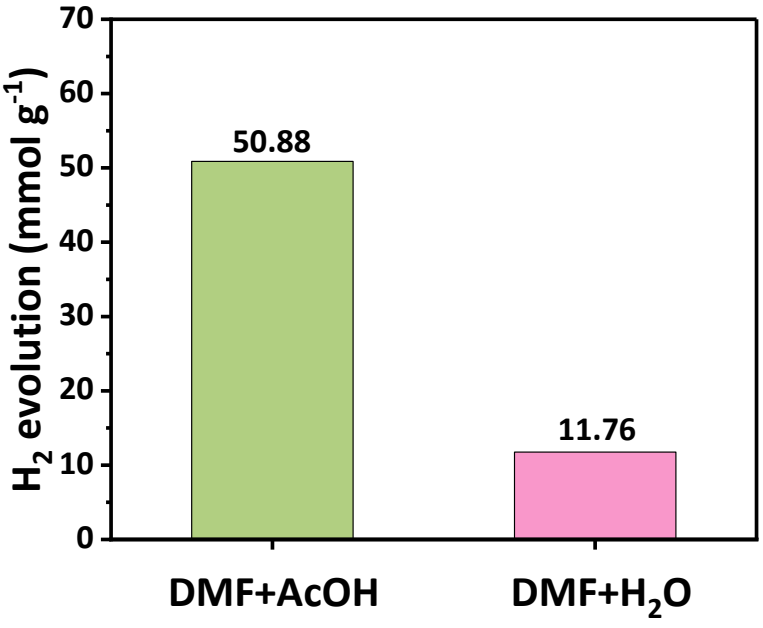

Figure S10. Photocatalytic H_2 evolution of TpBpy-Cu/Co under visible irradiation in 3 mL DMF/AcOH = 19/1 or 3 mL DMF/H_2O = 19/1. A 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as light source.

Table S2. Photocatalytic HER experiments in 6 hours.

Entry	Catalyst	H_2 (mmol g^{-1})	TON	TOF (h^{-1})
1	**TpBpy-Cu/Co**	50.88	339.2	56.5
2	**TpBpy-Cu**	13.44	/	/
3	**TpBpy**	1.60	/	/
4	**TpBpy-Cu** + $Co(bpy)Cl_2$	32.08	213.9	35.6
5	**TpBpy** + $[Cu(mestphen)(bpy)]^+$+$Co(bpy)Cl_2$	11.64	77.6	12.9

Unless noted, HER reactions were conducted with COF or homogeneous catalysts containing 0.136 μmol Cu site and 0.075 μmol Co site, and 90 mg BIH, in 45 μL AcOH + 2.955 mL DMF, a 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as the light source. $TON = \frac{no.of\ moles\ of\ H_2\ produced \times 2}{no.of\ moles\ of\ Co\ sites}$; $TOF = \frac{TON}{hours\ of\ irradiation}$.

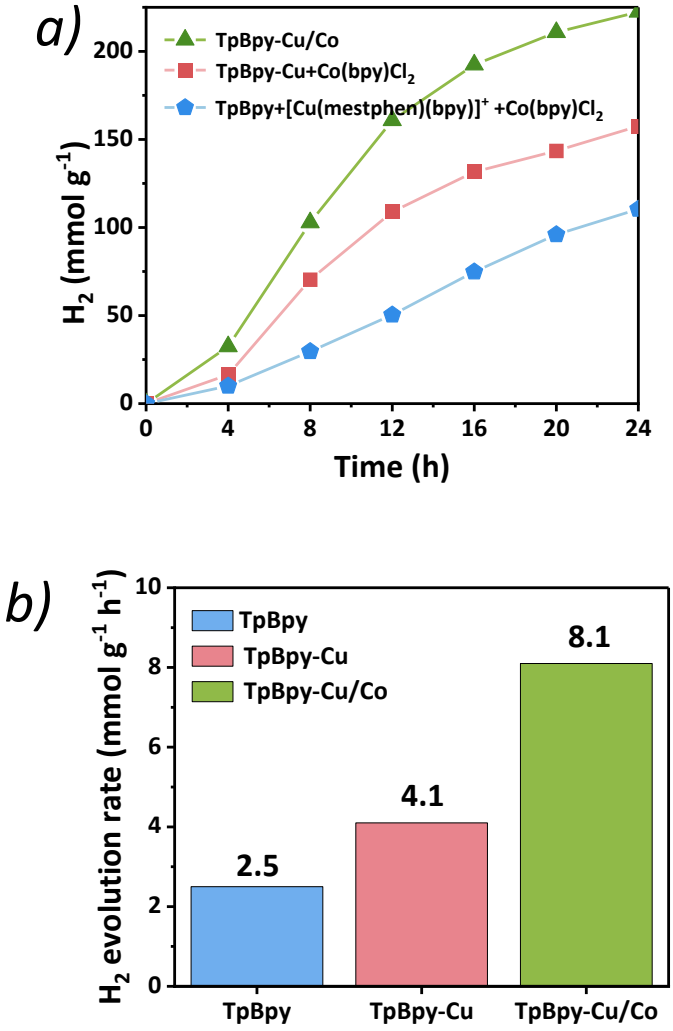

Figure S11. a) Time-dependent H_2 production under visible light irradiation and b) photocatalytic H_2 evolution initial rates (0.0136 μmol Cu site and 0.0075 μmol Co site, and 90 mg BIH, in 45 μL AcOH and 2.955 mL DMF). A 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as light source.

Table S3. Photocatalytic HER experiments at low concentrations in 24 hours.

Entry	Catalyst	H_2 (mmol g^{-1})	TON	TOF (h^{-1})
1	**TpBpy-Cu/Co**	222.40	1483	61.8
2	**TpBpy-Cu** + $Co(bpy)Cl_2$	157.60	1051	43.8
3	**TpBpy** + $[Cu(mestphen)(bpy)]^+$+$Co(bpy)Cl_2$	111.60	744	31
4	$[Cu(mestphen)(bpy)]^+$ + $Co(bpy)Cl_2$	78.74	267	11.1

Unless noted, HER reactions were conducted with COF or homogeneous catalysts containing 0.0136 μmol Cu site and 0.0075 μmol Co site, and 90 mg BIH, in 45 μL AcOH + 2.955 mL DMF, a 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as the light source. $TON = \frac{no.of\ moles\ of\ H_2\ produced \times 2}{no.of\ moles\ of\ Co\ sites}$; $TOF = \frac{TON}{hours\ of\ irradiation}$.

Table S4. Photocatalytic HER performance of some reported metalation COFs in water.

Entry	Catalyst	Metal	Light source (300 W Xe-lamp with filter)	Experimental conditions	Hydrogen production rate ($\mu mol\ h^{-1}\ g^{-1}$)	Ref
1	TpBpy-Cu/Co	Cu(I) Co(II)	>420 nm	BIH, DMF/AcOH (1.97:0.03)	12160	This work
2	Pt-Tpy-COF	Pt(II)	>400 nm	ascorbic acid, H_2O	7800	[1]
3	Ni-Py-COF	Ni(II)	>420 nm	ascorbic acid, H_2O	626	[2]
4	TpBpy–Ir	Ir(III)	>400 nm	ascorbic acid, H_2O	760	[3]
5	$CuCo_2O_4$/TpPa-COF	Cu(II) Co(II)	>420 nm	ascorbic acid, H_2O	8346	[4]
6	Co/Zn-Salen-COF	Co(II) Zn(II)	>420 nm	ascorbic acid, H_2O	1378	[5]
7	MoS_2-3%/TpPa-1-COF	Mo(IV)	>420 nm	ascorbic acid, H_2O	5585	[6]
8	20%CdS-CTF-1	Cd(II)	>420 nm	lactic acid, H_2O	11430	[7]
9	$Ni(OH)_2$-2.5%/TpPa-2	Ni(II)	>420 nm	Sodium ascorbate, PBS buffer solution	1896	[8]
10	ZnPor-DETH-COF	Zn(II) Pt(Co-catalyst)	>400 nm	TEOA, phosphate buffer solution	413	[9]
11	Pt_1@TpPa-1	Pt(II)	>420 nm	Sodium ascorbate, PBS buffer solution	719	[10]
12	Pd^0/TpPa-1-EosinY	Pd(0)	>420 nm	TEOA, H_2O	10400	[11]
13	Au100%-SAs-PAF-164	Au(δ) ($0 < \delta < 1$)	AM 1.5G filter	TEOA, MeCN/H_2O (3:1)	4820	[12]
14	Co0.4-SAC/Tp-Tta COF	Co(II)	320–780 nm	TEOA, H_2O	1798.5	[13]

15	Rh SAs/TpPa-1	Rh(0-III)	>420 nm	Sodium ascorbate, PBS buffer solution	1836.81	[14]
16	TpBpy-Cu/Co	Cu(I) Co(II)	>420 nm	BIH, DMF/H_2O (1.97:0.03)	2810	This work
17	UiO67-Ir-Cou 6/Co	Ir(III) Co(II)	>420 nm	BIH, MeCN/H_2O (43:7)	2440	[15]
18	N2-COF	Co(Co-catalyst)	AM 1.5G filter	TEOA, ACN/H2O (4:1)	782	[16]
19	[Co-1b]–COF	Co(II)	AM 1.5G filter	TEOA, MeCN/H_2O (4:1)	163	[17]

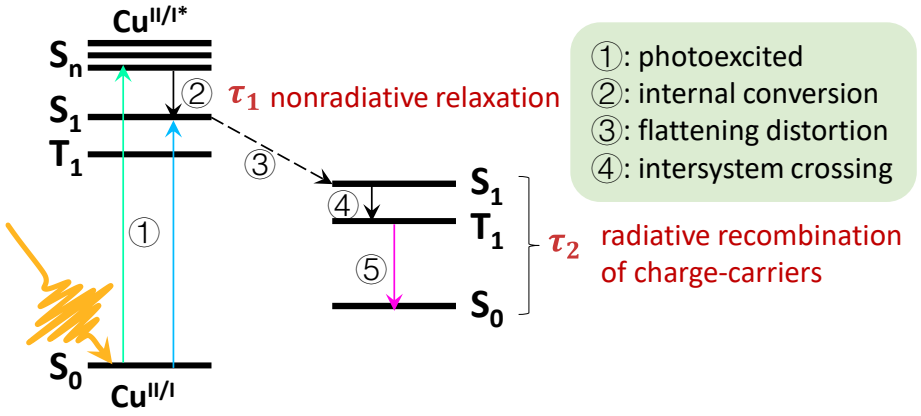

Figure S12. Proposed Perrin Jablonski diagram.

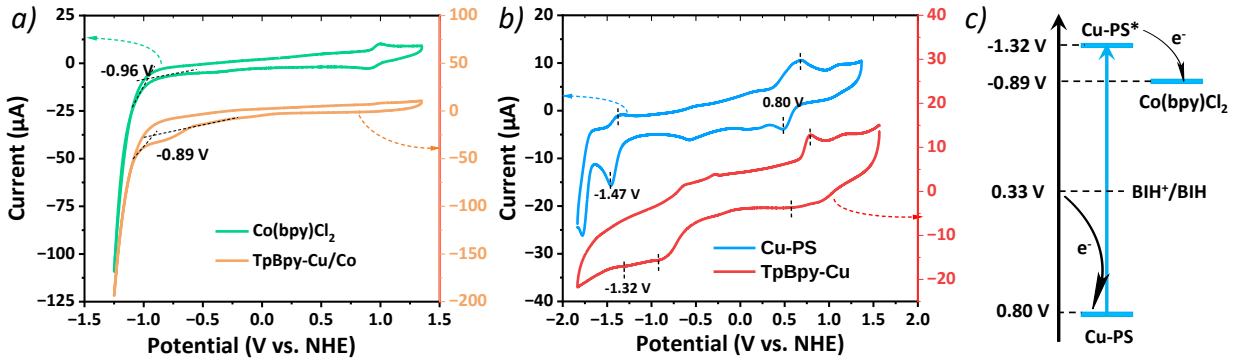

Figure S13. a) CVs of TpBpy-Cu/Co (0.05 mg) coated on electrode surface and $Co(bpy)Cl_2$ under photocatalytic HER conditions (10 mL 0.1 M $TBAPF_6/CH_3CN$ solution with 150 μL AcOH). b) CVs of TpBpy-Cu coated on electrode surface and $[Cu(mestphen)(bpy)]^+$ in 0.1M $TBAPF_6/CH_3CN$. c) Potential energy diagrams of TpBpy-Cu/Co catalyzed photocatalytic HER.

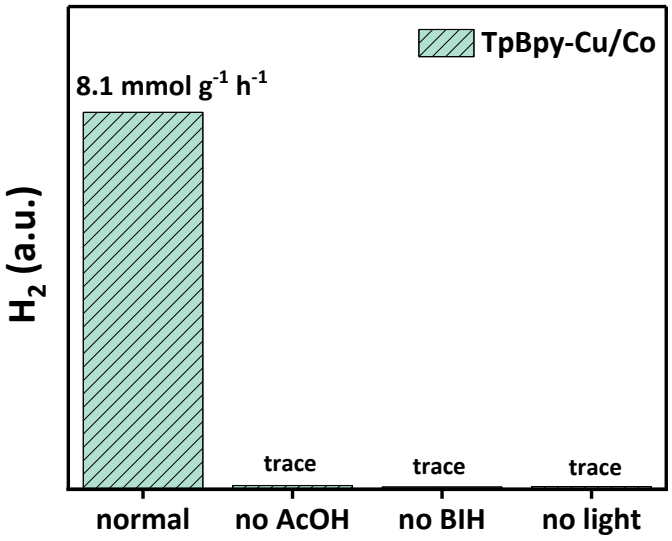

Figure S14. Control experiments of photocatalytic H_2 evolution under visible irradiation. (0.0136 μmol Cu site and 0.0075 μmol Co site, and 90 mg BIH, in 45 μL AcOH and 2.955 mL DMF). A 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as light source.

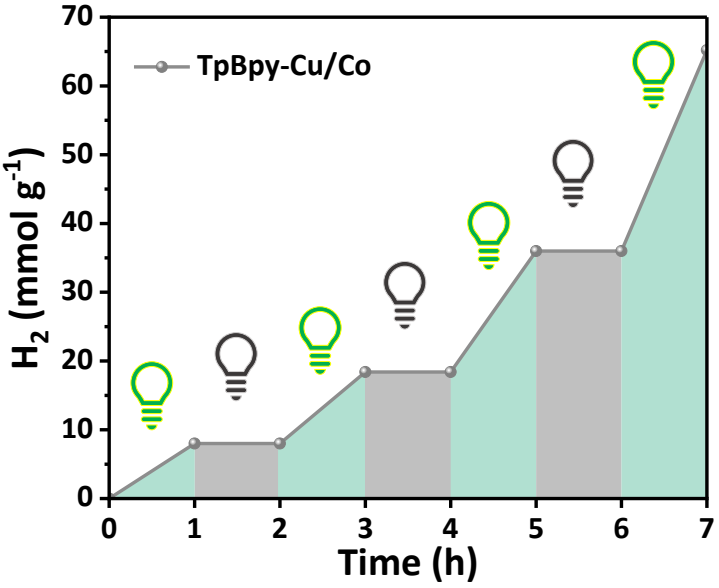

Figure S15. Light On-Off experiments for visible light-driven HER catalyzed by TpBpy-Cu/Co. (0.0136 μmol Cu site and 0.0075 μmol Co site, and 90 mg BIH, in 45 μL AcOH and 2.955 mL DMF). A 300W Xenon lamp with a 420 nm cut off filter (light intensity: 520 mW cm^{-2}) was used as light source.

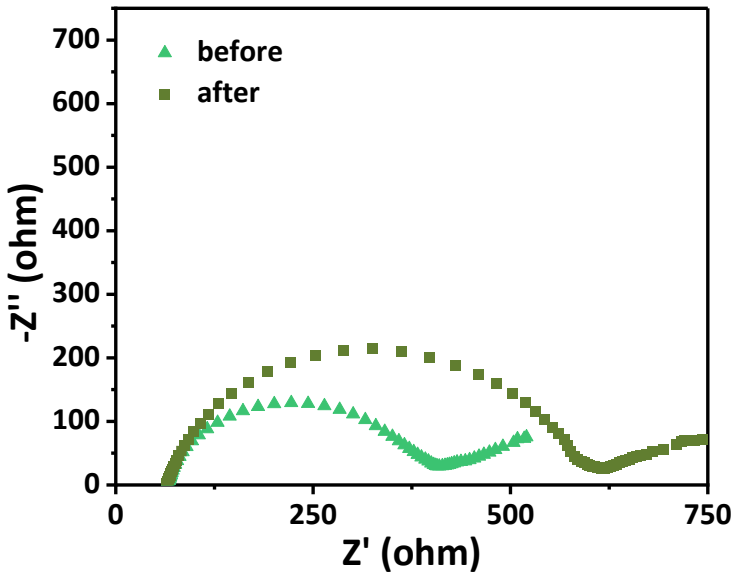

Figure S16. EIS Nyquist plots of TpBpy-Cu/Co before and after 24 h photocatalysis.

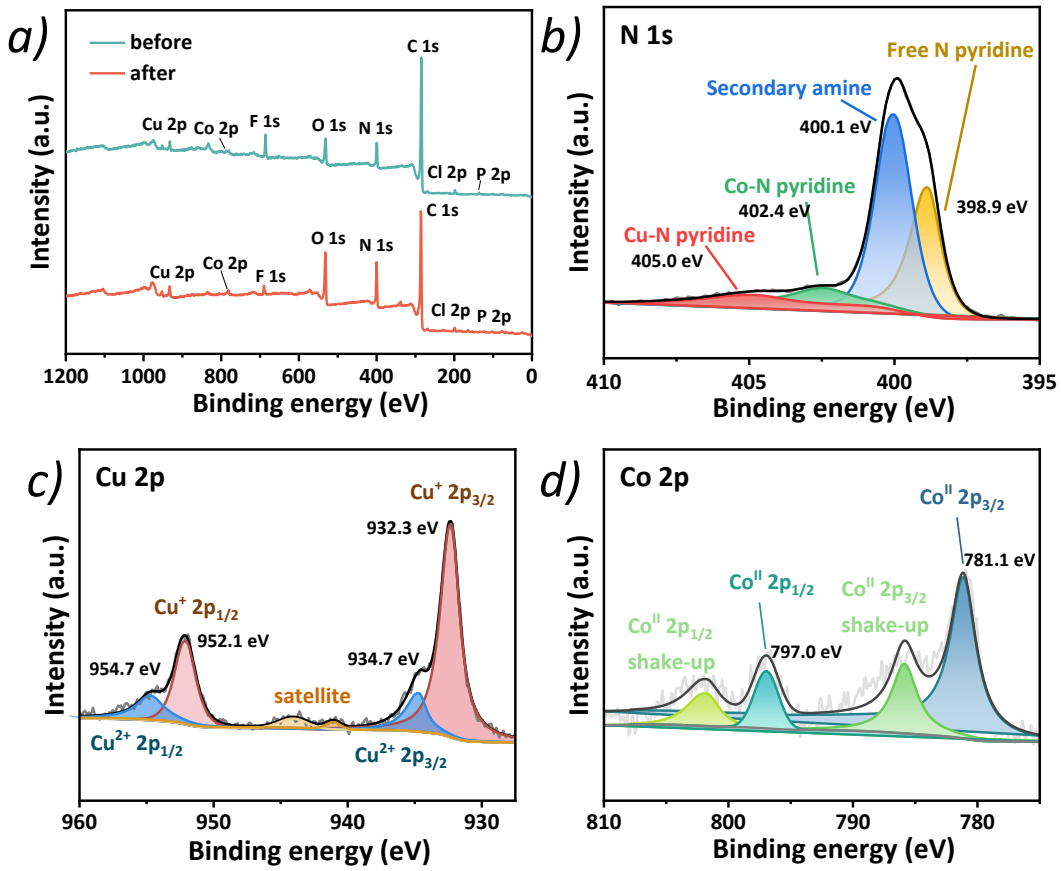

Figure S17. a) XPS survey, b) N 1s, c) Cu 2p, and d) Co 2p spectrum of TpBpy−Cu/Co after 24 h photocatalysis.

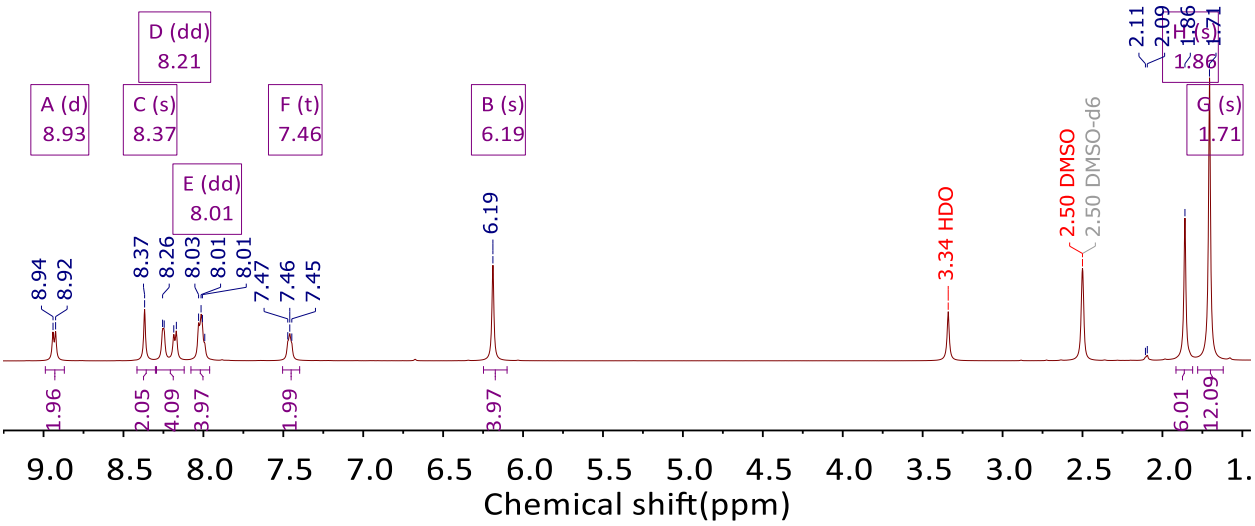

Figure S18. ^{1}H NMR spectrum of [Cu(mestphen)(bpy)]$^{+}$ in DMSO-d_6.

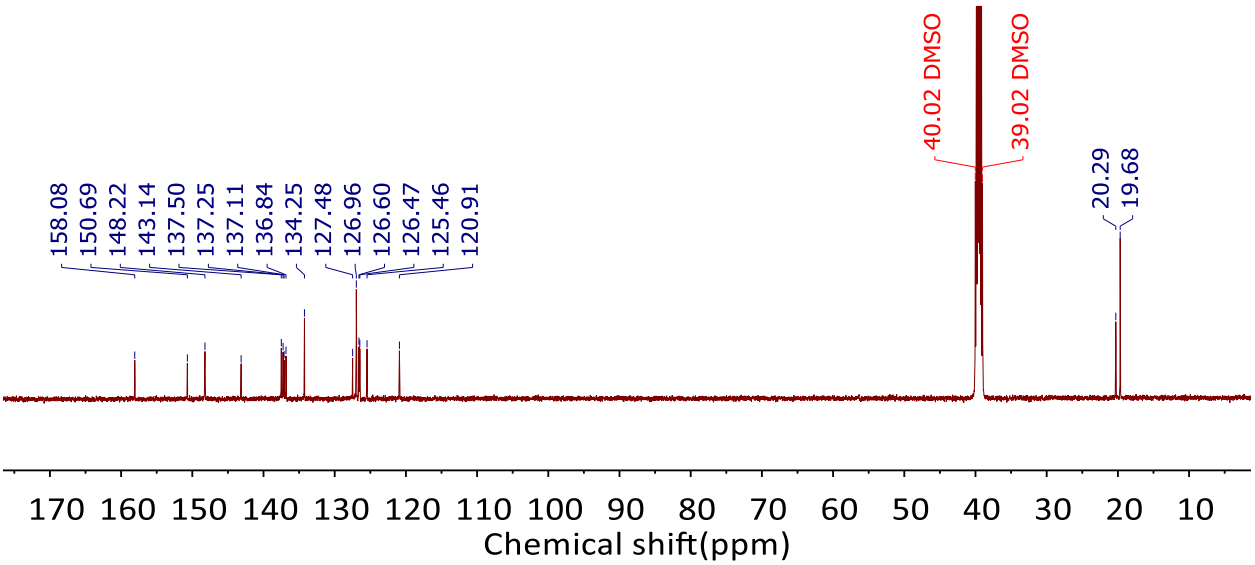

Figure S19. ^{13}C NMR spectrum of [Cu(mestphen)(bpy)]$^{+}$ in DMSO-d_6.

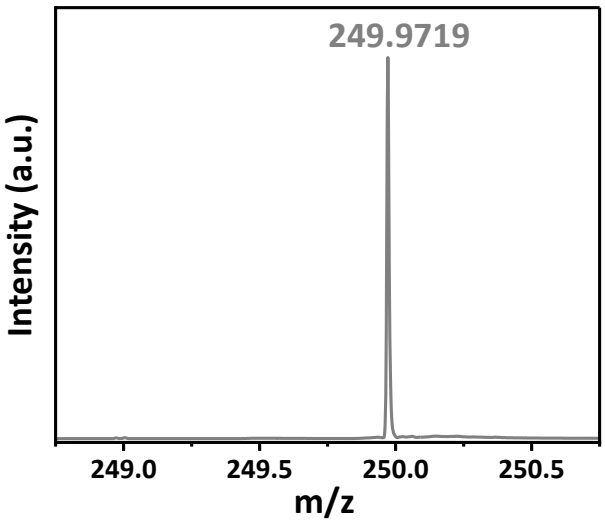

Figure S20. HRMS (ESI, positive mode) spectra of $CobpyCl_2$ in CH_3CN.

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