Supporting Information

Stable and improved visible light photocatalytic hydrogen evolution using copper(II)-organic framework: Engineering the crystal structures

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1. Experimental

1.1. Reagents

Copper(II) sulfate pentahydrate (CuSO₄ 5H₂O, 99.0%), triethanolamine (C₆H₁₅NO₃, 99.0%), ammonia (NH₃, 25.0-28.0%) were purchased from Aladdin Co. Ltd. Hydrochloric Acid (HCl) was purchased from Guangzhou Guoling Instrument Co. Ltd. The ligand H₂DSPTP was obtained from Jinan Camolai Trading Company. The materials were all utilized without furthermore purification and were all analytically pure. Deionized water was utilized throughout the experimental part.

1.2. Synthesis of compound 1

CuSO₄ 5H₂O (2.67 mg, 0.01 mmol), H₂DSPTP (5.00 mg, 0.01 mmol), H₂O (1.5 mL) were mixed and put in hydrothermal cell (20.0 mL) and heated for 48 h at 120 °C in the oven, and then the hydrothermal cell was cooled slowly (2 °C/h) to air temperature, affording as green block crystals. The opaque crystals were respectively washed with ethanol and deionized water. The yield was 38 % based on the H₂DSPTP organic ligand. Elemental analysis (%) calcd for compound 1: C, 43.39, N, 7.23, H, 3.99. Found: C, 43.44, N, 7.17, H, 3.95 %. Crystal structure data for compound 1 are given in Table S1 by single-crystal diffraction.

1.3. Synthesis of compound 2

CuSO₄ 5H₂O (2.67 mg, 0.01 mmol), H₂DSPTP (5.00 mg, 0.01 mmol), H₂O (1.5 mL) were mixed and put in hydrothermal cell (20.0 mL) and pH regulated to 5.0 with NH₃ (0.25 mol/L), and heated for 48 h at 120 °C in the oven. Finally, the hydrothermal cell was cooled slowly (2 °C/h) to air temperature, affording as blue block crystals. The opaque crystals were respectively washed with ethanol and deionized water. The yield was 67 % based on the H₂DSPTP organic ligand. Elemental analysis (%) calcd for compound 2: C 43.11, N, 7.18 H, 3.27. Found: C, 43.14, N, 7.16, H, 3.29 %. Crystal structure data for compound 2 are given in Table S1 by single-crystal diffraction.

1.4. Characterization

To measure the structural variations, XRD patterns (X-ray diffraction, Bruker D8

Advance) were obtained by using graphite monochromatized Cu-Ka ($\lambda = 1.5406$ Å) radiation in the 20 range from 5° to 55°. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 C analytical instrument. Thermogravimetric analyses were performed on Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C/min in flowing nitrogen atmosphere. Microstructural characterization and the elemental mapping of desired regions were performed by field-emission scanning electron microscopy (FESEM, Hatachi, S-4800) and energy dispersive X-ray analyzer (EDX), respectively. The UV-VIS-NIR spectrophotometer (Lambda950, PerkinElmer Company) using BaSO₄ as a reference at room temperature. X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) measurements were carried out with a monochromatic X-ray source (Al Ka, 15 kV, 200 W). Diffraction intensity data for single crystals of compounds were collected on a Bruker Smart Apex II diffractometer equipped with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The data reduction, multi-scan absorption corrections, solution, and refinement were performed with the programs SHELXL-97. All the non-hydrogen atoms were refined with anisotropic thermal parameters while hydrogen atoms were placed in calculated positions and refined using a riding model.

1.5. Photocatalytic H₂ production

Photocatalytic experiments for H_2 evolution were carried out in a Pyrex reaction cell connected by a closed gas evacuation and circulation system. The composites (0.005 g) were sonicated for 5 min in a triethanolamine aqueous solution (7.8 mL TEOA, 70 mL deionized water) and pH adjusted to 7.0. Then the suspension aqueous solution was degassed for 1 h and irradiated by 300 W Xe lamp with an ultraviolet cut-off filter (λ >420nm)(PLS-SXE300, Trusttech). To analyze photocatalytic H₂ evolution at near infrared region, various monochromatic filters were used including 700, 800, and 900 nm. A flow of cooling water was used to maintain the reaction temperature on the room temperature. The content of H₂ generated was determined by online gas chromatography (GC7900, Tian Mei, Shanghai) equipped with a 5 Å molecular sieve column and a thermal conductivity detector (TCD) by using nitrogen as the carrier gas, as shown in Figure S1.

1.6. Photoelectrochemical measurements

Electrochemical measurements (CHI660C electrochemical Instruments) utilized a standard three-electrode system with Na₂SO₄ (1 mol L⁻¹) aqueous solution as the electrolyte. Ag/AgCl (saturated KCl) and platinum flake were used as the reference electrodes and counter electrodes, respectively. The sample electrodes separately served as the working electrode that was obtained by using the doctor-blade coating method to make the suspensions deposited onto Indiumtinoxide (ITO). The visible light source employs a 300 W Xe lamp with an ultraviolet cut-off filter (λ >420 nm) (PLS-SXE300, Trusttech). The working electrodes were prepared through the ways: compounds (0.005 g) were ground with 0.5 mL deionized water and 0.02 g polyethylene glycol to make a slurry. Next, the slurry was coated onto ITO glass electrodes and these electrolytes were dried at 80 °C for 1 h.

1.7. The apparent Quantum Efficiency Measurement

The apparent quantum efficiency (QE) was measured using the same experimental setup for the photocatalytic hydrogen evolution, but with an additional band-pass filter to obtain monochromatic light. Band-pass filters (900 nm) were equipped when conducting reactions under photons of different wavelengths and collecting quantum efficiency (QE) results. The amount of H_2 produced in the first 3 h was used to calculate quantum efficiency using the equation below. The quantum efficiency (QE) was calculated by using the following equation:

 $QE = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\%$

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Figure S1 The photocatalytic H_2 production equipment with the gas chromatography (GC7900, Tian Mei, Shanghai) by nitrogen as a carrier gas.



Figure S2 Picture of the ligand H₂DSPTP.



Figure S3 SEM images of the H₂DSPTP Ligand.



Figure S4 TG curve for compound 1.







Figure S6 XRD for simulated, as-synthesized compound 1.



Figure S7 XRD for simulated, as-synthesized compound 2.



Figure S8 The $(\alpha hv)^{1/2}$ versus hv curve of the compound 1 and 2; The band structure of the compounds are calculated by the KubelKa-Munk (KM) method according to the following equation: $\alpha hv=A(hv-Eg)^2$, where α is the absorption coefficient, hv is the photo energy, Eg is the direct band gap, and A is a constant.



Figure S9 The VB XPS of compound 2.



Figure S10 XRD patterns of simulated 2 and after the stability test (24h).



Figure S11 SEM morphology of compound 2 before ((a), (c)) and after ((b), (d)) the stability test (24h).



Figure S12 A possible mechanism for the photocatalytic H_2 evolution about compound 2.



Figure S13 A possible active sites for the photocatalytic H_2 evolution about compound 2.

Table S1	Crystallographic	data for	compound	1 and 2
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Compound	1	2
Formula	$C_{42}H_{46}CuN_6O_{21}S_4$	$C_{21}H_{19}CuN_3O_9S_2$
Fw	1162.65	585.07
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a, Å	10.901(3)	12.762(2)
b, Å	15.230(4)	7.941(14)
c, Å	15.633(4)	23.131(4)
α, deg	97.984(4)	90
β, deg	99.498(4)	102.437(2)
γ, deg	105.188(4)	90
V, Å ³	2424.7(12)	2289.3(7)
Z	2	4
D_{calcd} , g cm ⁻³	1.593	1.695
μ, mm ⁻¹	0.711	1.197
R _{int}	0.71073	0.0394
Data / restraint / parm	8411 / 0 / 667	5162 / 0 / 334
GOF	1.015	0.995
$\mathbf{R}_{1}\left[I=2\sigma(\mathbf{I})\right]^{\alpha}$	0.1223	0.0479
$WR_2[I=2\sigma(I)]^b$	0.2438	0.1408

 ${}^{\alpha}\mathbf{R}_{1} = \Sigma ||F_{o}| - |F_{c}|| / |F_{o}|, \ {}^{\mathbf{b}}\mathbf{w}\mathbf{R}_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2}]^{1/2}, \ \text{where } w = 1 / [\sigma^{2}(F_{o}^{2}) + (\alpha P)_{2} + bP]. \ P = (F_{o}^{2} + 2F_{c}^{2}) / 3.$

bond lengths (Å)						
Cu(1)-O(1W)	1.986(8)	Cu(1)-N(3)	2.043(9)			
Cu(1)-O(3W)	2.045(10)	Cu(1)-O(4)#1	2.397(10)			
Cu(1)-N(4)	2.035(9)	Cu(1)-O(2W)	2.420(10)			
bond angles ()						
O(1W)-Cu(1)-O(3W)	176.8(4)	N(4)-Cu(1)-O(4)#1	87.3(3)			
O(1W)-Cu(1)-N(4) 87.5(4)		N(3)-Cu(1)-O(4)#1	92.9(4)			
O(3W)-Cu(1)-N(4)	95.2(4)	O(1W)-Cu(1)-O(2W)	92.5(4)			
O(1W)-Cu(1)-N(3)	89.7(4)	O(3W)-Cu(1)-O(2W)	86.0(4)			
O(3W)-Cu(1)-N(3)	87.6(4)	N(4)-Cu(1)-O(2W)	87.7(4)			
N(4)-Cu(1)-N(3)	177.2(5)	N(3)-Cu(1)-O(2W)	92.7(4)			
O(1W)-Cu(1)-O(4)#1	O(1W)-Cu(1)-O(4)#1 100.6(4)		165.8(4)			
O(3W)-Cu(1)-O(4)#1	81.2(5)					

 Table S2. Selected bond lengths (Å) and bond angles () for compound 1 at 296K.

Symmetry transformations used to generate equivalent atoms: # 1 x, y, z + 1, #2 x, y, z-1.

bond lengths (Å)						
Cu(1)-N(3)	1.993(3)	Cu(1)-O(2W)	2.009(2)			
Cu(1)-O(6)#1	1.998(2)	Cu(1)-O(1W)	2.394(3)			
Cu(1)-N(1)#2	Cu(1)-N(1)#2 1.997(3)					
bond angles ([°])						
N(3)-Cu(1)-O(6)#1	86.82(11)	N(1)#2-Cu(1)-O(2W)	89.59(11)			
N(3)-Cu(1)-N(1)#2 177.10(12)		N(3)-Cu(1)-O(1W)	91.59(11)			
O(6)#1-Cu(1)-N(1)#2 90.54(11)		O(6)#1-Cu(1)-O(1W)	104.24(11)			
N(3)-Cu(1)-O(2W) 92.74(11)		N(1)#2-Cu(1)-O(1W)	90.22(11)			
O(6)#1-Cu(1)-O(2W) 168.12(10)		O(2W)-Cu(1)-O(1W)	87.64(11)			

 Table S3. Selected bond lengths (Å) and bond angles () for compound 2 at 296K.

Symmetry transformations used to generate equivalent atoms: #1 - x + 3/2, y + 1/2, -z + 1/2, #2 - x + 1, -y, -z + 1, #3 - x + 3/2, y - 1/2, -z + 1/2.

Table S4. The comparison of photocatalytic H_2 production activity, experimental conditions, the loaded catalysts, and photosensitizer among MOFs reported in the literature and **this work**.

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	MOFs photocatalyst	Metal node	Linker	co- catalys	Photose nsitizer	Conditions	Activity	stability
$ \frac{1}{ $	Al(OH)(bpydc)-0.5PtCl ₂ MOF-253-Pt ¹	AI	2,2'-bipyridin e-5,5'-dicarb oxylic acid	Pt	No	TEOA,pH=8.5 CH ₃ CN/H ₂ O=1:1; Visible light	100-200 μmol g ⁻¹ h ⁻¹	No
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			-			Near-infrared light	No	
	Pt/NH ₂ -MIL-101(Cr) ²	Cr	2-aminotere	Pt	Rhodamin e B	TEOA, H ₂ O Visible light	TON of 110 mol _{H2} mol _{ca}	5 times; One time for 6h
$\begin{array}{c c c c c c c c c c c c c c c c c c c $						Near-infrared light	No	
$\frac{Ptel D(D-Be')}{rbox} \left[\frac{2}{rb} \ berezenedica} \left[\frac{Pt}{rbox} \ e B \right] \\ \frac{2}{rbox} \left[\frac{2}{rbox} \left[\frac{2}{rbox} \left[\frac{1}{rbox} \left[\frac{1}{rb$		_	1,4-	Pt	Rhodamin e B	TEOA, pH=7	116.0 µmol g '	3 times;
	Pt@UiO-66°	∠r	benzenedica			$\Lambda \ge 420 \text{ nm}$	h'	One time for 5h
2 - aminoter phthalars of the phtha			rboxylic acid			Near-Infrared light		
$ \begin{array}{c c} \operatorname{Ce} \mathbb{Q} \operatorname{NH}_{-}\operatorname{ML}(-125 (T)) & \operatorname{II} \operatorname{II} \operatorname{II} \operatorname{P} \operatorname{ML} \operatorname{Id} \operatorname{III} \operatorname{III} \operatorname{P} \operatorname{A} \operatorname{Id} \operatorname{III} \operatorname{III} \operatorname{A} \operatorname{A} \operatorname{A} \operatorname{III} \operatorname{A} \operatorname{A} \operatorname{A} \operatorname{A} \operatorname{A} \operatorname{A} \operatorname{A} A$			2-aminotere	Co-dioxi	No	H ₂ O,CH ₃ CN,triethyla	TOF of 0.8 h	3 times;
	Co@NH ₂ -MIL-125(Ti) [*]	Ti	phthalate	me-			101 24 m	One time for 24h
$ \begin{bmatrix} [Ni_{2}(PymS)]_{2}]_{1}^{5} & Ni & Primidine - 1 \\ 1 & Ni & Ni & Primidine - 1 \\ 1 & Ni & P$				diimine		Near-infrared light	No	
$ \left[N_{15}(PymS)_{1,1}^{(h)} \\ N_{10}(PymS)_{1,1}^{(h)} \\ N_{1}(PymS)_{1,1}^{(h)} \\ N_{1}(P_{1,1},P_{1}) \\ P_{1,1}(P_{1,1},P_{1}) \\ P_{1,1}(P_{1,1},P_{1}) \\ P_{1,1}(P_{1,1},P_{1,1}) \\ P_{1,1}(P_{1,1},P_{1,1})$			Pyrimidine-2	No	fluorescei	TEA;	TOF of 6 µmol	4 times;
$\frac{1}{ Cu^{1} _{L^{1}} _{L^{1$	[Ni ₂ (PymS) ₄] _n	Ni	-		n	white-light-diode	h'	One times for 60
$ \begin{array}{c} \begin{array}{c} P_{1} P_{1} P_{2} P_{3} P_{3}$			thio			Near-Infrared light	No	min
$ \begin{array}{c c} P_{l_{u}} r_{B} u 0^{6} \\ P_{l_{u}} r_{B} v r_{B} u 0^{6} \\ P_{l_{u}} r_{B} v r_{B} v r_{B} v r_{B} \\ P_{l_{u}} r_{B} v $			2,2'-bipyridin	Pt(H ₂ L) Cl ₂		DMF:H ₂ O:DMA		
$\frac{ _{ } _{ } _{ } _{ } _{ } _{ } _{ } _{ } _{ } _{ } _{ } _{ $	Pt _n _Ir_BuiO ⁶	Zr	e-5,5'-dicarb oxylic acid		No	8:2:2 V/V	10F of 2.9 h	No
$\frac{\left[\operatorname{Co}^{\dagger}(\operatorname{TPA})\operatorname{CI}\left[\operatorname{CI}\right]^{+}}{\operatorname{MIL}-125-\operatorname{NH}_{2}^{-7}}\right]_{1}^{7}} \operatorname{Tr} \\ \frac{2-\operatorname{aminotere}}{\operatorname{phthalic acid}} \operatorname{Co}^{\dagger}(\operatorname{TPA})\operatorname{CI}\left[\operatorname{CI}\right]^{+}}{\operatorname{phthalic acid}} \operatorname{No}^{\dagger} \operatorname{Co}^{\dagger}(\operatorname{TPA})\operatorname{CI}\left[\operatorname{CI}\right]^{+}}{\operatorname{phthalic acid}} \operatorname{No}^{\dagger} N$						Near infrared light	No	
$ \begin{bmatrix} [Co^{II}[TPA]CI][C]]_{MIL-125-NH_{2}^{\prime\prime}} \\ MIL-125-NH_{2}^{\prime\prime} \\ MIL-125-NH_{2}^{$							INU	
$ \begin{array}{ c c c c c c } \begin{tabular}{ c c c c c } & No & No & A & 380 \mm & No & A & 380 \mm & No & $	[Co ^{ll} (TPA)CI][CI]-		2 aminatoro				553 µmol g ^{−1}	3 times;
	MIL-125-NH ₂ ⁷	Ti	phthalic acid	(C0 (TP A)CI][CI]	No	$\lambda > 380 \text{ nm}$	h^{-1}	One time for 150
$\frac{\left[\text{Cu-RSH}^{\$} \ \text{Cu} - \text{RSH}^{\$} \ \text{Cu} \ \frac{3}{3} \text{formyl-4-h} \\ \text{ydroxybenzo} \\ \text{ic acid} \ \text{ic acid} \ \text{No} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{formyl-4-h} \\ \text{ydroxybenzo} \\ \text{ic acid} \ \text{No} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{A20 nm} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{A20 nm} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{A20 nm} \ \frac{3}{2} \text{A20 nm} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{A20 nm} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{3}{2} \text{A20 nm} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \\ \frac{10\% \text{TEOA}(\text{y/y})}{2 \text{ci acid}} \ \frac{10\% \text{TEOA}(\text{y/y})$						Near-infrared light	No	min
$ \begin{array}{c c} Cu-RSH^{\theta} \\ Cu-RSH^{\theta} \\ Cu \\ P^{0} \\ P^{0}$		3 Cu yı	3-formyl-4-h ydroxybenzo ic acid	No	Eosin Y	10% TEOA (v/v)		
$ \begin{array}{c c} Cu-RSH^3 & Cu & ydroxyberzo ic acid \\ & & & & & & & & & & & & & & & & & & $						at pH 13	7.88 mmol $a^{-1} h^{-1}$	4 times:
	Cu-RSH ⁸					$\lambda > 420 \text{ nm}$		One time for 5h
$ \begin{bmatrix} Zr_{6}(\mu_{3}-O)_{4}(\mu_{3}-OH)_{4}(L1)_{6}](CO_{2}\\ CF_{3})_{6}^{9} \end{bmatrix} Z^{r} \begin{bmatrix} Ir(py)_{2}(bpy)\\ C \\ derived\\ dicarboxylic\\ acids \end{bmatrix} \begin{bmatrix} I(-C_{4}H_{9}\\)_{4}N]_{10}[Ni_{4}\\ (H_{2}O)_{2}(P)\\ W_{9}O_{3},1]_{2} \end{bmatrix} \\ No \qquad \frac{10\% \text{ methanol}}{Near-infrared light} \end{bmatrix} No \qquad \frac{4.4 \text{ mmol } h^{-1} \text{ g}^{-1}}{Net \text{ mol } h^{-1} \text{ g}^{-1}} \\ A > 400 \text{ nm} \end{bmatrix} \\ Simes; One time for 20h \\ Near-infrared light \end{bmatrix} No \qquad \frac{3 \text{ times};}{No} = \frac{10\% \text{ methanol}}{Near-infrared light} No \qquad \frac{118 \text{ mL acetonitrile}}{No} \\ Pt^{0}[Cu^{1}Cu^{1}_{2}-c^{-1}]_{2} + \frac{2-amino-1,4-}{benzenedica} \frac{Pt}{boxylic acid} \end{bmatrix} \\ Pt \qquad \frac{2-amino-1,4-}{benzenedica} \frac{Pt}{boxylic acid} Pt \qquad No \qquad \frac{118 \text{ mL acetonitrile}}{No} \\ \frac{118 \text{ mL acetonitrile}}{Nad 2 \text{ mL}} \\ \frac{3 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{3 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{3 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{10\% \text{ mL methanol}}{Nad 2 \text{ mL}} \\ \frac{3 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{4 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{10\% \text{ mL methanol}}{Nad 2 \text{ mL}} \\ \frac{32 \text{ mol } \text{ m}}{Nad 2 \text{ mL}} \\ \frac{32 \text{ mol } \text{ m}}{Nad 2 \text{ mL}} \\ \frac{32 \text{ mol } \text{ m}}{Nad 2 \text{ mL}} \\ \frac{32 \text{ mol } \text{ m}}{Nad 2 \text{ mL}} \\ \frac{4 \text{ times};}{Nad 2 \text{ mL}} \\ \frac{4 \text{ times};}{(Cu(\text{ HDSPTP})_{2}(H_{2}O)_{3}.6H_{2}O)}{N_{n} \text{ timpyridine}} \\ \frac{4 \text{ timpyridine}}{(Cu(\text{ DSPTP})(H_{2}O)_{3}.2H_{2}O)_{3}} \\ \frac{4 \text{ timpyridine}}{(Cu(\text{ DSPTP})(H_{2}O)_{3}.2H_{2}O)_{3}} \\ \frac{4 \text{ timpyridine}}{(Cu(\text{ mSPTP})(H_{2}O)_{2}.H_{2}O)_{3}} \\ \frac{4 \text{ timpyridine}}{(Cu(\text{ mSPTP})'(H_{2}O)_{3}.2H_{2}O)_{3}} \\ \frac{8 \text{ times};}{(Gine 1 \text{ m} for 3H)} \\ \frac{10\% \text{ m}}{Nad 2 \text{ mol } h^{-1}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ mol } h^{-1}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ mol } h^{-1}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ m}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ m}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ m}} \\ \frac{10\% \text{ m}}{Nad 2 \text{ m}$						Near-infrared light	No	
$ \begin{bmatrix} [Zr_{6}(\mu_{3}-O)_{4}(\mu_{3}-OH)_{4}(L1)_{6}](CO_{2}\\ CF_{3})_{6}^{9} \end{bmatrix} 2^{\Gamma} \begin{bmatrix} T^{1} \\ 0 \\ erived \\ dicarboxylic \\ acids \end{bmatrix} \frac{1}{V_{9}} \begin{bmatrix} [(n-C_{4}H_{9})\\]_{A}N]_{10}[Ni_{4}\\ (H_{2}O)_{2}(P)\\ W_{9}O_{34})_{2} \end{bmatrix} \\ Pt@UiO-66-NH_{2}^{10} \end{bmatrix} \begin{bmatrix} T^{1} \\ 2r \end{bmatrix} \begin{bmatrix} T^{1} \\ 2r \end{bmatrix} \begin{bmatrix} T^{1} \\ 0 \\ risk \\ risk$		Zr	[lr(ppy) ₂ (bpy)			10% methanol		
$\frac{\left L^{2} f_{6} (\mu_{3} - O)_{4} (\mu_{3} - OH)_{4} (L_{1})_{6} [(CO_{2} \\ CF_{3})_{8}^{9} - 0^{9} - 0^{9} - 0^{1} + 0$]Cl- derived dicarboxylic acids	[(n-C ₄ H ₉) ₄ N] ₁₀ [Ni ₄ (H ₂ O) ₂ (P W ₉ O ₃₄) ₂]	No	pH=1.2	4.4 mmol h ⁻¹ g ⁻¹	a
$\frac{\left(H_{2} \cup j_{2} (P) \\ W_{3} \cup g_{3} j_{2}\right)}{\left(H_{2} \cup j_{2} (P) \\ W_{3} \cup g_{3} j_{2}\right)} \left(\frac{H_{2} \cup j_{2} (P) \\ W_{3} \cup g_{3} j_{2}\right)}{\left(H_{3} \cup j_{3} (P) \\ P^{+} (P^{+} $	$[2r_6(\mu_3-O)_4(\mu_3-OH)_4(L1)_6](CO_2)$					λ > 400 nm		3 times;
$\frac{Pt}{Pt} (UiO-66-NH_2^{10}) = \frac{1}{2r} \left\{ \frac{2-amino-1,4-}{benzenedica} rboxylic acid \right\} Pt \left\{ Pt + \frac{No}{2r} \left\{ \frac{18 \text{ mL acetonitrile,}}{nd 2 \text{ mL deioned water}}{rboxylic acid} + \frac{18 \text{ mL acetonitrile,}}{nd 2 \text{ mL deioned water}}{nd 2 \text{ mL triethanolamine}} + \frac{257.38 \ \mu mol \ g^{-1}}{h^{-1}} \right\} \left\{ \frac{4 \text{ times;}}{One \text{ time for 2.5h}} \right\}$ $\frac{Pt}{(DcTP)_2 NO_3 \cdot 1.5DMF_n^{11}} \left\{ \frac{4' \cdot (3,5-\text{dicar}}{DcTP)_2 (H_2O)_3 \cdot 1.5DMF_n^{11}} + \frac{4' \cdot (3,5-\text{dicar}}{DcTP)_2 (H_2O)_3 \cdot 1.5DMF_n^{11}} + \frac{4' \cdot (3,5-\text{dicar}}{DcTP)_2 (H_2O)_3 \cdot 1.5DMF_n^{11}} + \frac{4' \cdot (2,4-\text{disulf}}{DcTP)_2 (H_2O)_3 \cdot 1.5DMF_n^{11}} + \frac{4' \cdot (2,4-\text{disulf}}{DcTP)_2 (H_2O)_3 \cdot 1.5DMF_n^{11}} + \frac{4' \cdot (2,4-\text{disulf}}{DcTP} + \frac{4' \cdot (2,4-\text{disulf}}{DcTP} + \frac{10\% \text{ TEOA; pH=7}}{DcTP} + \frac{5.77 \text{ and } 6.99}{M + 20 \text{ mm l} \text{ mol } $	CF ₃) ₆ °					Near-infrared light	No	One time for 20h
$\frac{Pt}{Pt} (UiO-66-NH_{2}^{10}) X_{2}^{10} $						18 mL acetonitrile		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2-am Zr benz rbox			No	0.2 mL deioned water	-1	
$\begin{array}{cccc} Pt@UiO-66-NH_2^{10} & Zr & benzenedica rboxylic acid & Pt & No & triethanolamine h^h & One time for 2.5h \\ \hline h^h & h^h & h^h & h^h & One time for 2.5h \\ \hline h^h & h^h & h^h & h^h & h^h & One time for 2.5h \\ \hline h^h & H^h &$	10		2-amino-1,4-			and 2 mL	257.38 µmol g ⁻¹	4 times;
$\frac{ Pt {[Cu Cu _{2}^{-}]}}{[(Cu Cb]_{2}]NO_{3}\cdot 1.5DMF]_{n}^{11}} = \frac{ Pt }{Cu Cu _{2}^{-}} \left(\frac{4'\cdot(3,5-\text{dicar})}{boxyphenyl)} + \frac{4'\cdot(3,5-\text{dicar})}{boxyphenyl)} + \frac{4'\cdot(3,5-\text{dicar})}{4,2':6',4''-} + \frac{Pt}{terpyridine} + \frac{Pt}{Pt} + \frac{10 \text{ mL methanol}}{90 \text{ mL H}_{2}O} + \frac{32 \text{ µmol g}^{-1}}{h^{-1}} + \frac{32 \text{ µmol g}^{-1}}{h^{-1}} + \frac{h^{-1}}{h^{-1}} + $	Pt@UiO-66-NH ₂ ¹⁰		benzenedica	Pt		triethanolamine	h'	One time for 2.5h
$\frac{\left \begin{array}{c c c c c c c } \hline \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $			rboxylic acid			λ > 380 nm		
$\frac{Pt/\{[Cu Cu ^{I}_{2^{-}}\\(DCTP)_{2}]NO_{3}\cdot 1.5DMF\}_{n}^{11}}{(DCTP)_{2}[NO_{3}\cdot 1.5DMF\}_{n}^{11}} \left\{ \begin{array}{c} u\\ $						Near-infrared light	No	
$\frac{Pt/\{[Cu^{l}Cu^{l}_{2}-}{(DCTP)_{2}]NO_{3}\cdot 1.5DMF\}_{n}^{11}} \left(\begin{array}{c} Cu \\ 4,2^{\prime}:6^{\prime},4^{\prime-} \\ terpyridine \end{array} \right) + \frac{Pt}{4,2^{\prime}:6^{\prime},4^{\prime-}} \left(\begin{array}{c} Pt \\ No \end{array} \right) + \frac{90 \text{ mL } H_{2}O}{320-780 \text{ mm}} \left(\begin{array}{c} 0.52 \text{ priver } g \\ h^{-1} \end{array} \right) + \frac{1}{No} \right) + \frac{1}{No} + \frac{1}{No} \left(\begin{array}{c} 0.52 \text{ priver } g \\ h^{-1} \end{array} \right) + \frac{1}{No} \right) + \frac{1}{No} +$	Pt/{[Cu ^l Cu ^{ll} ₂ - (DCTP) ₂]NO ₃ ·1.5DMF} _n ¹¹	Cu 4'-(3,5-dic boxypheny 4,2':6',4' terpyridin	4'-(3,5-dicar	4'-(3,5-dicar boxyphenyl)- 4,2':6',4''- terpyridine	No	10 mL methanol	32 µmol a ⁻¹	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			boxyphenyl)-			90 mL H₂O	52 μποι g	No
$\frac{([Cu(HDSPTP)_{2}(H_{2}O)_{3}]\cdot 6H_{2}O)}{(h_{2}O)_{2}[\cdot H_{2}O)_{3}} \cdot 6H_{2}O} \xrightarrow{L}{Cu} \begin{array}{c} terpyridine \\ \lambda^{'}(2,4-disulf ophenyl)-3,2' \\ (Cu(DSPTP)(H_{2}O)_{2}]\cdot H_{2}O)_{n} \\ (This worK) \end{array} \begin{array}{c} \lambda^{'}(2,4-disulf ophenyl)-3,2' \\ \cdot 6',3'' \cdot terpyrid \\ dine \end{array} \begin{array}{c} No \end{array} \begin{array}{c} No \end{array} \begin{array}{c} 10\% TEOA; pH=7 \\ \lambda > 420 nm \\ Noarther infrared light \\ Near-infrared light \\ (OOnerrol) \end{array} \begin{array}{c} 0.64 and 1.43 \\ \mumol h^{-1} \\ \mumol h^{-1} \end{array} \begin{array}{c} 8 times; \\ One time for 3h \end{array} \end{array}$			4,2':6',4"- terpyridine			320-780 nm		NO
$ \begin{cases} [Cu(HDSPTP)_{2}(H_{2}O)_{3}] \cdot 6H_{2}O \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$						Near-infrared light	No	
$\begin{array}{c c} \lambda > 420 \text{ nm} & \mu \text{mol } h^{-1} \\ \hline \lambda > 420 \text{ nm} & \mu \text{mol } h^{-1} \\ \hline \lambda > 420 \text{ nm} & \mu \text{mol } h^{-1} \\ \hline (\text{Cu}(\text{DSPTP})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}_{\text{n}} \\ \hline (\text{This worK}) & \text{dine} & \text{No} & \text{No} \\ \end{array} \begin{array}{c c} \lambda > 420 \text{ nm} & \mu \text{mol } h^{-1} \\ \hline \lambda > 420 \text{ nm} & \mu \text{mol } h^{-1} \\ \hline \text{Near-infrared light} & \mu \text{mol } h^{-1} \\ \hline (\text{Cu} \cap h^{-1}) & \text{One time for 3h} \\ \hline \ \ \text{One time for 3h} \\ \hline \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	{[Cu(HDSPTP) ₂ (H ₂ O) ₂] ₂ 6H ₂ O		4'-(2,4-disulf ophenyl)-3,2' :6',3''-terpyri			10% TEOA; pH=7	5.77 and 6.99	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	}_ and	-				λ > 420 nm	µmol h ⁻¹	8 times; One time for 3h
(This worK) dine Near-infrared light µmol h '	{[Cu(DSPTP)(H ₂ O) ₂]·H ₂ O} _n	Cu		No	No		0.64 and 1.43	
	(This worK)		dine			Near-Intrared light		

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