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A metal-organic framework with in-situ generated low-coordinate binuclear Cu(I) units as the highly effective catalyst for photodriven hydrogen production†

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Experimental section

Materials and Methods.

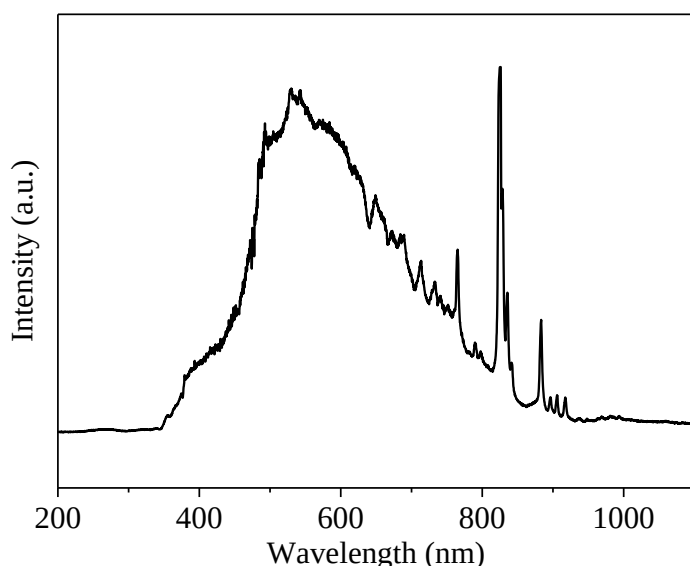
All reagents were commercially available and used without further purification. 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole (H₂bbta) was synthesized according to literature method.^[*J. Org. Chem.*, 1986, 51, 979-986] X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Scientific ESCALAB 250 instrument. Electron paramagnetic resonance measurements were performed at 9.7 GHz (X-band) using a Bruker BioSpin A300 spectrometer at 77 K. The spin concentrations in the samples were determined from the second integral of the spectra using CuSO₄·5H₂O as a standard. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8-Advance diffractometer with Cu K α radiation and a LynxEye detector. Thermogravimetry (TG) analyses were performed on a TA Q50 thermogravimetric analyzer under nitrogen gas at a heating rate of 10 °C/min. Scanning electron microscope (SEM) images were obtained from an Ultra-high Resolution electron microscope (FE-SEM, SU8010). Gas sorption isotherms were measured on a Micromeritics ASAP 2020M instrument. Before the sorption experiments, the as-synthesized samples were first solvent exchanged by MeOH, and then activated for 12 h at 150 °C under vacuum. N₂ (99.999%) was used for the measurement. The temperature was controlled by a liquid nitrogen bath (77 K). Inductively coupled plasma-mass spectrometry (ICP-MS) was conducted on an iCAP-Qc instrument (Thermo Fisher). Electron paramagnetic resonance measurements were performed at 9.7 GHz (X-band) using a Bruker BioSpin A300 spectrometer at 77 K. The spin concentrations in the samples were determined from the second integral of the spectra using CuSO₄·5H₂O as a standard. Raman spectra were measured at 200 °C by using a Renishaw model 1000 spectrometer with a 20 mW air-cooled argon ion laser (514.5 nm) as the excitation source.

Synthesis of [Cu₂Cl₂(bbta)(H₂O)₂]·guest (denoted as Cu₂-Cl₂-bbta or MAF-X29).

A mixture of CuCl₂ (0.033 g, 0.252 mmol), H₂bbta (0.020 g, 0.126 mmol), DMF (4 mL), methanol (4 mL), and 12 M HCl (0.2 mL) was placed in a 15-mL Teflon reactor and heated at 70 °C for 72 h. Crystalline powders were collected by filtration, washed with isopropanol and dried in air (apparent yields 50-80%).

Photocatalytic Measurements.

The photocatalytic HER experiments were carried out in a 250 mL Pyrex reaction vessel via an online photocatalytic H₂ evolution activity evaluation system. For each experiment, 20 mg of the catalysts were dispersed in 100 mL mixture solvent (MeCN/H₂O/TEOA = 65 mL/25 mL/10 mL) and immersed in an ultrasonic bath for 20 min. To make sure the reaction system was under vacuum, the whole system was vacuumed for at least 30 min with vacuum bump before the reactions. The reaction mixture, which was kept at room temperature with circulating water, was constantly stirred and irradiated by a 200 W Xenon light source with a 420 nm filter (light intensity = 100 mW/cm²). The emission spectra of the light source was shown as follow:



The generated product was analyzed *in-situ* by a Techcomp 7900 gas chromatography equipped with a thermal conductivity detector (TCD) and a 5A molecular sieves column. The concentration of Cu in the filtrate was detected by the inductively coupled plasma–mass spectrometry. After photocatalytic reaction (20 mg catalysts in 100 mL solution), 1 mL of the filtrate was digested and diluted to 100 mL for tests. The concentration of Cu in the concentrated filtrate was detected as 20.2 ng/mL. Therefore, the dissolved Cu ions of the MOF was $(20.2 \text{ ng mL}^{-1} \times 100 \text{ mL})/0.20 \text{ mg} = 1.01\%$.

Computational Methods.

All simulations/calculations were performed by the Materials Studio 5.0 package. All energies were calculated by the periodic density functional theory (PDFT) method by the Dmol3 module. Full geometry optimizations with fixed cell parameters were performed to

the systems. The widely used generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and the double numerical plus d-functions (DNP) basis set, TS for DFT-D correction as well as the Effective Core Potentials (ECP) were used. The energy, force and displacement convergence criteria were set as 1×10^{-5} Ha, 2×10^{-3} Ha and 5×10^{-3} Å, respectively.

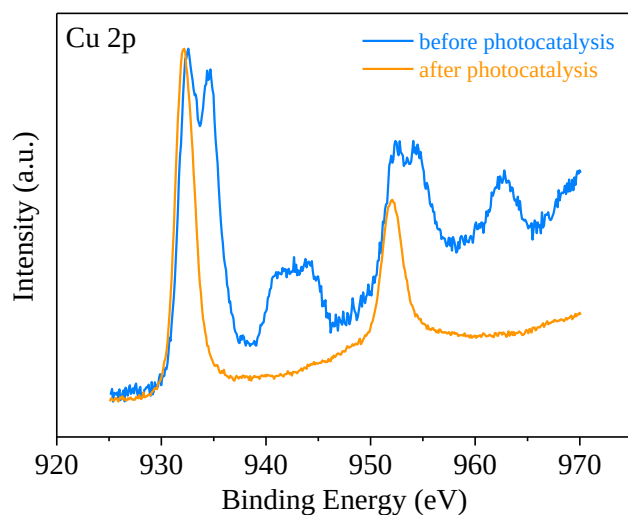


Fig. S1. XPS spectra of **Cu₂-Cl₂-bbta**.

Before photocatalysis, The observation of the satellite peaks at 940-945 eV and 960-965 eV indicate the Cu ions in **Cu₂-Cl₂-bbta** before photocatalysis are Cu(II). After photocatalytic experiments, the absence of satellite peaks indicate most of the Cu ions turn from Cu(II) to Cu(I).

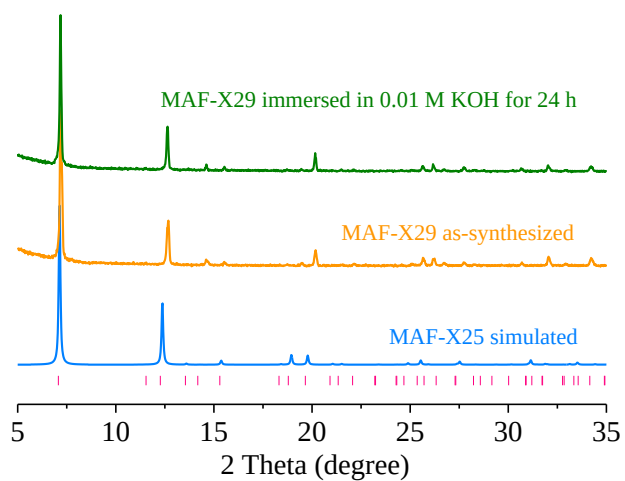


Fig. S2. PXRD patterns of **Cu₂-Cl₂-bbta**.

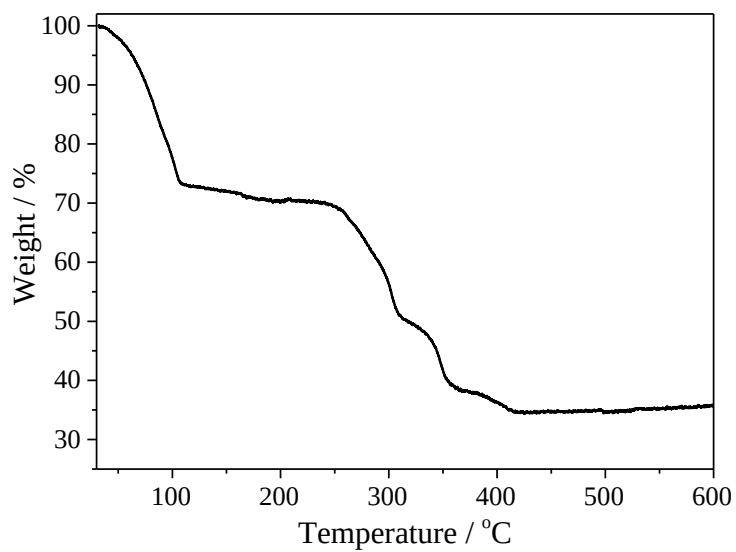


Fig. S3. TG curves of $\text{Cu}_2\text{-Cl}_2\text{-bbta}$.

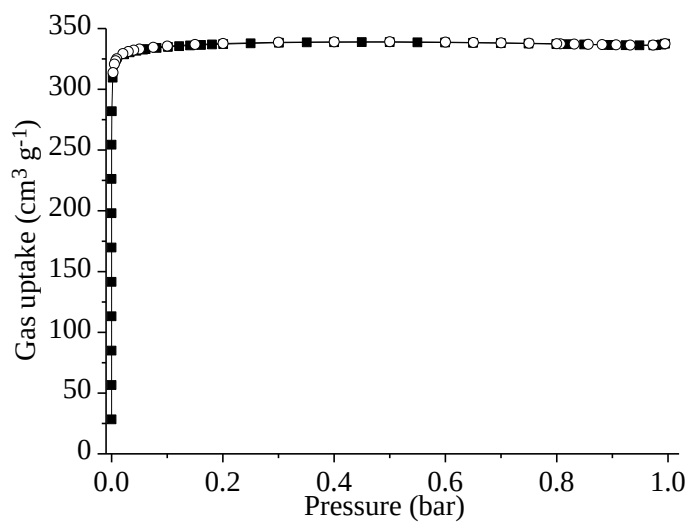


Fig. S4. N_2 adsorption and desorption isotherms of $\text{Cu}_2\text{-Cl}_2\text{-bbta}$ at 77 K.

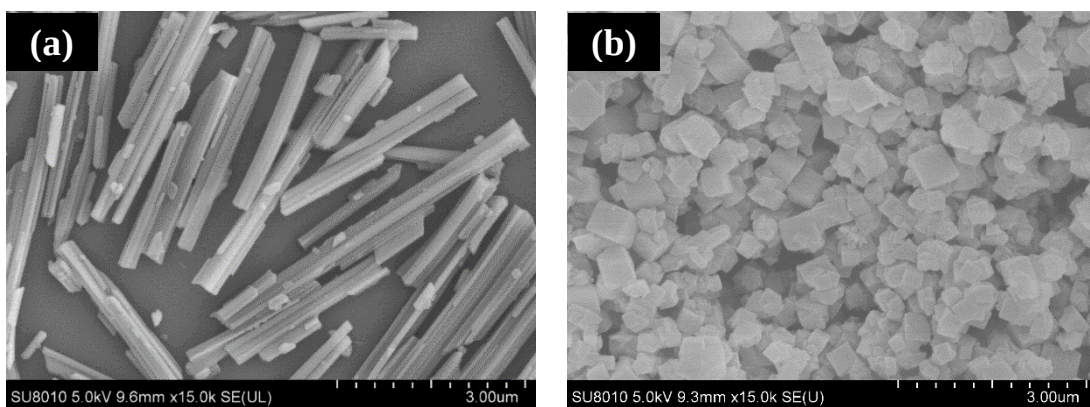


Fig. S5. SEM images of the (a) $\text{Cu}_2\text{-Cl}_2\text{-bbta}$ and Cu-Cl-btdd .

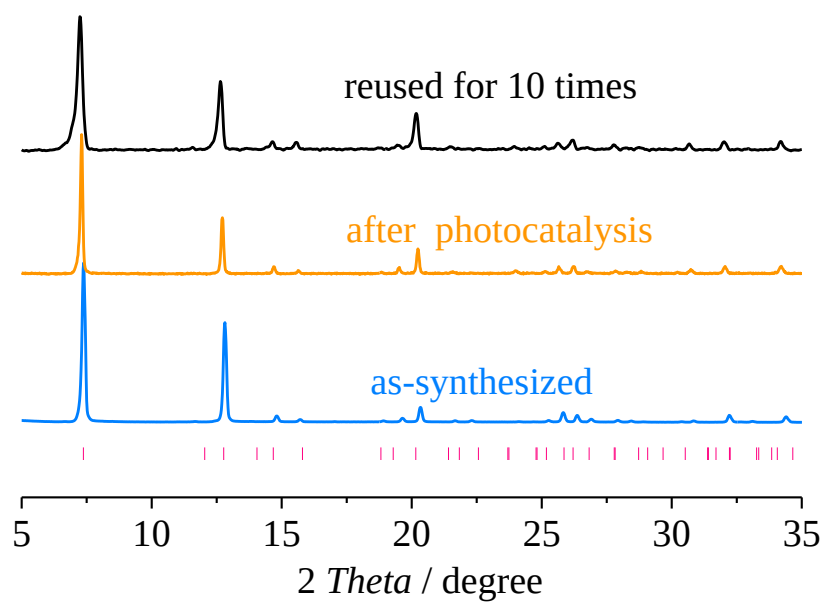


Fig. S6. PXRD patterns of $\text{Cu}_2\text{-Cl}_2\text{-bbta}$ before and after photocatalytic reaction (pink vertical lines indicate the theoretical Bragg diffractions of the crystal structure).

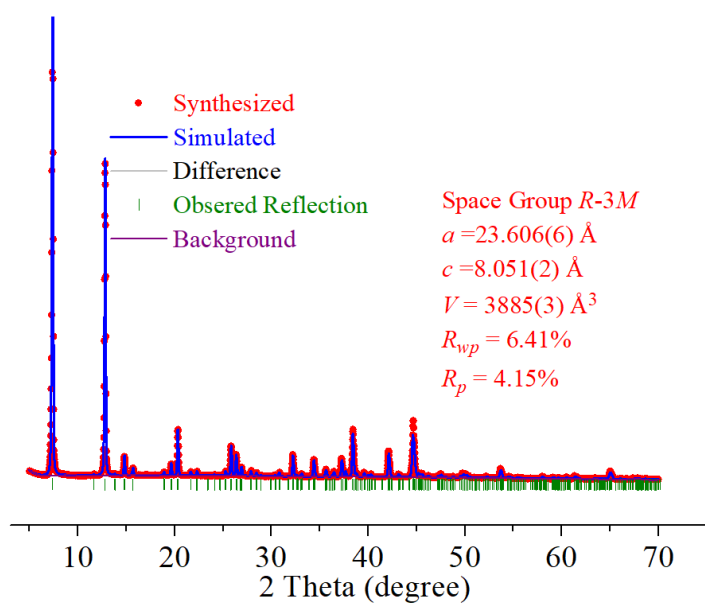


Fig. S7 Final Rietveld refinement results of **Cu₂-bbta**.

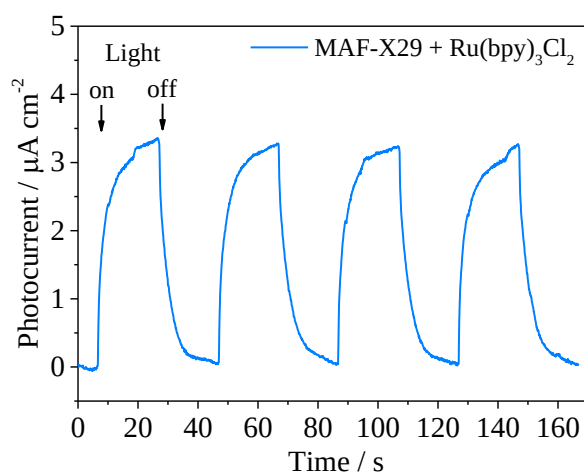


Fig. S8. Photocurrent measurements for **Cu₂-Cl₂-bbta** in the presence of [Ru(bpy)₃]Cl₂.

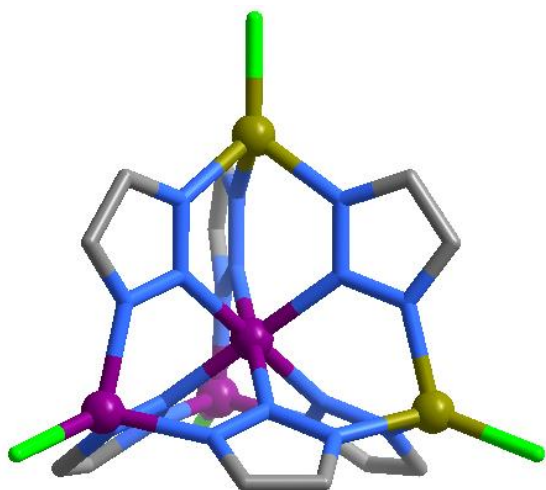


Fig. S9. Coordination environment of **Cu-btdd**. Color code: Purple, Zn; Yellow, Cu; Blue, N; Green, Cl; Gray, C.

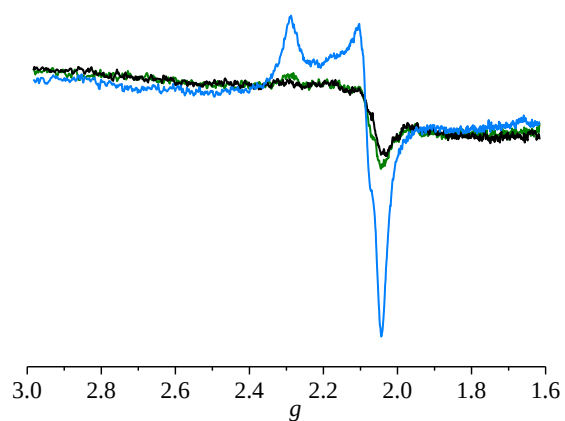


Fig. S10. *in situ* EPR spectra of **Cu-Cl-btdd** measured before (blue) and after photocatalytic hydrogen evolution reaction for 60 (green) and 120 (black) min, respectively.

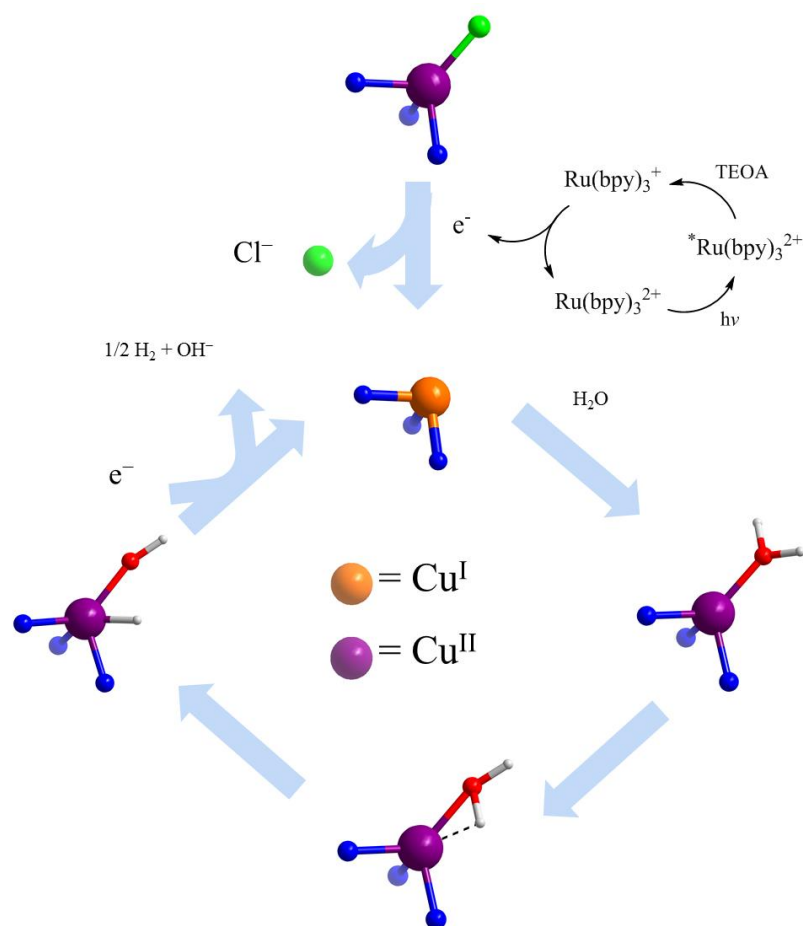


Fig. S11. The proposed mechanism for photocatalytic hydrogen evolution using **Cu-Cl-btdd** as catalyst.

Table S1. Comparison of the photocatalytic hydrogen evolution performances of **Cu₂-Cl₂-bbta** and other MOF catalysts.

Materials	Sacrificial agents	Photosensitizers	Co-cat alyst	Irradiation	H ₂ production rate / mmol g ⁻¹ h ⁻¹	AQY	Ref.
Cu₂-bbta	TEOA	Ru(bpy) ₃ Cl	—	> 420 nm	102.8	10.1%	This work
Pt@2	TEA	Ir ^{III} (ppy) ₂ (bpy)	Pt	> 420 nm	144.4	—	<i>J. Am. Chem. Soc.</i> , 2012 , 134, 7211
Pt@1	TEA	Ir ^{III} (ppy) ₂ (bpy)	Pt	> 420 nm	1.98	—	
CdS/MIL-101 (Cr)	Lactic acid	—	Pt	> 420 nm	75.5	—	<i>Chem. Commun.</i> , 2013 , 49, 6761
RCGO/U6N	TEOA	ErB	Pt	> 420 nm	41.4	8.8%	<i>J. Mater. Chem. A</i> , 2017 , 5, 20136
Ni@MOF-5	TEOA	Eosin Y	Ni	> 420 nm	30.22	16.7%	<i>Appl. Catal. B: Environ.</i> 2016 , 190 12
Au@CdS/MI L-101	Na ₂ S/ Na ₂ SO ₃	—	—	> 420 nm	25.0	8.8%	<i>Appl. Catal. B: Environ.</i> 2016 , 185, 307
MOF-199/Ni	TEOA	Eosin Y	Pt	> 420 nm	24.4	—	<i>J. Mater. Chem. A</i> 2016 , 4, 7174
MOF-199/Ni	TEOA	Eosin Y	—	> 420 nm	8.0	—	
NH ₂ -UiO-66/ TpPa-1-COF	Ascorbate	—	Pt	> 420 nm	23.41	—	<i>Angew. Chem. Int. Ed.</i> 2018 , 57, 12106
[Ni ₂ (PymS) ₄] _n	TEA	Fluorescein	—	2.02 W LED	18.7	—	<i>J. Mater. Chem. A</i> , 2015 ,3, 7163
GOWPt@U6 N-8 mL	TEOA	ErB	Pt	> 420 nm	18.15	1.80 %	<i>ChemSusChem</i> 2018 , 11, 666
NiS/Zn _{0.5} Cd _{0.5} S	Na ₂ S/ Na ₂ SO ₃	—	—	> 420 nm	16.78	—	<i>Angew. Chem. Int. Ed.</i> 2018 , 57, 9790
[Cu(RSH)(H ₂ O)] _n	TEOA	Eosin Y	—	> 420 nm	7.88	~4%	<i>Angew. Chem. Int. Ed.</i> 2016 , 55, 2073
Cu-I-bpy	TEA	—	—	UV	7.09	—	<i>Angew. Chem. Int. Ed.</i> 2017 , 56, 14637
Ni₄P₂@MOF- 1	MeOH	Ir ^{III} (ppy) ₂ (bpy)	—	> 400 nm	4.4	0.002%	<i>Angew. Chem. Int. Ed.</i> , 2016 , 55, 6411
Ni₄P₂@MOF- 2	MeOH	[Ru(bpy) ₃] ²⁺	—	> 400 nm	0.03	—	
WD-POM@S MOF-1	TEOA	[Ru(bpy) ₃] ²⁺	—	> 420 nm	3.55	—	<i>Nat. Commun.</i> 2016 , 7 11580

*Calculation of apparent quantum yield (AQY)

All photocatalytic experiments in this work were carried out under exposure to monochromatic light beam with an excitation wavelength of 420 nm. The number of incident photons (N) is calculated as

$$N = (I \times S \times \lambda) / (h \times c) = (100 \times 10^{-3} \times 32.15 \times 3600 \times 4 \times 420 \times 10^{-9}) / (6.626 \times 10^{-34} \times 3 \times 10^8) = 9.78 \times 10^{28}$$

where Light intensity (I) = 100 mW/cm². Area (S) = 32.15 cm². λ = 420 nm.

h is Planck constant = 6.626×10^{-34} J·s, c is velocity of light = 3×10^8 m/s.

The apparent quantum yield (AQY) of **Cu₂-Cl₂-bbta** was calculated as:

$$\text{AQY} = [2 \times (\text{number of the produced molecule}) / (\text{number of incident photons})] \times 100\% \\ = 2 \times 8.22 \times 10^{-3} \times 6.022 \times 10^{23} / (9.78 \times 10^{28}) \times 100\% = 10.1\%$$

Note that the apparent quantum yield calculation does not consider the catalyst amount and many other aspects (such as the transparency of the reaction container), meaning that only the experiments carried out with the same setting are suitable for comparison of the apparent quantum yields.

****Calculation of Solar to hydrogen (STH) conversion efficiency**^[*Science* **2015**, 347, 970; *J. Mater. Chem. A*, **2015**, 3, 2485]

During 4 h of illumination, the total incident power over 32.15 cm² irradiation area was 3.2 W, so that the total input energy in 4 hours was:

$$E_{\text{Solar}} = 4.61 \times 10^4 \text{ J}$$

During the photocatalytic reaction, 8.22 mmol H₂ was detected by gas chromatography (GC), which indicated that the energy generated by water splitting was:

$$E_{\text{F}} = 8.22 \times 10^{-3} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} = 1217.3 \text{ J}$$

Where 2.46 eV is the free energy of water splitting.

STH = (Energy of generation of hydrogen by water splitting)/(Solar energy irradiating the reaction cell) = $E_{\text{F}}/E_{\text{Solar}} = 1217.3 \text{ J} / 4.61 \times 10^4 \text{ J} = 2.64\%$

Table S2. The summary of photocatalytic hydrogen evolution performances of **Cu₂-Cl₂-bbta** with different ratios of solvents.

Materials	Solvent	Sacrificial agents	Photosensitizers	Irradiation	H ₂ production rate / mmol g ⁻¹ h ⁻¹
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 80:10	TEOA	Ru(bpy) ₃ Cl ₂	> 420 nm	55.2
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 65:25	TEOA	Ru(bpy) ₃ Cl ₂	> 420 nm	102.8
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 45:45	TEOA	Ru(bpy) ₃ Cl ₂	> 420 nm	29.0
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 25:65	TEOA	Ru(bpy) ₃ Cl ₂	> 420 nm	3.1

Table S3. The summary of photocatalytic hydrogen evolution performances of **Cu₂-Cl₂-bbta** with different sacrificial agents.

Materials	Solvent	Sacrificial agents	Photosensitizers	Irradiation	H ₂ production rate / mmol g ⁻¹ h ⁻¹
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 65:25	TEOA	Ru(bpy) ₃ Cl ₂	> 420 nm	102.8
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 65:25	ascorbic acid	Ru(bpy) ₃ Cl ₂	> 420 nm	18.1
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 65:25	methanol	Ru(bpy) ₃ Cl ₂	> 420 nm	22.0
Cu₂-Cl₂-bbta	MeCN:H ₂ O = 65:25	oxalic acid	Ru(bpy) ₃ Cl ₂	> 420 nm	6.0