

Supporting Information

Noble-Metal-Free Photocatalyst System via BODIPY-Based MOFs for Highly Efficient Visible-Light-Driven H₂ Evolution

Heng Yang,^{‡,a} Ming Zhao,^{‡,a} Jing Zhang,^a Ji Ma,^a Pengyan Wu,^{*,b} Wenlong Liu^c and
Lili Wen^{*,a}

^a Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, 430079, China.

^b School of Chemistry and Materials Science & Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, 221116, China.

^c College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China.

[‡] Heng Yang and Ming Zhao contributed equally to this work.

Corresponding Authors. E-mails: wenlili@mail.ccnu.edu.cn (L. L. Wen),
wpyan@jsnu.edu.cn (P. Y. Wu)

Materials and Instrumentation

The reagents and solvents applied were commercially available and employed without further purification. Ligand BODIPY was synthesized according to the literature.¹⁻² Proton reduction catalyst tris(bipyridine)cobalt ($[\text{Co}(\text{bpy})_3]\text{Cl}_2$) was prepared based on the published procedure.³⁻⁴ IR spectra were recorded on KBr discs on a Bruker Vector 22 spectrophotometer in the 4000 – 400 cm^{-1} region. The power X-ray diffraction (PXRD) patterns were recorded on a Siemens D 5005 powder diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 5-35°. Thermogravimetric analyses (TGA) were performed on TA-SDT 2960 under N_2 atmosphere with a heating rate of 10 $^\circ\text{C min}^{-1}$. Gas sorption experiments were performed with a Quantachrome IQ₂ system. The UV/Vis diffused reflectance spectra (DRS) were obtained on Agilent Cary 60 spectrophotometer with BaSO_4 as the reference for the baseline correction. Steady-state photoluminescence (PL) emission spectra were obtained over VARIAN Cary Eclipse Fluorescence spectrophotometer. Time-resolved photoluminescence (TRPL) spectra were recorded on FLS1000 photoluminescence spectrophotometer (Edinburgh Instruments, UK). Cyclic voltammetry and transient photocurrent measurements were performed on a CHI 760E electrochemical analyzer (CH Instruments, Inc., Shanghai).

Experimental Section

Synthesis of Cd-BPDC. Cd-BPDC was synthesized according to the literature.⁵ A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (61.6 mg, 0.20 mmol), H_2BPDC (24.2 mg, 0.10 mmol) was suspended in DMF (4 mL) in a 5 mL glass vial, and stirred for 30 min. White turbid liquid was obtained. The resulting solution was transferred into autoclave and heated at 90 $^\circ\text{C}$ for 2 days. After cooling to room temperature naturally, colorless crystals were obtained. FT-IR (KBr, cm^{-1}): 3185m, 1610m, 1600s, 1580s, 1520s, 1395s, 1180w, 1030w, 1000w, 850w, 820w, 765m, 690w.

Synthesis of Cd-SDB. Cd-SDB was synthesized according to the literature.⁶ A mixture of Cd(NO₃)₂·4H₂O (0.310 g, 1 mmol), H₂BPDC (0.296 mg, 1 mmol) were dissolved in 12 g of ethanol and stirred for 2 hours to achieve homogeneity. The resultant solution was heated at 140°C for 3 days. Colorless crystals were recovered. FT-IR (KBr, cm⁻¹): 3486s, 3079w, 2967m, 2865w, 2366w, 1951w, 1628s, 1564m, 1398s, 1296m, 1167s, 1100m, 1013w, 856m, 734s, 686w, 618m, 496m.

X-ray Crystallography. The crystallographic data for **CCNU-11** and **CCNU-12** was measured using a Bruker Smart Apex CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. The structure was solved by direct methods and refined anisotropically with SHELXTL using full-matrix least-squares procedures based upon F^2 values.⁷ In the structure, free solvent molecules were removed using the SQUEEZE routine of PLATON,⁸ the subsequent refinements were based on the new data generated. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre: CCDC 1935387-1935388. Select bond lengths and angles are provided in Table S1 and S2.

Activated CCNU-11 and CCNU-12.⁹ **CCNU-11** or **CCNU-12** (*ca.* 40 mg) initially washed with DMF (3 \times 20 mL) was first exchanged with CH₂Cl₂. The crystals were soaked in 20 mL of CH₂Cl₂ 3 times over 1 h. The crystals were then immersed in 20 mL of dry hexane over 1 h replacing the solvent every 20 min. Once the solvent exchange is complete, the material was isolated by decanting the hexane and the crystals were evacuated under dynamic vacuum for 3 h at 40°C. The PXRD profiles of the simulated form, as-synthesized and activated **CCNU-11** or **CCNU-12** suggest that the evacuated samples maintain the integrity of structure (Fig. S2). And then, the dynamic vacuum activated samples were evacuated again by using the “degas” function of the surface area analyzer for 10 h at 313 K before N₂ isotherm measurement.

Cyclic Voltammetry Measurement for [Co(bpy)₃]Cl₂.¹⁰ Cyclic voltammetry was

performed on a conventional three electrode system. Glassy carbon electrode (GCE, 5 mm in diameter), an Ag/AgCl with saturated KCl, and a Pt wire were used as the working electrode, reference and counter electrode, respectively. The electrolyte solution was made up of CH₃CN (working as solvent) and 0.1 M [(n-Bu)₄N][PF₆] (working as the supporting electrolyte). The solution was saturated with N₂ prior to experiment.

Fluorescence Measurements.¹¹ 3 mg of CCNU-11 or CCNU-12 powders were dispersed in 3.00 mL of [Co(bpy)₃]Cl₂ (common proton reduction catalyst) in water with different concentrations. The finely ground powder of CCNU-11 and CCNU-12 is dispersed well in water, which enables substrates to be closely adhered to the surface of the MOF particles and facilitates possible host-guest interactions. To obtain the luminescent spectra, the emulsions were treated by ultrasonication for 30 min and then aged for 1 day to form stable emulsions before fluorescence study. Each PL emission spectra were measured at least three times and the emission intensities were found basically unvaried.

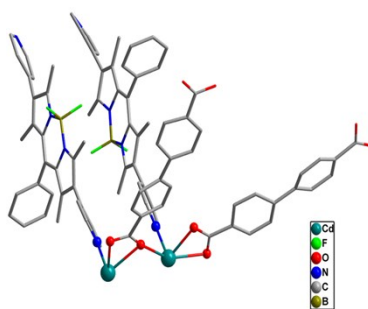
In addition, the samples contained 0.2 g/L CCNU-11 (CCNU-12) + 0.34 mM [Co(bpy)₃]Cl₂ were positioned in aqueous suspension and were treated by ultrasonication for 30 min, the lifetime of which was measured excited by 440 nm pulsed laser.

Photoelectrochemical measurements. Transient photocurrent measurements were performed on a CHI 760E electrochemical work station in a standard three-electrode system with the photocatalyst-coated fluorin-tin oxide (FTO) as the working electrode, Pt plate serve as the counter electrode, Ag/AgCl as the reference electrode and 0.4 M Na₂SO₄ solution was used as the electrolyte. A 420 nm LED (3W) lamp (Shenzhen LAMPLIC Science Co. Ltd. China) was used for excitation. The mixture of CCNU-11(15 mg) or CCNU-12 (15 mg) and [Co(bpy)₃]Cl (15 mg) was added into 10 μL Nafion and 1.2 mL mixed solution of methanol and distilled water (v/v=1), and the working electrode was prepared by dropping the suitable amount of the

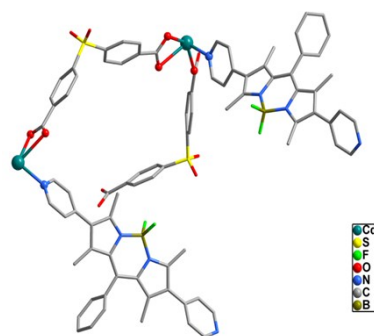
suspension onto the surface of an FTO plate. The working electrode was dried at room temperature, and the photo-responsive signals of the samples were measured under chopped light at 0.5 V.

Photo-induced Hydrogen Production. For photo induced hydrogen evolution, each sample was made in a 10 mL flask with a volume of 5 mL in ethanol/water. Typically, the sample contained 0.2 g/L CCNU-11 or CCNU-12, [Co(bpy)₃]Cl₂, and TEA as the sacrificial electron donor. The flask was sealed with a septum and protected from light, then degassed by bubbling nitrogen for 25 min under atmospheric pressure at room temperature. After that, the samples were irradiated by a 500 W Xe lamp equipped with a UV cut-off filter (>420 nm), the reaction temperature was 293 K by using a water filter to absorb heat. Hydrogen gas was measured by gas chromatography (GC 7890T, nitrogen as a carrier gas) using a thermal conductivity detector (TCD) and a 5 Å molecular sieve column (0.6 m × 3 mm). The amount of hydrogen generated was determined by the external standard method. Hydrogen in the resulting solution was not measured and the slight effect of the hydrogen gas generated on the pressure of the flask was neglected for calculation of the volume of hydrogen gas.

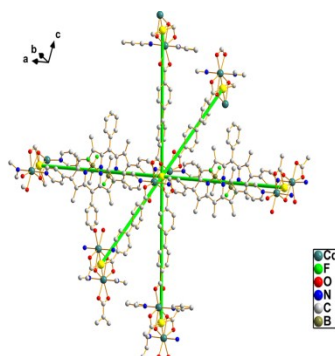
Results and Discussion



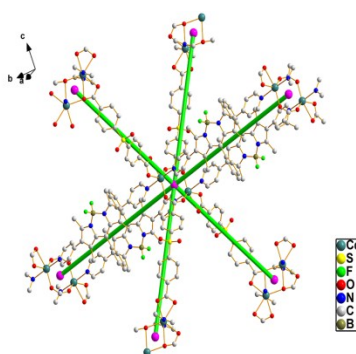
(a)



(b)



(c)



(d)

Fig. S1 The asymmetric unit for (a) **CCNU-11** and (b) **CCNU-12**. 6-connected nodes represented by $\{\text{Cd}_2\}$ units: (c) yellow spheres represent the centers of neighboring Cd1 and Cd2 atoms in **CCNU-11** and (d) purple spheres represent the centers of two symmetry-related Cd atoms in **CCNU-12**.

Table S1. The partial bond length (Å) and bond angle (°) of **CCNU-11**.

CCNU-11			
Cd(1)-O(1)#1	2.453(11)	Cd(1)-O(2)	2.331(11)
Cd(1)-O(6)#1	2.326(11)	Cd(1)-O(7)	2.400(11)
Cd(1)-O(8)	2.311(12)	Cd(1)-N(5)	2.263(11)
Cd(1)-N(8)#2	2.265(15)	Cd(2)-N(4)#2	2.298(13)

Cd(2)-O(2)	2.460(10)	Cd(2)-O(1)#1	2.322(11)
Cd(2)-N(1)	2.264(11)	Cd(2)-O(4)#3	2.388(11)
Cd(2)-O(3)	2.307(11)	Cd(2)-O(5)#3	2.273(12)
O(6)#1-Cd(1)-O(7)	84.8(4)	O(8)-Cd(1)-O(2)	92.1(4)
N(5)-Cd(1)-O(1)#1	89.9(4)	O(6)#1-Cd(1)-O(2)	128.8(4)
N(5)-Cd(1)-O(8)	89.2(5)	N(8)#2-Cd(1)-O(7)	88.3(5)
N(8)#2-Cd(1)-O(1)#1	91.7(5)	O(1)#1-Cd(2)-O(3)	129.0(4)
O(4)#3-Cd(2)-O(3)	84.6(4)	O(5)#3-Cd(2)-O(1)#1	92.4(4)
O(5)#3-Cd(2)-N(4)#2	89.6(5)	O(3)-Cd(2)-N(1)	93.4(4)
O(4)#3-Cd(2)-N(1)	94.4(4)	O(2)-Cd(2)-N(4)#2	89.8(5)

Symmetry codes: #1 +x, -y, -1/2+z; #2 -1+x, +y, +z; #3 +x, 1-y, -1/2+z.

Table S2. The partial bond length (Å) and bond angle (°) of CCNU-12

CCNU-12			
Cd(1)-O(3)	2.287(7)	Cd(1)-O(4)	2.514(8)
Cd(1)-O(10)#2	2.265(7)	Cd(1)-O(9)	2.197(7)
Cd(1)-N(4)#1	2.362(7)	Cd(1)-N(3)	2.313(7)
Cd(2)-O(5)	2.628(6)	Cd(2)-O(5)#3	2.336(7)
Cd(2)-O(6)	2.307(6)	Cd(2)-O(11)#4	2.468(7)
Cd(2)-N(7)	2.297(7)	Cd(2)-O(12)#4	2.319(6)
Cd(2)-N(8)#5	2.323(7)	O(9)-Cd(1)-O(4)	87.0(3)
O(10)#2-Cd(1)-N(4)#1	89.6(3)	O(3)-Cd(1)-N(4)#1	90.9(3)
N(3)-Cd(1)-O(4)	95.2(3)	O(9)-Cd(1)-N(3)	90.7(3)
O(10)#2-Cd(1)-O(3)	94.0(3)	N(7)-Cd(2)-O(12)#4	98.7(3)
O(5)#3-Cd(2)-N(8)#5	90.6(3)	O(5)-Cd(2)-O(6)	52.4(2)
O(11)#4-Cd(2)-N(8)#5	89.4(3)	O(11)#4-Cd(2)-O(6)	88.9(2)
O(12)#4-Cd(2)-O(5)	164.0(2)	N(7)-Cd(2)-O(5)#3	91.1(2)

Symmetry codes: #1 -1/2+x, -1/2+y, +z; #2 -x, 1-y, -z; #3 -x, 2-y, 1-z; #4 -x, 1-y, 1-z; #5 -1/2+x, 1/2+y, +z.

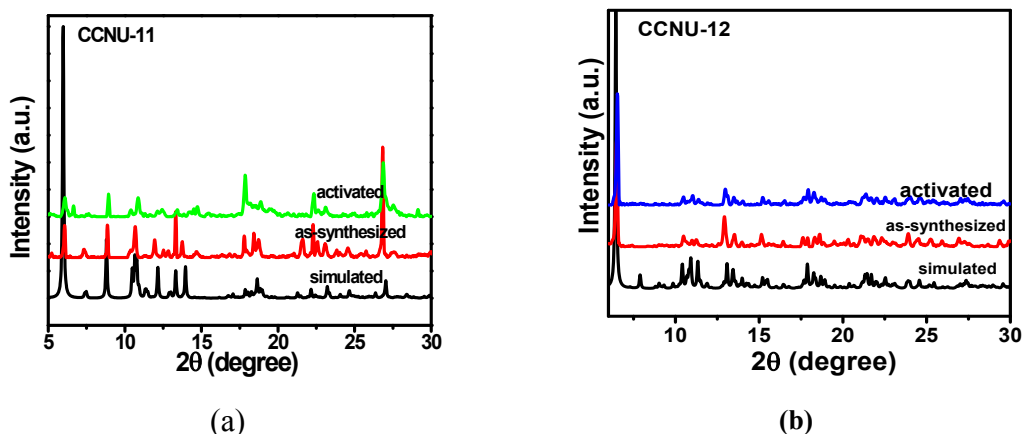


Fig. S2 The PXRD patterns of (a) CCNU-1 and (b) CCNU-12. Simulated spectrum was calculated from the single crystal data, respectively.

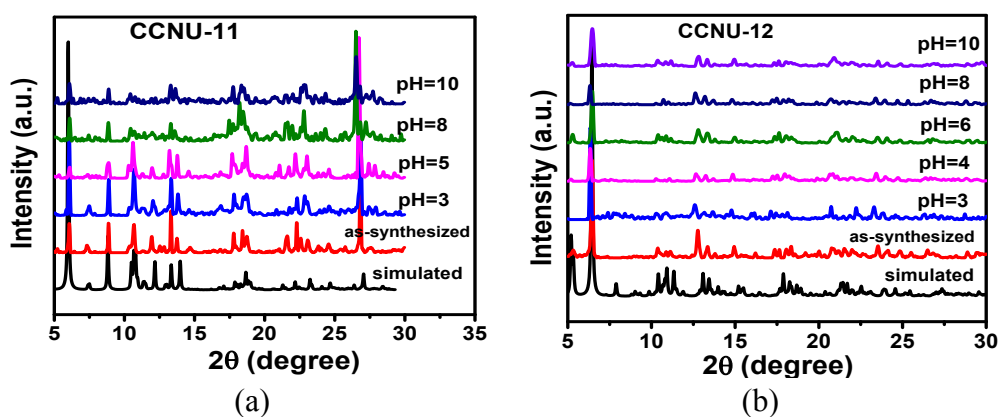


Fig. S3 PXRD patterns of (a) CCNU-11 and (b) CCNU-12 soaked in aqueous solution with different pH (3–10) for 24 h. Simulated spectrum was calculated from the single crystal data, respectively.

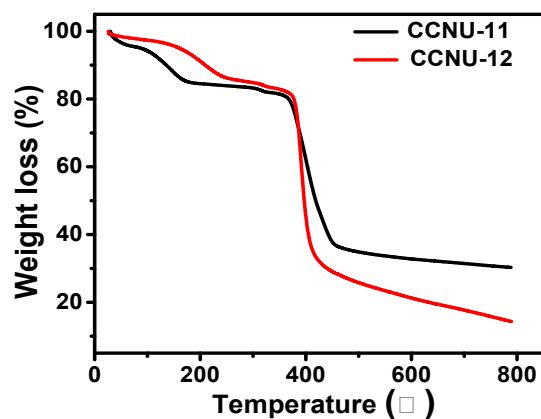


Fig. S4 TGA curves of CCNU-11 and CCNU-12.

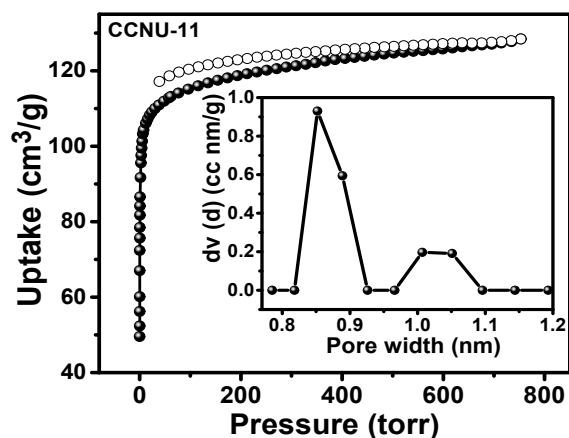


Fig. S5 N_2 adsorption and desorption isotherm for CCNU-11 at 77 K. The inset is the pore distribution analysis by the nonlocal density functional theory (NLDFT).

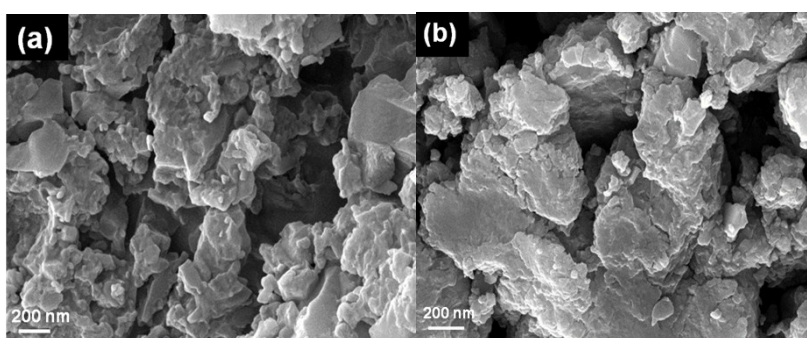


Fig. S6 The TEM and SEM images for CCNU-11 (a) and CCNU-12 (b).

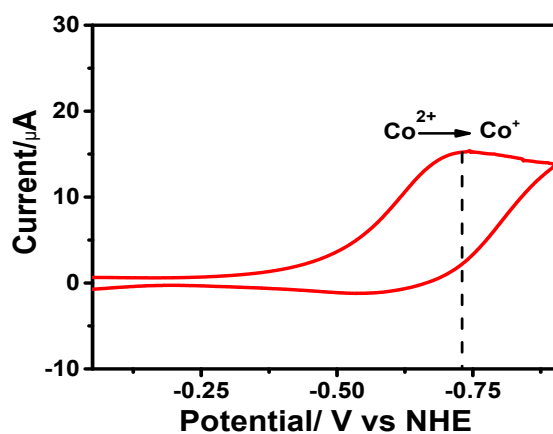


Fig. S7 CVs of 1 mmol/L of $[Co(bpy)_3]Cl_2$ in MeCN + 0.1 mol/L Bu_4NPF_6 at a glassy carbon electrode under N_2 . Reference electrode: Ag/AgCl; counter electrode: platinum (Pt) wire; scan rate: 50 mV/s.

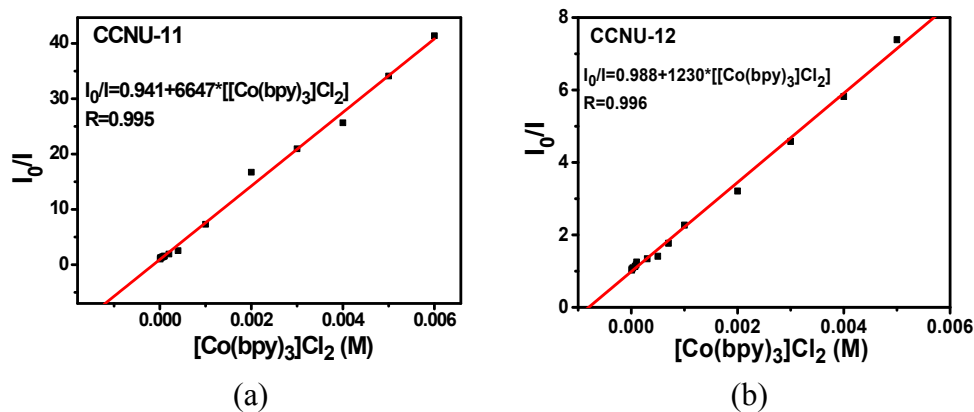


Fig. S8 Stern–Volmer plot of compounds **CCNU-11** (a) and **CCNU-12** (b) quenched by $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ aqueous solution, where I_0 and I are the fluorescence intensity ratio before and after metal ion incorporation, respectively.

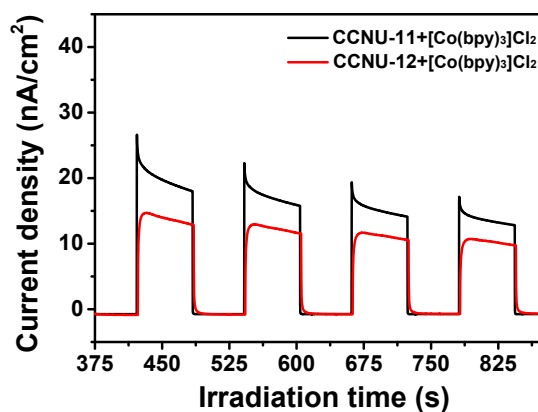


Fig. S9 Transient photocurrent-time profiles for **CCNU-11**+ $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ and **CCNU-12**+ $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ in the 0.4 M Na_2SO_4 aqueous solution.

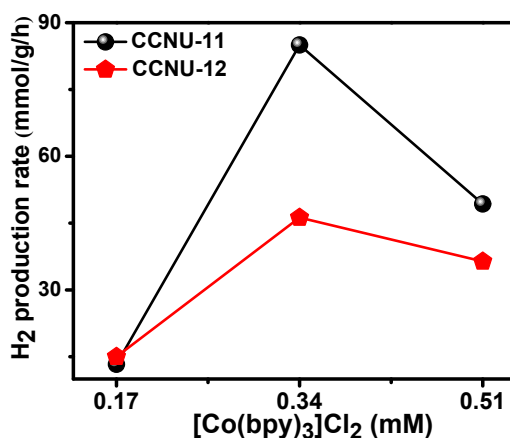


Fig. S10 Influence of the $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ content on photo-induced hydrogen production from the system comprising 0.2 g/L **CCNU-11** or **CCNU-12** and 5% TEA in a pH=9 (**CCNU-11**) or pH=10 (**CCNU-12**) ethanol/water solution after 5 h of

irradiation.

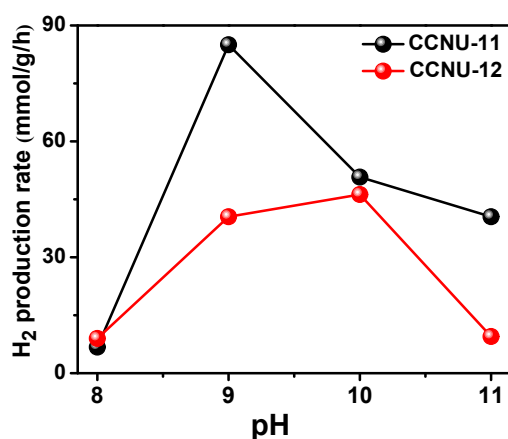


Fig. S11 Influences of the pH on photo-induced hydrogen production from the system comprising 0.2 g/L CCNU-11 or CCNU-12 and $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ (0.34 mM) in a 5% TEA.

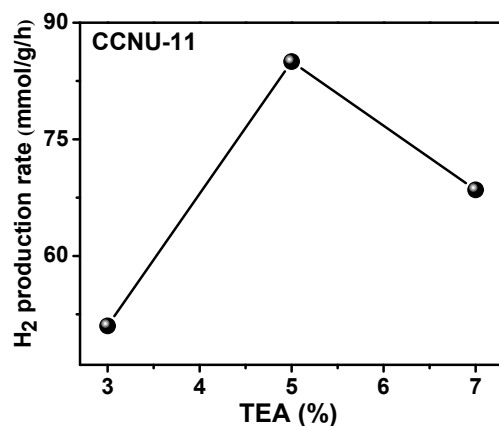


Fig. S12 Influence of the TEA content on photo-induced hydrogen production from the system comprising 0.2 g/L CCNU-11 and $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ (0.34 mM) in a pH=9 ethanol/water solution after 5 h of irradiation.

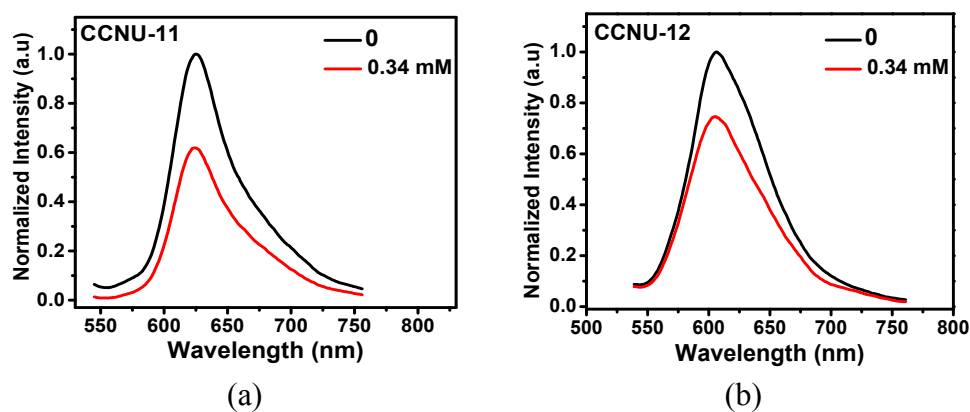


Fig. S13 Fluorescence intensity changes of (a) CCNU-11 and (b) CCNU-12 upon the addition of $[\text{Co}(\text{bpy})_3]\text{Cl}_2$.

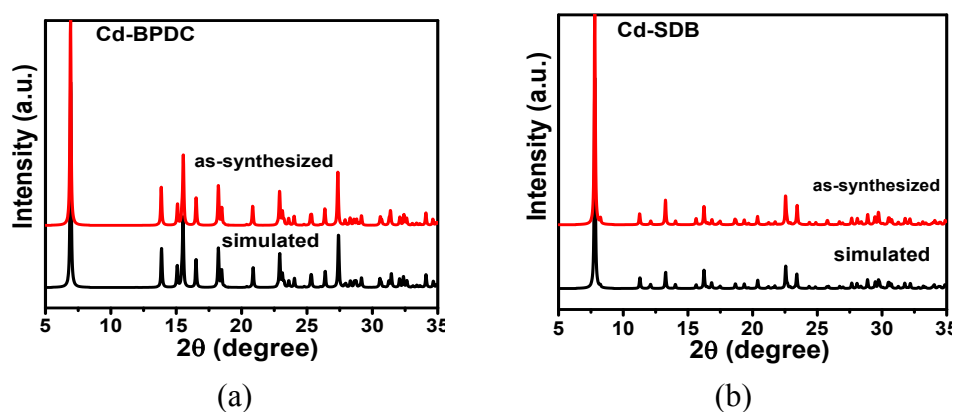


Fig. S14 The PXRD patterns of (a) Cd-BPDC and (b) Cd-SDB. Simulated spectrum was calculated from the single crystal data.⁵⁻⁶

Table S3. Comparison of hydrogen production.^a

Entry	Photocatalyst	H ₂ Production Rate (mmol/g/h)	Note
1	CCNU-11	60.4	---
2	Cd-BPDC	1.43	No BODIPY
3	CCNU-11	n. d.	No [Co(bpy) ₃]Cl ₂
4	CCNU-11	n. d.	In dark
5	---	n. d.	No CCNU-11
6	CCNU-11	n. d.	No TEA
7	CCNU-12	44.5	---
8	Cd-SDB	2.06	No BODIPY
9	CCNU-12	n. d.	No [Co(bpy) ₃]Cl ₂
10	CCNU-12	n. d.	In dark
11	---	n. d.	No CCNU-12
12	CCNU-12	n. d.	No TEA

^aReaction conditions: Photosensitizer CCNU-11 and CCNU-12 (0.2 g/L), [Co(bpy)₃]Cl₂ (0.34 mM), TEA 5%, pH = 9 (for CCNU-11) and pH = 10 (for CCNU-12), 5 mL ethanol/H₂O = 1/1 solvent irradiated using an Xe lamp (500 W) at ambient temperature for 10 h (CCNU-11) and 6 h (CCNU-12).

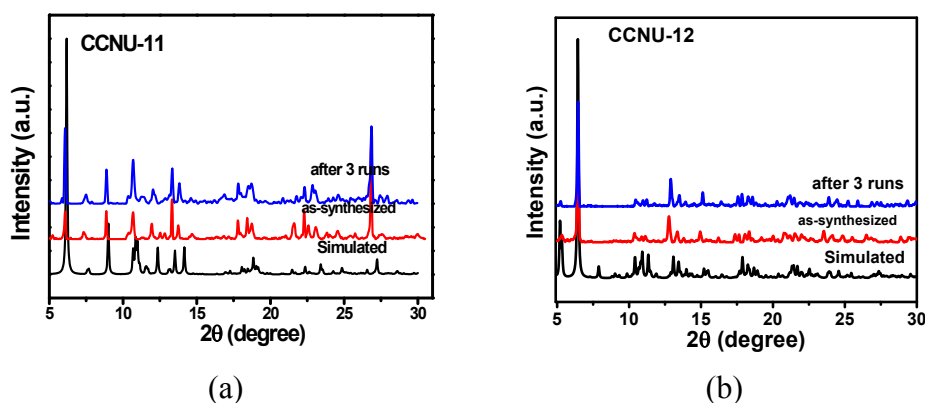


Fig. S15 The PXRD patterns of CCNU-11 (a) and CCNU-12 (b) before and after reaction.

References

- 1 D. Zhang, Y. G. Wen, Y. Xiao, G. Yu, Y. Q. Liu and X. H. Qian, *Chem. Commun.*, 2008, **39**, 4777.
- 2 C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 15858.
- 3 V. Artero, M. Chavarot-Kerlidou, and M. Fontecave. *Angew. Chem. Int. Ed.*, 2011, **50**, 7238.
- 4 J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T.H. Anderson, and S. Bernhard, *J. Am. Chem. Soc.*, 2005, **127**, 7502.
- 5 L.Y. Wang, R. Q. Fan, P. Wang, Y. L. Yang, *Inorg. Chem. Commun.*, 2012, **23**, 54.
- 6 A. M. Plonka, D. Banerjee, W. R. Woerner, Z. J. Zhang, J. Li and J. B. Parise, *Chem. Commun.*, 2013, **49**, 7055.
- 7 G. M. Sheldrick, *WI*, 2001.
- 8 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- 9 J. L. Ma, A. P. Kalenak, A. G. Wong-Foy, and A. J. Matzger, *Angew. Chem. Int. Ed.*, 2017, **56**, 14618.
- 10 Z. Li, J. D. Xiao and H. L. Jiang, *ACS Catal.*, 2016, **6**, 5359.
- 11 Y. Zhao, X. Y. Xu, L. Qiu, X. J. Kang, L. L. Wen and B. G. Zhang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 15164.