

## 2D photosensitive porphyrin-based MOFs integrated Pd cocatalyst with fast charge transfer for efficient photocatalytic hydrogen evolution

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### Materials and experimental Section

#### Materials

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%), Copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99%), Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%), Cadmium nitrate trihydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 98%), Polyvinylpyrrolidone (PVP), Pyrazine (99%) and Trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ , 99%) was purchased from Alfa Aesar. Pyrrole ( $\text{C}_4\text{H}_5\text{N}$ , 99%), Methyl 4-Formylbenzoate ( $\text{C}_9\text{H}_8\text{O}_3$ , 98%) were purchased from Adamas. Palladium chloride ( $\text{PdCl}_2$ , 99.9%, Pd 59.5%), Methyl Alcohol ( $\text{CH}_3\text{OH}$ , 99.9%), Propionic Acid ( $\text{C}_3\text{H}_6\text{O}_2$ , 99.5%), N, N-Dimethylformamide (DMF) ( $\text{C}_3\text{H}_7\text{NO}$ ,

98%), KOH (90%) were purchased from Chron Chemicals. All the materials were used as received without further purification.

## **Experimental Section**

### **5,10,15,20-tetrakis(4-methoxycarbonylphenyl) porphyrin (TMCPP).**

Methyl 4-formylbenzoate (14.410 g, 0.086 mol) was completely dissolved in propionic acid (250 mL) in a round-bottom flask, then slowly added pyrrole (6.09 mL, 0.086 mol) dissolved in 20 mL propionic acid, and finally refluxed the mixture at 150 °C for 12 hours. After cooling to room temperature, the obtained precipitate was washed with a large amount of ethanol, ethyl acetate and a small amount of THF, successively. The collected purple precipitate was dried at 70 °C for 12 hours. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*): δ 8.82 (s, 8H), 8.44 (d, J=8, 8H), 8.31 (d, J=8, 8H), 4.12 (s, 12H), 2.80 (s, 2H) (Figure S1).

### **5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP)**

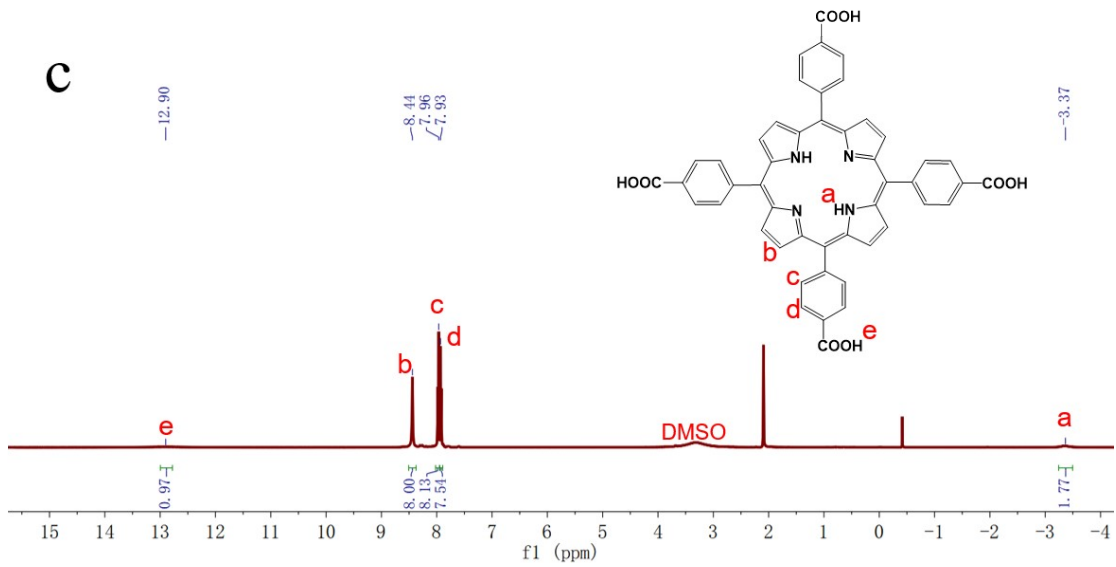
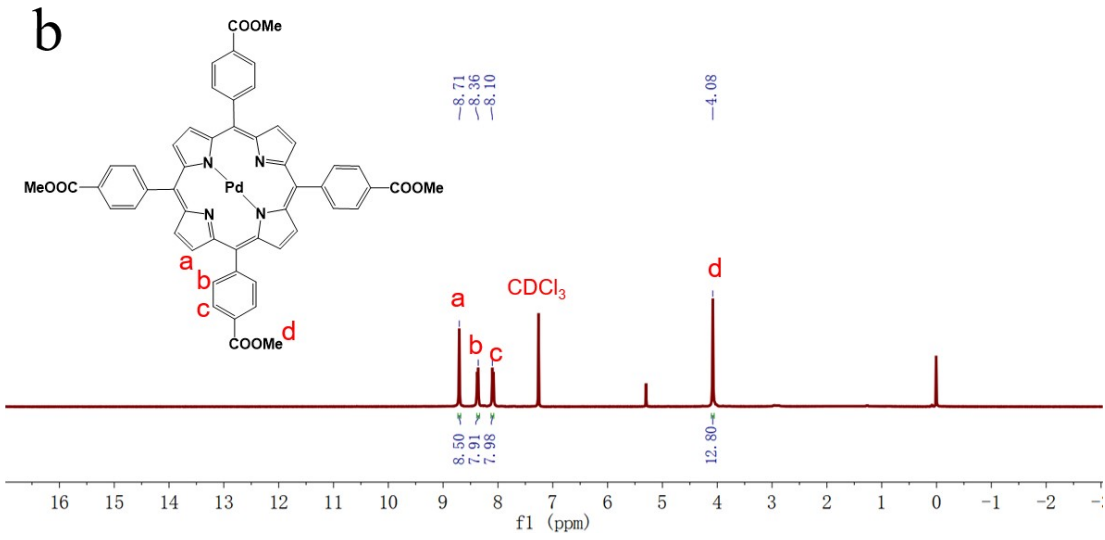
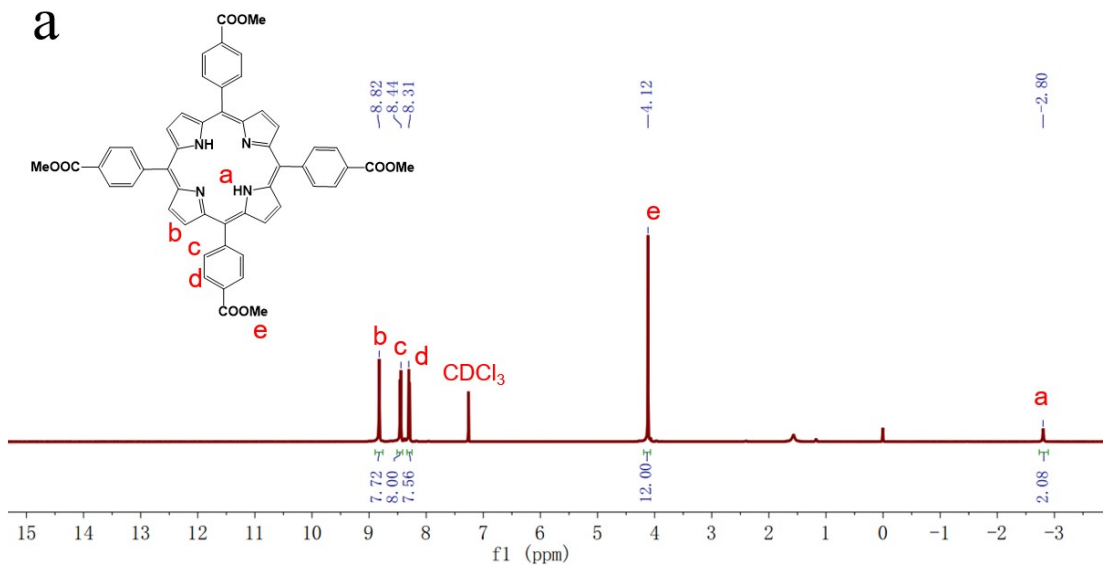
Put TMCPP (500 mg) into the 250 mL round bottom flask with 40 mL THF and 40 mL MeOH, and 40 mL of water dissolved with 3 g KOH was added, then reflux the mixture solution at 90 °C for 12 h. After cooling to room temperature, part of the solvent was removed, then filtered to obtain a clear solution, subsequently the solution was acidified with 1M HCl until no more precipitate was formed (pH≈2), finally the collected precipitate was obtained via centrifugation and washed with water several times, and dried at 80 °C under vacuum for 8 hours. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 12.90 (s, 4H), 8.44 (s, 8H), 7.96 (d, J=8, 8H), 7.93 (d, J=8, 8H), -3.37 (s, 2H) (Figure S1).

### **5,10,15,20-tetrakis(4-methoxycarbonylphenyl) porphyrin-Pd (PdTMCPP)**

Dissolve the TMCPP (300mg) in 100 mL DMF and put it into 250 ml round bottom flask, then PdCl<sub>2</sub>·2H<sub>2</sub>O (135 mg) was added, stirred well and later refluxed for 6 h. After the solution was cooled to room temperature, about 100 mL H<sub>2</sub>O was added to carry out suction filtration. During the suction filtration, the solid obtained was washed with water until the filtrate was clear. Finally, the washed solid was dried in a vacuum drying oven at 80 °C overnight to obtain PdTMCPP. <sup>1</sup>H NMR (400 MHz, Chloroform-d): δ 8.71 (s, 8H), 8.36 (d, J=8, 8H), 8.10 (d, J=8, 8H), 4.08 (s, 12H) (Figure S1).

### **5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin-Pd (PdTCPP)**

The obtained PdTMCPP (300 mg) were dissolved in a mixed solution of 26 mL (THF/MeOH=1:1), to which KOH aqueous solution (13 mL, 2 mol/L) was added and refluxed at 90 °C for 12 h. After cooling to room temperature, part of the solvent was removed, then filtered to obtain a clear solution, subsequently the solution was acidified with 1M HCl until no more precipitate was formed (pH≈2), finally the collected precipitate was obtained via centrifugation and washed with water several times, and dried at 80 °C under vacuum for 8 hours. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 13.05 (s, 4H), 8.72 (s, 8H), 8.28 (d, J=8, 8H), 8.21 (d, J=8, 8H) (Figure S1).



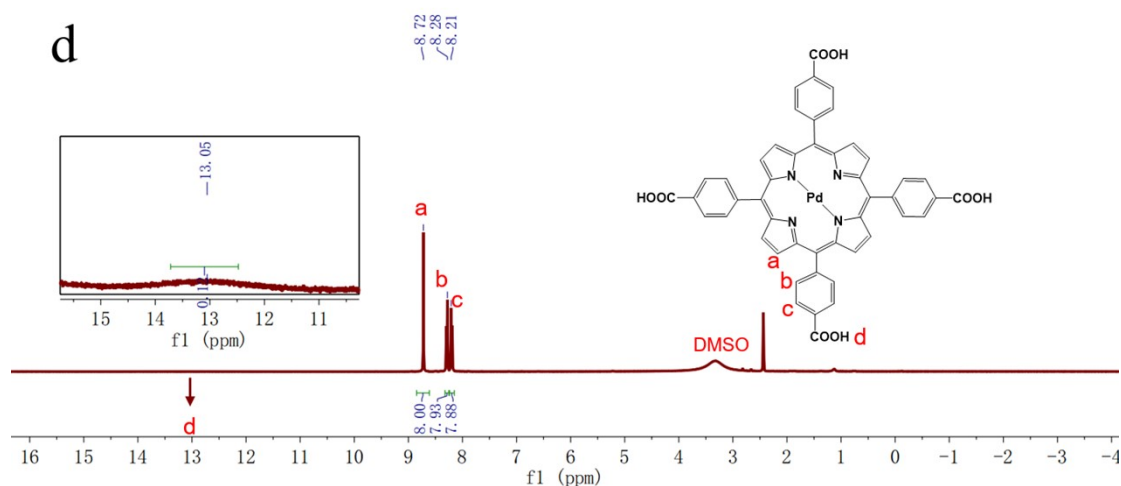


Figure S1 (a-b)  $^1\text{H}$  NMR spectrum (400 MHz) of TMCPP and PdTMCPP in  $\text{CDCl}_3$ ; (c-d)  $^1\text{H}$  NMR spectrum (400 MHz) of TCPP and PdTCPP in  $\text{DMSO-D}_6$

**Synthesis of Co-TCPP(2H)/Co-TCPP(Pd) nanosheets.**  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (4.4 mg, 0.015 mmol), pyrazine (0.8 mg, 0.01 mmol) and PVP (20.0 mg) in 12 mL of the mixture of DMF and ethanol (V: V=3:1) were dissolved in a 20 mL capped vial. Then TCPP (4.0 mg, 0.005 mmol)/ PdTCPP (4.5 mg, 0.005 mmol) dissolved in 4 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwisely under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept the reaction for 24 h. The resulting red nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Co-TCPP/Co-TCPP(Pd) nanosheets were dried in a vacuum drying oven at 60 °C for 12 h.

**Synthesis of Cu-TCPP(Pd) nanosheets.**  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (3.6 mg, 0.015 mmol), Trifluoroacetic acid (1.0 M  $\times$  10  $\mu\text{L}$ ) and PVP (10.0 mg) in 12 mL of the mixture of DMF and ethanol (V:V=3:1) were dissolved in a 20 mL capped vial. Then PdTCPP (4.5 mg, 0.005 mmol) dissolved in 4 mL of the mixture of DMF and ethanol (V: V=3:1)

were added dropwisely under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept the reaction for 3 h. The resulting red nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Cu-TCPP(Pd) nanosheets were dried in a vacuum drying oven at 60 °C for 12 h.

**Synthesis of Cd-TCPP(Pd) nanosheets.** Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (4.6 mg, 0.015 mmol), pyrazine (0.8 mg, 0.01 mmol) and PVP (20.0 mg) in 12 mL of the mixture of DMF and ethanol (V:V=3:1) were dissolved in a 20 mL capped vial. Then PdTCPP (4.5 mg, 0.005 mmol) dissolved in 4 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwisely under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept the reaction for 24 h. The resulting dark green nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Cd-TCPP(Pd) nanosheets were dried in a vacuum drying oven at 60 °C for 12 h.

**Synthesis of Zn-TCPP(Pd) nanosheets.** Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (4.5 mg, 0.015 mmol), pyrazine (0.8 mg, 0.01 mmol) and PVP (20.0 mg) in 12 mL of the mixture of DMF and ethanol (V: V=3:1) were dissolved in a 20 mL capped vial. Then PdTCPP (4.5 mg, 0.005 mmol) dissolved in 4 mL of the mixture of DMF and ethanol (V: V=3:1) were added dropwisely under stirring. After that, the solution was sonicated for 10 min. The vial was heated to 80 °C and then kept the reaction for 16 h. The resulting purple nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Zn-TCPP(Pd) nanosheets were dried in a

vacuum drying oven at 60 °C for 12 h.

### **Characterizations and Measurements**

The microstructure and morphology of M-TCPP(Pd) composites were characterized by X-ray powder diffraction (XRD) patterns (XPD-6100, Shimadzu, Japan), Fourier transform infrared (FT-IR) spectra (IRPrestige-21, Shimadzu, Japan), Scanning electron microscopy (SEM) micrographs (Zeiss Merlin, Germany), Atomic force microscope AFM (Dimension ICON, Brooklyn), Transmission electron microscope TEM (Talos F200 S, USA), X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, USA), Brunauer-Emmett-Teller (BET) measurements (ASAP 2020, USA). Photocatalytic properties and mechanisms were investigated by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) (UV-vis DRS, Shimadzu, Japan), Photoluminescence spectrum (PL spectrum) (F-7000, HITACHI, Japan and FLS1000, Edinburgh instruments), Transient photocurrent response curve (PEC 1000), Electrochemical impedance spectroscopy (EIS) (PEC 1000).

### **Photocatalytic H<sub>2</sub> generation experiments**

Under the ambient temperature, a 300 W Xe lamp equipped with a UV cut filter ( $\lambda \geq 420$  nm) was used to carry out the photocatalytic hydrogen production experiment in a 100 mL optical reaction vessel. Usually, 5 mg sample reagent was dispersed in 25 mL deionized water containing ascorbic acid (AH<sub>2</sub>, 1M) was used as a sacrificial reagent, then the suspension was bubbled with nitrogen for 15 min to remove air. A constant temperature cooling circulating pump was used to maintain the test

temperature at 6 °C, and in a closed system illuminated by a 300 W Xe lamp equipped with a 420 nm cut-off filter, a gas chromatograph (GC 7920, Nitrogen was used as carrier gas) was used to detect the formation of H<sub>2</sub> online every hour. The AQE was measured through the equation below :

$$\text{AQE (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$
$$= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

### **Electrochemical measurements**

An electrochemical instrument with a three-electrode system was used to analyze electrochemical measurements. The working electrode was prepared as follows: added 50 μ L of H<sub>2</sub>O, 450 μ L of ethanol, 10 μ L of Nafion, reagent to the sample (1 mg) and ultrasonic dispersion for 30 min, and then transferred 100 μ L of suspension to coat the ITO. The electrode was dried in air at room temperature. The reference electrode was calomel electrode and the counter electrode was platinum electrode. Electrochemical impedance spectroscopy (EIS) and transient photocurrent tests were conducted in Na<sub>2</sub>SO<sub>4</sub> (0.2 M). A xenon lamp (300 W) was treated as the light irradiation for photocurrent test.



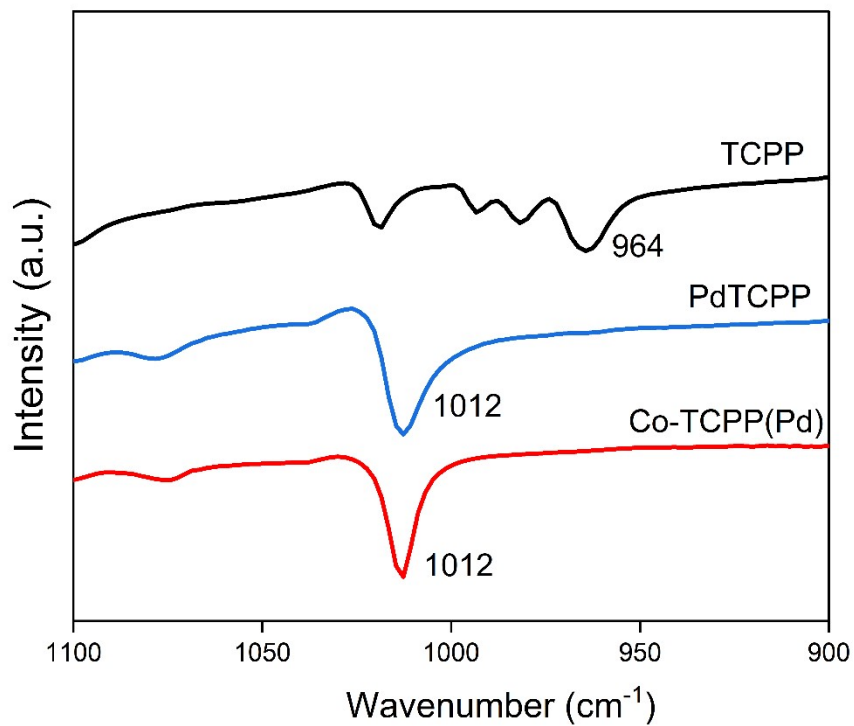


Figure S2. FTIR spectrums of TCPP, PdTCPP and Co-TCPP(Pd) at 1100-900  $\text{cm}^{-1}$ .

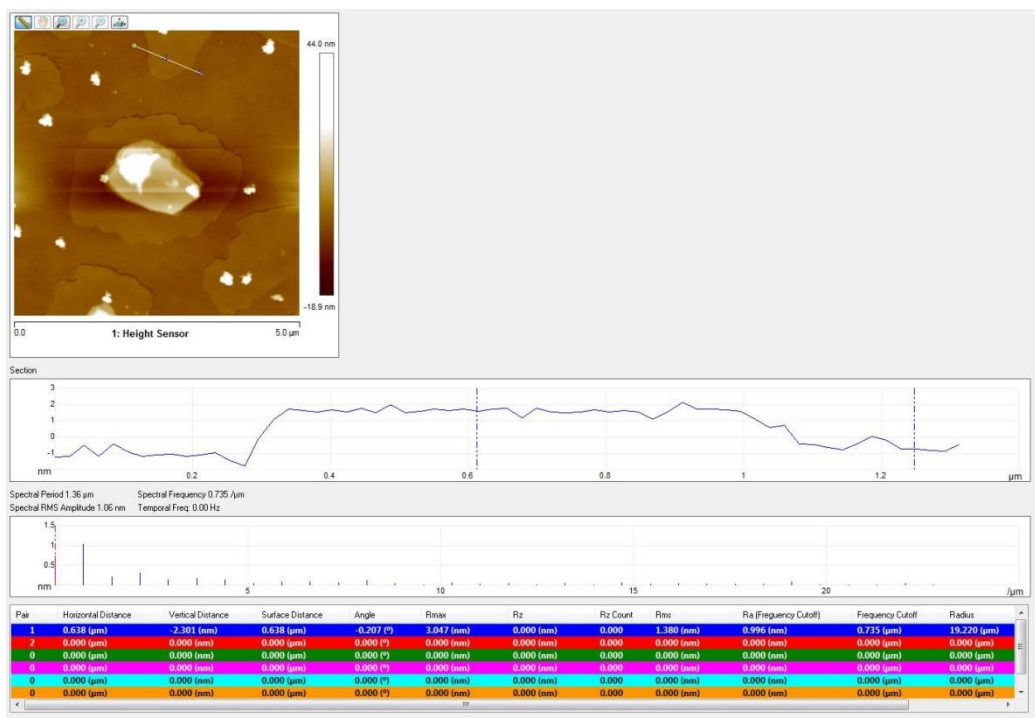


Figure S3. The AFM of Co-TCPP(Pd).

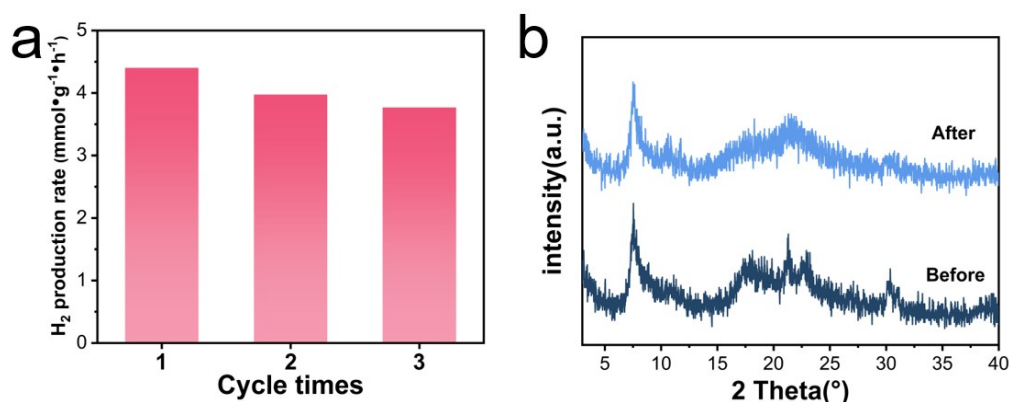


Figure S4. (a) Cycling performance of Co-TCPP(Pd); (b) XRD comparison of Co-TCPP(Pd)

before and after activity testing.

photocatalysts	Light source	Activity	Journal
Co-TCPP(Pd)	300 W Xe lamp, $\lambda > 420$ nm	4403 $\mu\text{mol/g/h}$	This work
Pd/TiO <sub>2</sub> <sup>1</sup>	300 W Xe lamp, 780 $>\lambda>$ 320 nm	979 $\mu\text{mol/g/h}$	Appl. Catal. B: Environ.
CdS-YS <sup>2</sup>	300 W Xe lamp, $\lambda > 420$ nm	3051 $\mu\text{mol/g/h}$	J. Mater. Chem. A.
Pt-TiO <sub>2</sub> <sup>3</sup>	300 W Xe lamp, $\lambda > 420$ nm	1023 $\mu\text{mol/g/h}$	New J Chem.
Co-doped CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> <sup>4</sup>	300 W Xe lamp, $\lambda > 380$ nm	1077 $\mu\text{mol/g/h}$	J Colloid Interf Sci.
Co-AgInS <sub>2</sub> <sup>5</sup>	350 W Xe lamp, $\lambda > 400$ nm	66 $\mu\text{mol/g/h}$	J Alloy Compd.
MoS <sub>2</sub> -RGO/ZnO <sup>6</sup>	300 W Xe lamp, $\lambda > 380$ nm	288 $\mu\text{mol/g/h}$	Chem Eng J.
Bi <sub>2</sub> O <sub>2</sub> Se/TiO <sub>2</sub> <sup>7</sup>	300 W Xe lamp, $\lambda > 420$ nm	1240 $\mu\text{mol/g/h}$	Chem Eng J.

Table S1. The comparison of the photocatalytic H<sub>2</sub> production rate of Co-TCPP(Pd)

with those of other reported photocatalysts.

photocatalysts	Light source	Activity	Journal
Co-TCPP(Pd)	300 W Xe lamp, $\lambda > 420$ nm	4403 $\mu\text{mol/g/h}$	This work

2% Pt/Zr-TCPP(Pd) <sup>8</sup>	300 W Xe lamp, $\lambda > 420$ nm	3348 $\mu\text{mol/g/h}$	Chem Eng J.
Al-PMOF <sup>9</sup>	300 W Xe lamp, $\lambda > 420$ nm	200 $\mu\text{mol/g/h}$	Angew. Chemie - Int. Ed.
Ti-MOF-NH <sub>2</sub> <sup>10</sup>	300 W Xe lamp, $\lambda > 420$ nm	510 $\mu\text{mol/g/h}$	Catal Sci Technol.
Al-TCPP-0.1Pt <sup>11</sup>	300 W Xe lamp, $\lambda > 380$ nm	129 $\mu\text{mol/g/h}$	Adv. Mater.
HNTM-Ir/Pt <sup>12</sup>	300 W Xe lamp, $\lambda > 400$ nm	201.9 $\mu\text{mol/g/h}$	Angew. Chemie - Int. Ed.
Pt@UiO-66-NH <sub>2</sub> <sup>13</sup>	300 W Xe lamp, $\lambda > 380$ nm	257.38 $\mu\text{mol/g/h}$	Angew. Chemie - Int. Ed.
USTC-8(In) <sup>14</sup>	300 W Xe lamp, $\lambda > 420$ nm	341 $\mu\text{mol/g/h}$	ACS Catal.

Table S2. The comparison of the photocatalytic H<sub>2</sub> production rate of Co-TCPP(Pd) with those of other reported MOF-based photocatalysts

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