Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A Novel BODIPY-based-MOF Photocatalyst for Efficient Visible-Light-Driven Hydrogen Evolution

Heng Yang,[a] Jinming Wang,[b] Ji Ma,[a] Hong Yang,[a] Jing Zhang,[a] Kangle Lv,[c] Lili Wen*,[a] and Tianyou Peng*,[b]

[a] Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, 430079, China.
[b] College of Chemistry & Molecular Science, Wuhan University, Wuhan 430072, China.
[c] College of Resources & Environmental Science, Key Laboratory of Catalysis & Materials Science of State Ethnic Affairs Commission, South-Central University Nationalities, Wuhan 430074, China.

Corresponding Authors. E-mails: wenlili@mail.ccnu.edu.cn (L. L. Wen), typeng@whu.edu.cn (T. Y. Peng).

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] The power X-ray diffraction (PXRD) patterns were recorded on a Siemens D 5005 powder diffractometer using Cu Kα radiation (λ = 1.5406 Å) over a 2θ range of 5-40°. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific Escalab 250Xi-XPS photoelectron spectrometer with an Al Kα X-ray resource. The binding energies were calibrated by the C1s binding energy of 284.7 eV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was recorded on Vavian 715-ES. Transmission electron microscope (TEM) was performed on a FEI Tecnai G2 F30 electron microscope operating at 300 kV. Thermogravimetric analyses (TGA) was performed on TA-SDT 2960 under N_2 atmosphere with a heating rate of 10 °C min^{-1}. The UV/Vis diffused reflectance spectra (DRS) were obtained on a UV/Vis spectrophotometer (Agilent Cary 60) with $BaSO_4$ as the reference for the baseline correction. Photoluminescence (PL) spectra were obtained with a Fluorescence Spectrophotometer (VARIAN Cary Eclipse). FLS1000 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) was employed to record time-resolved photoluminescence (TRPL) spectra.

Experimental Section

Synthesis of CCNU-1. A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (7.4 mg, 0.025 mmol), BODIPY (6.0 mg, 0.0125 mmol), H_2BPDC (3.1 mg, 0.025 mmol), N,N'-Dimethylacetamide (DMA) (2 mL) and CH_3OH (1 mL) was added into a 5 mL vial, which was followed by adding one drop of 0.1 M nitric acid as the modulator. Then the final mixture was transferred to an oven and heated to 90 °C for 2 days. After cooling to ambient temperature, the resulting orange crystals were recovered by filtration (yield: 67% based on BODIPY). IR spectrum (cm^{-1}): 3435w, 2066w, 2927w, 2355w, 1643s, 1618s, 1528s, 1462w, 1397s, 1315w, 1241w, 1177s, 1110w, 1061w, 1013m, 840w, 775m, 726w, 677w, 587w, 439w.

Fabrication of Pt/CCNU-1 composite. Typically, **CCNU-1** (150 mg) was grinding to powder in an agate mortar and then dispersed into deionized water (20 mL). Sequently, 105 μL of H_2PtCl_6 (0.1 g·mL^{-1}) aqueous solution was mixed briefly under stirring over 0.5 h. The resulting mixture was collected through filtration, washed with deionized water, and then redispersed in 20 mL deionized water, and followed by an aqueous solution of $NaBH_4$ (1500 μL, 3.8 mg·mL^{-1}). After an extra reaction time of 0.5 h, the resultant dark orange precipitates (denoted as **Pt/CCNU-1** hereafter) were separated, washed by deionized water, and then dried in air. The loading amount of Pt (0) is *ca*. 0.13 wt% determined by ICP-AES for **Pt/CCNU-1** composite. Additionally, in order to optimize the loading amounts of Pt, the different volumes (50, 150 and 200 μL) of 0.1 g·mL^{-1} H_2PtCl_6 aqueous solution were mixed with **CCNU-1** (150 mg). The corresponding loading amounts of Pt NPs are *ca*. 0.04, 0.18 and 0.21 wt% (determined by ICP-AES), after treated by $NaBH_4$ chemical reduction.

Fabrication of Zn-BPDC. Zn-BPDC was synthesized according to the literature.[3] A mixture of $Zn(NO_3)_2·6H_2O$ (59.4 mg, 0.20 mmol), H_2BPDC (19.0 mg, 0.074 mmol) and N,N'-Diethylformamide (DEF) (4.5 mL) was heated in a 5 mL vial at 80 °C for 12 h. After cooling to ambient temperature, transparent colorless crystal **Zn-BPDC** was collected. **Fabrication of Pt/Zn-BPDC. Pt/Zn-BPDC** was obtained by the similar procedure to that for **Pt/CCNU-1**. Firstly, **Zn-BPDC** (150 mg) was grinding to powder in an agate mortar and then dispersed into deionized water (20 mL). Subsequently, 105 μL H_2PtCl_6 (0.1 g·mL^{-1}) was mixed briefly under stirring over 0.5 h. The resulting mixture was collected through filtration, washed with deionized water, and then re-dispersed in 20 mL deionized water, and followed by an aqueous solution of $NaBH_4$ (1500 μL, 3.8 mg·mL^{-1}). After an extra reaction time of 0.5 h, the resultant precipitates (denoted as **Pt/Zn-BPDC** hereafter) were separated, washed by deionized water, and then dried in air. The loading amount of Pt (0) was determined by ICP-AES, is up to *ca*. 0.11 wt% for **Pt/Zn-BPDC**.

Photoelectrochemical measurements. Transient photocurrent measurements were performed on a CHI 760E electrochemical work station (CHI760E China) 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 Na_2SO_4 solution was used as the electrolyte. A 420 nm LED (3W) lamp (Shenzhen LAMPLIC Science Co. Ltd. China) was used for excitation. The as-synthesized sample (6 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. The electrochemical impedance spectroscopy (EIS) was record by CHI 760E in a standard three-electrode system with the photocatalyst-coated glassy carbon ($\Phi = 3$ cm) as the working electrode, Pt plate as the counter electrode, Ag/AgCl as the reference electrode and 0.4 M Na_2SO_4 solution was used as the electrolyte. The as-synthesized sample (6 mg) was added into 10 μL Nafion and 1.2 mL co-solvent (methanol/H_2O at 1:1, v/v), and the working electrode was prepared by dropping 2 drops of the above suspension onto the surface of the glassy carbon electrode, and the working electrode was dried at room temperature. Then the EIS measurement was performed with a bias potential of 0.22 V in the dark with a frequency range from 10^{-1} to 10^{5} Hz, and the cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 1 $mV\cdot s^{-1}$.

Photocatalytic hydrogen production. The photocatalytic hydrogen production experiments were conducted in a Pyrex photoreaction device connected to a closed gas circulation and evacuation system. Typically, 50 mg of photocatalyst was dispersed in 50 mL aqueous solution with 0.1 M L-ascorbic acid (H_2A) as sacrificial agent. Then the mixture was homogenously dispersed by ultrasonication for 5 min and degassed thoroughly in the photoreaction vessel prior to photoirradiation by a 300 W Xenon arc lamp (Perfect light, Beijing) coupled with a UV cut-off filter ($\lambda > 420$ nm). Finally, the reaction solution was stirred continuously and the amount of H_2 generation was detected using online gas chromatograph (Agilent; GC-7890A).

$$TON = \frac{moles\ of\ evolved\ H_2}{moles\ of\ Pt\ on\ photocatalyst}$$

$$TOF = \frac{TON}{reaction\ time\ (hours)}$$

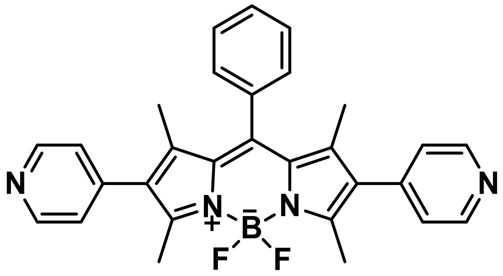
Measurement of apparent quantum efficiency (AQE). The apparent quantum efficiency (AQE) measurements of **Pt/CCNU-1** were carried out under different wavelengths of monochromatic light (420, 450, 475, 500, 550, 600, 635, 685 and 750 nm) with the similar reaction conditions. The number of photons reaching the reaction solution was measured using a FZ-A irradiatometer (A40094, Beijing Normal University Photoelectric Instruments Co., LTD).

$$AQE(\%) = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= 2 \times \frac{the\ numner\ of\ evolved\ H_2 molecules}{the\ number\ of\ incident\ photons} \times 100\%$$

X-ray Crystallography. The crystallographic data for **CCNU-1** was measured using a Bruker Smart Apex CCD area-detector diffractometer with Mo-K*a* radiation (λ = 0.71073 Å) at 173 K (Table S1). The structure was solved by direct methods and refined anisotropically with SHELXTL using full-matrix least-squares procedures based upon F^2 values.[4] In the structure, free solvent molecules were removed using the SQUEEZE routine of PLATON,[5] the subsequent refinements were based on the new data generated. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre: CCDC 1898260. Select bond lengths and angles are provided in Table S2.

Results and Disscussion



Scheme S1. Pyridine-functionalized boron dipyrromethene (BODIPY).

Table S1. Crystallographic data for **CCNU-1**.

	CCNU-1
Formula	$C_{57}H_{43}BF_2N_4O_9Zn_2$
Weight	1107.50
Crystal system	monoclinic
Space group	*I2/a*
a /Å	17.6239(12)
b /Å	18.1600(12)
c /Å	20.5219(13)
α /º	90.00
β /º	101.767 (6)
γ /º	90.00
V /Å^3	6430.0(7)
Z	4
ρ_{calcd}/g cm^{-3}	1.144
μ /mm^{-1}	0.801
Collected Reflections	25055
Unique reflections	5890
R_1 [I >2σ (I)]	0.0506
wR_2(all data)	0.1069

Table S2. The partial bond length (Å) and bond angle (°) of **CCNU-1**.

CCNU-1			
Zn(1)−Zn(1)#1	2.9295(8)	Zn(1)−O(5)#3	1.990(2)
Zn(1)−O(2)	2.054(2)	Zn(1)−N(2)	2.018(3)
Zn(1)−O(3)#1	2.002(2)	Zn(1)−O(4)#2	2.072(2)
O(2)−Zn(1)−O(4)#2	158.21(11)	Zn(1)#1−Zn(1)−N(2)	174.08(8)
O(5)#3−Zn(1)−O(3)#1	160.26(11)		

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

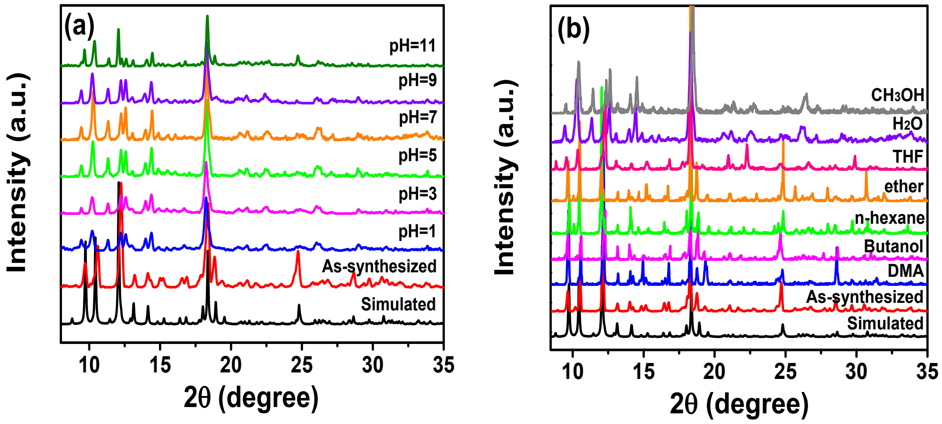


Fig. S1 PXRD patterns of **CCNU-1** soaked in aqueous solution with different pH for 24 h (a) and in different organic solvents for 24 h (b). Simulated spectrum was calculated from the single crystal data.

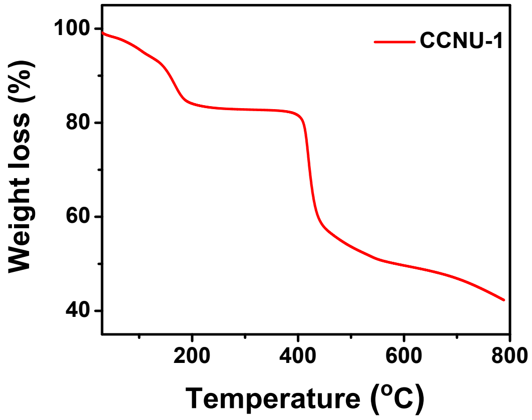


Fig. S2 TGA curve of **CCNU-1**.

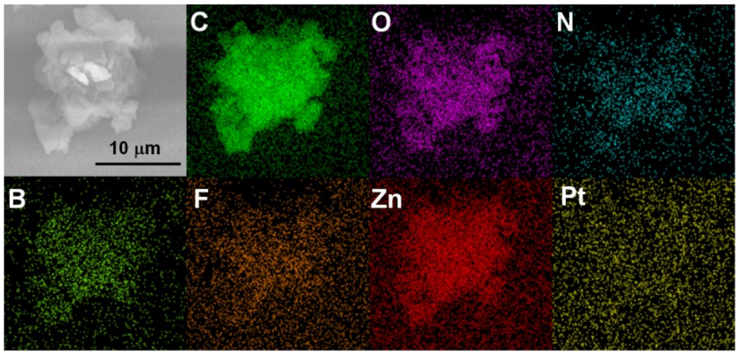


Fig. S3 SEM-EDS elemental mapping pattern for **Pt/CCNU-1**.

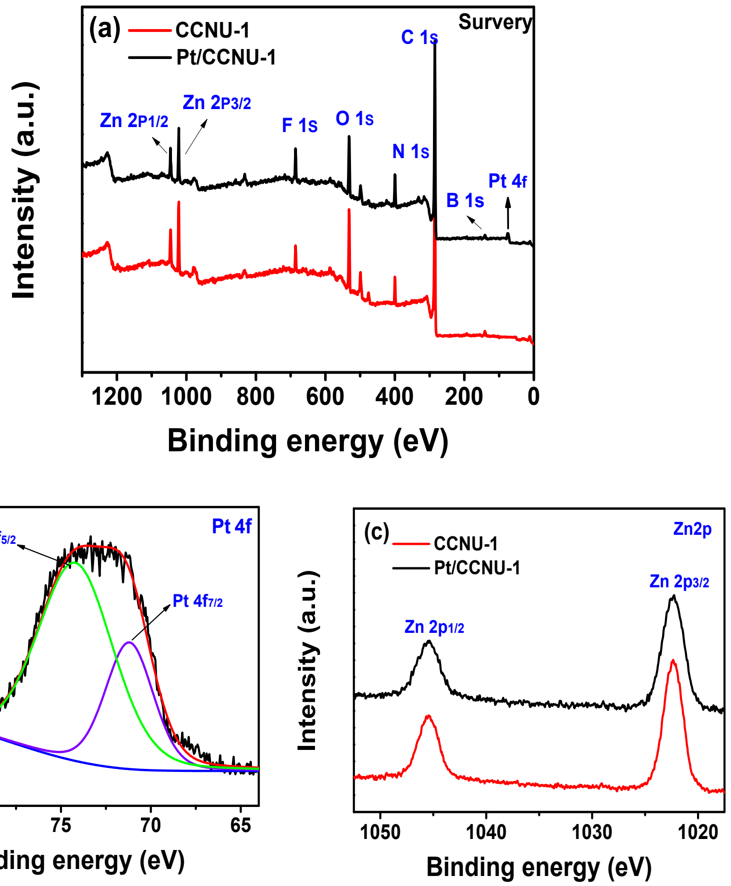


Fig. S4 XPS spectra of **CCNU-1** and **Pt/CCNU-1**: (a) survey spectrum and high-resolution (b) Pt 4f, (c) Zn 2p spectra.

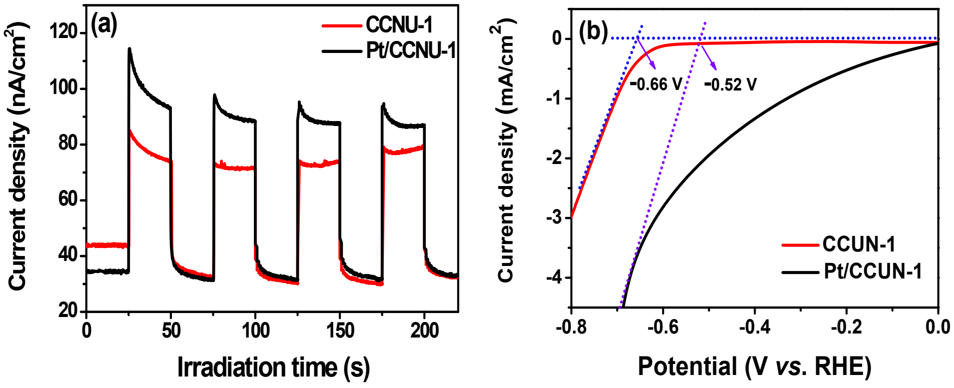


Fig. S5 Transient photocurrent-time profiles (a) and linear sweep voltammetry curves (b) for **CCNU-1** and **Pt/CCNU-1** in 0.4 M Na_2SO_4 aqueous solution.

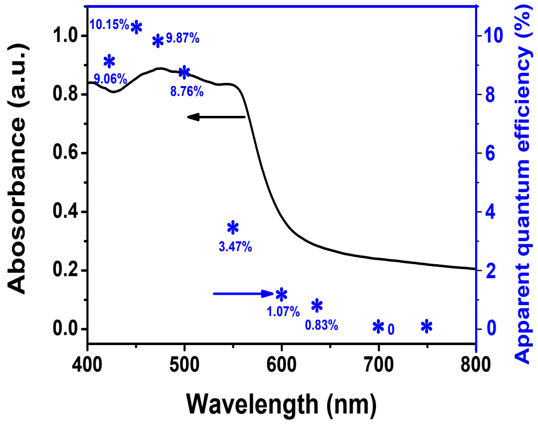


Fig. S6 Wavelength-dependent apparent quantum efficiency tests of H_2 evolution over **Pt/CCNU-1** (blue star), along with the UV–Vis absorption spectrum of **Pt/CCNU-1**.

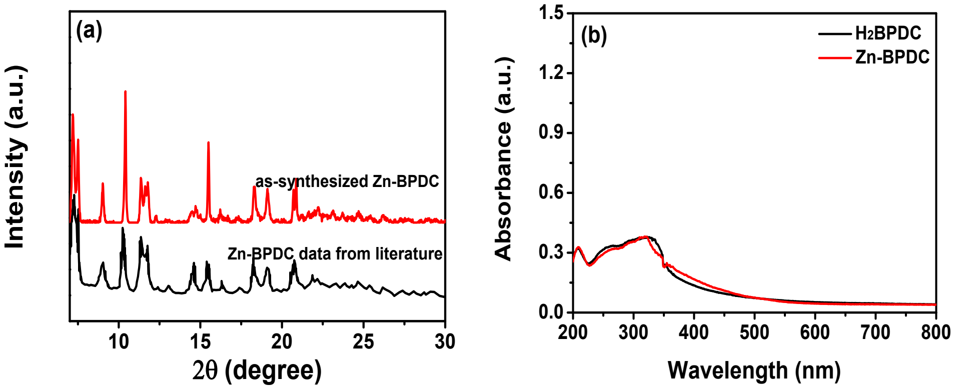


Fig. S7 (a) The PXRD profile of **Zn-BPDC** (reference 3), (b) UV/Vis Diffuse reflectance spectra of **H_2BPDC** and **Zn-BPDC**.

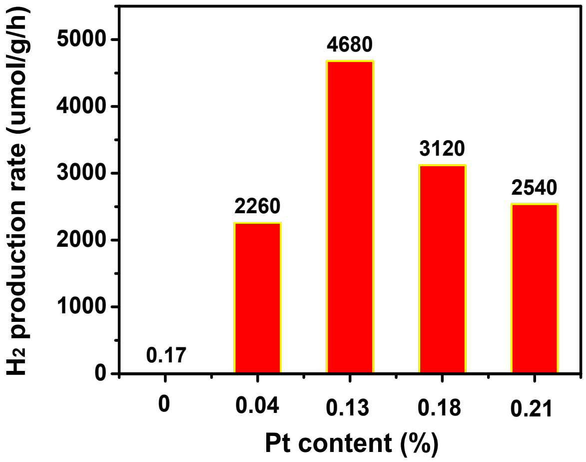


Fig. S8 Photocatalytic H_2 production of **Pt/CCNU-1** composites with variable Pt contents.

Samples with variable Pt contents (0.04, 0.13, 0.18 and 0.21 wt%) exhibit excellent H_2 production rate in comparison to pristine **CCNU-1**. Obviously, **Pt/CCNU-1** with 0.13 wt% content, which was prepared with 105 μL of 0.1 g·mL^{-1} H_2PtCl_6 aqueous solution, exhibits the maximum H_2 production rate of 4680 μmol·g^{-1}·h^{-1}.

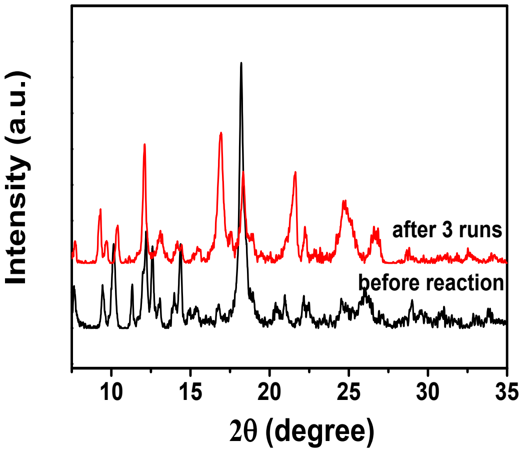


Fig. S9 The PXRD of **Pt/CCNU-1** before and after reaction.

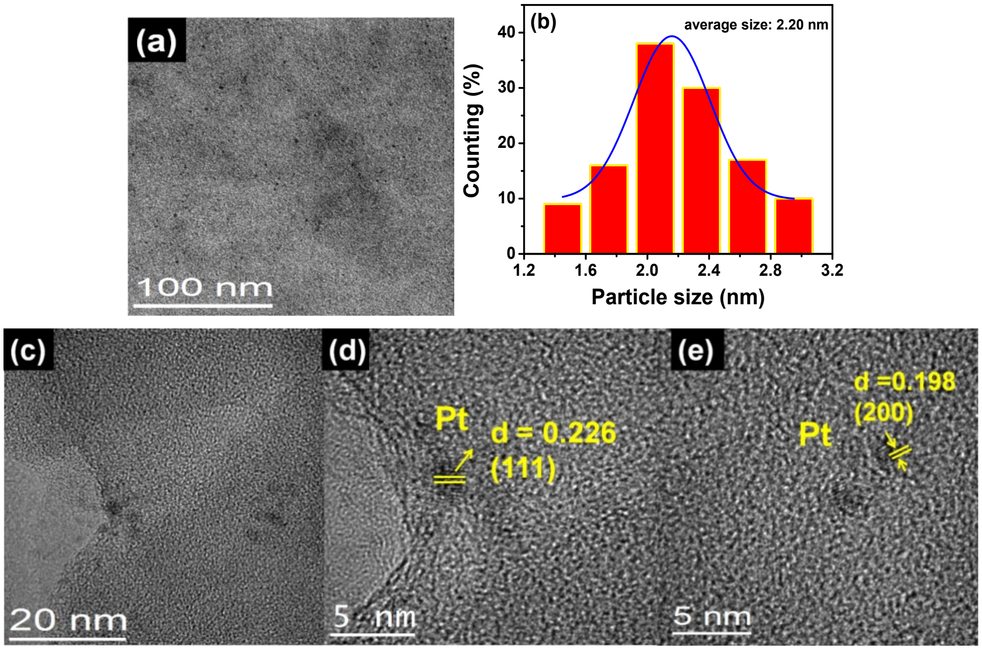


Fig. S10 (a-b) TEM images and statistical analysis of the size distribution of Pt NPs in **Pt/CCNU-1** after reaction and TEM and HRTEM images of **Pt/CCNU-1** after reaction (c-e).

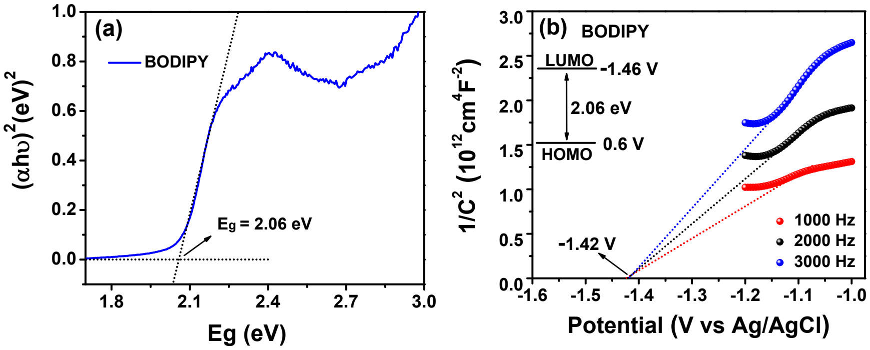


Fig. S11 (a) Tauc plot of BODIPY, (b) Mott-Schottky plots for BODIPY in a 0.4 M Na_2SO_4 aqueous solution, Inset: Energy diagram of the HOMO and LUMO levels**.**

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 K. Sugikawa, Y. Furukawa and K. Sada, *Chem. Mater.*, 2011, **23**, 3132.

4 G. M. Sheldrick, *WI*, 2001.

5 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.