Supporting information

Promoting H$_2$ generation of BiFeO$_3$ photocathode by a catalyst-sensitizer dyad linked with Sn(dipicolinate)$_2$

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Experimental section

Materials

Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, 98%), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, 99%), and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (F108) were purchased from Aladdin®. High-purity water (18.2 MΩ·cm-1) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments. Fluorine-doped tin oxide (FTO, NSG 10 Ω, 10 mm × 25 mm × 2.2 mm) substrates were purchased from a local foreign trade company and were ultrasonically cleaned in deionized water, acetone, and ethanol for 15 min, respectively. 4-Pinacolboryl-2,6-diacetylpyridine, and catalyst (C1) were synthesized according to the literature.[1] The starting material di-tert-butyl pyridine-2,6-dicarboxylate was purchased from Aladdin®. All other related reagents were commercially available and used as received. Organic solvents used during the experiment were analytical reagent grade and were of the highest available purity.

Physical Characterization Instruments

The morphology and transmission electron microscopy (TEM) images of all films were characterized by field emission scanning electron microscopy (HITACHI UHR FE-SEM SU5000, operated at 5 and 15 kV) and field emission transmission

electron microscope (JEM-F200, Japan), respectively. A Smart Lab 9KW diffractometer using Cu Kα radiation (Rigaku Corp., Japan) was used to detect X-ray diffraction (XRD) patterns. The absorption spectra of photocathodes were obtained by a solid UV-visible (UV-vis) spectrometer (Thermo Scientific Evolution 200). ^{1}H-NMR spectra were taken by a Bruker DRX-500 instrument at 298 K. Fourier transform infrared spectra (FT-IR) were measured by Nicolet 6700 Flex (Thermo Fisher™). The binding energy of relevant elements was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB™ Xi+).

The simulated solar light was provided by an XES-40S3-TT solar simulator (SAN-EI ELECTRIC CO., LTD) with an AM 1.5G filter (AAA spectral match), power intensity of 100 mW cm−2 was calibrated by an optical power meter with silicon photodiode (PM 100D, Thorlabs). The external quantum efficiency (IPCE) of electrodes was directly measured by the Zahner photoelectrochemical workstation (CIMPS-2). The wavelength scan range was from 365 to 630 nm.

Fabrication of BiFeO$_3$ photocathode

A solution was prepared by mixing 0.8 g of Bi(NO$_3$)$_3$·5H$_2$O, 0.6 g of Fe(NO$_3$)$_3$·9H$_2$O and 0.5 g of F-108 in 2 mL of 2-methoxyethanol.[2] The solutions were stirred at room temperature for 30 min until the powders were completely dissolved. 0.1 mL of ethanolamine and 1 mL of acetic anhydride were added to the solution and stirred for another 60 min. The solution was deposited onto FTO substrates by spin coating at 3000 rpm for 30 seconds. For pre-annealing, the thin films were placed onto a hot plate at 100 °C for 5 min before being transferred onto another hot plate at 350 °C for another 5 min. The as-deposited films were heated at 600 °C for 2 hours in the air (ramping rate = 5 °C/min) to form BiFeO$_3$ (BFO) electrodes.

Synthesis of PDI molecules

The PDI dye was synthesized according to the synthetic route in *Figture S1*. Anthra[2,1,9-def:6,5,10-def]diisoquinoline-1,3,8,10(2H,9H)-tetrone, 5-bromo-2,9-bis(2-ethylhexyl) (773 mg, 1 mmol), 4-pinacolboryl-2,6-diacetylpyridine (101 mg, 2.5 mmol), and Cs_2CO_3 (814 mg, 2.5 mmol), tetrakis(triphenylphosphine)palladium (115 mg, 0.1 mmol) were added to the solution of toluene/MeOH (10:1) (10 mL). The reaction was stirred for 12 h at 120°C under Ar atmosphere. After removed the solvents, the residues were washed by water and MeOH. The residues were dissolved in a mixed solvent of trifluoroacetate/CH_2Cl_2 (1:2, 6 mL) at room temperature, and stirred for 12 h. The fuchsia precipitated was collected as the desired product, which was washed with MeOH and dried in vacuum yielding red powder as the desired product (690.2 mg, yielding 73%). HRMS (MALDI, TOF) calculated for C54H48N4O12: 944.3269; found:944.3211. 1H-NMR (500 MHz, d4-trifluoroacetate) δ 9.10-8.99 (m, 6H), 8.46 (s, 2H), 7.99 (s, 2H), 4.22 (m, 4H), 1.92 (m, 2H), 1.37-1.25 (m, 17H), 0.90-0.80 (m,12H). FT-IR (u cm^{-1}): 2955, 1699, 1657, 1590, 1326.
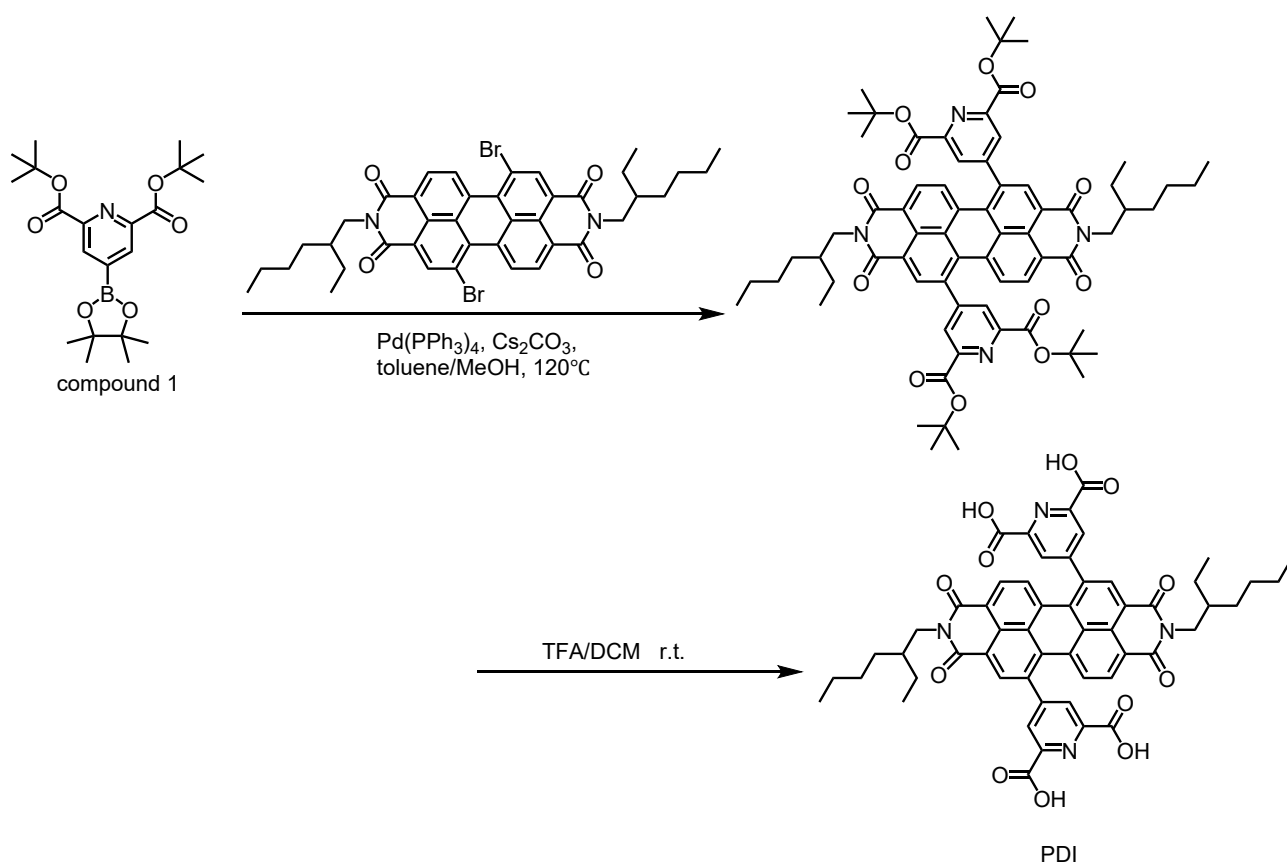

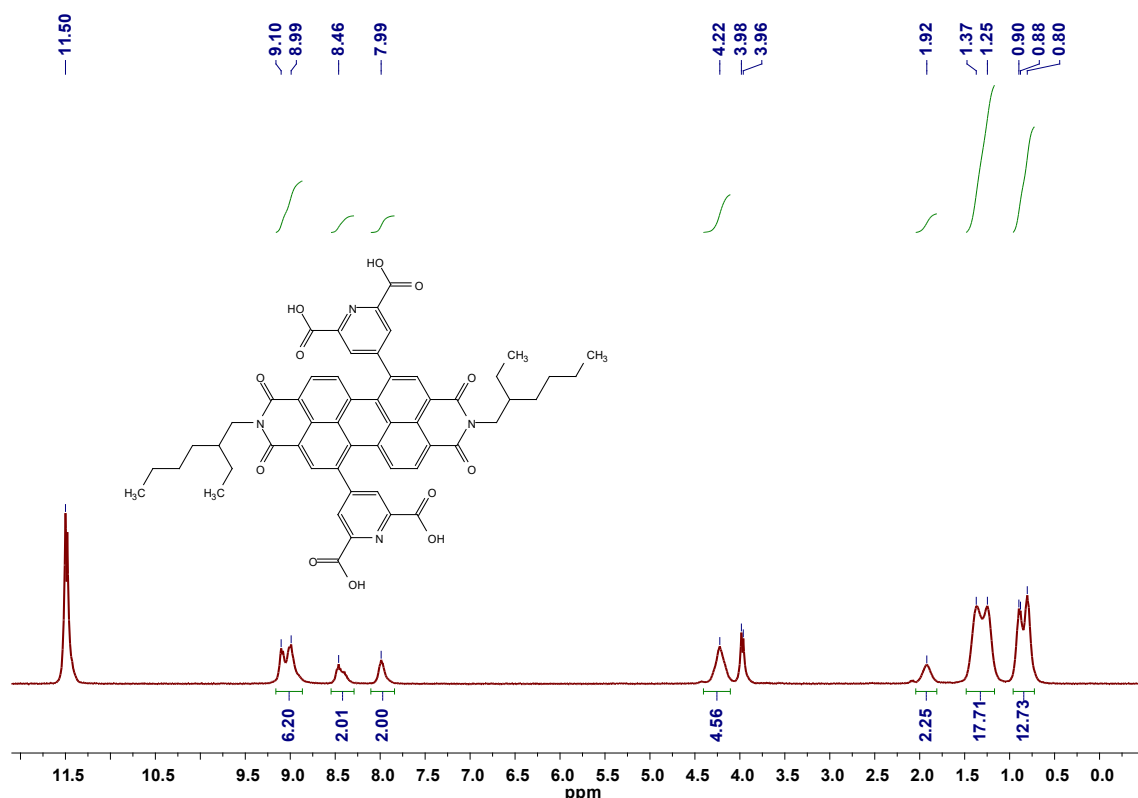**Figure S1.** Synthetic route of PDI.

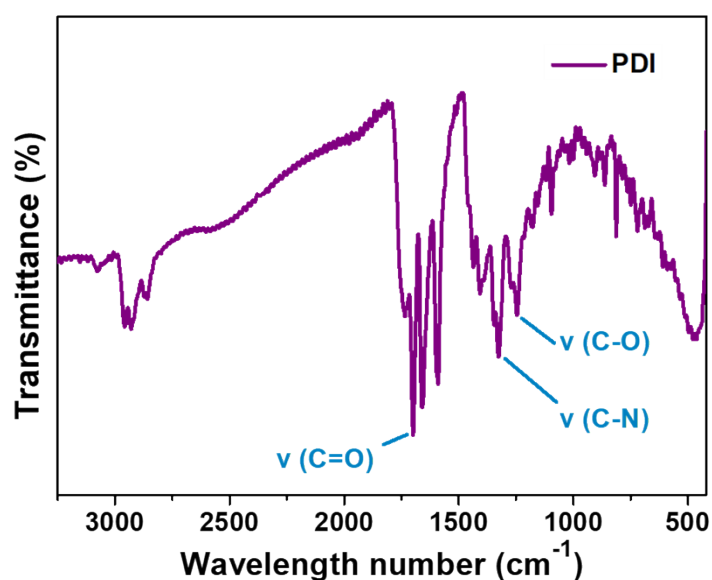**Figure S2.** ^{1}H-NMR spectrum of PDI.

Figure S3. Fourier transform infrared (FT-IR) spectra of PDI.

Preparation of photocathodes

PDI@BFO was fabricated via the adsorption method. BFO electrodes were sensitized by immersion in a PDI solution (1.5 mM in methanol/triethylamine 9/1) for 45 min to give PDI@BFO. The catalyst was immobilized on the PDI@BFO photocathodes using Sn^{4+} to link the pyridine-2,6-dicarboxylic group of the PDI and catalyst. After dipping the PDI@BFO electrodes into a solution of in methanol (10% in volume) and 2 mM $SnCl_4$ solution (methanol/triethylamine 100/1 in volume ratio

as the solvent), respectively, the resulting $(PDI+Sn^{4+})@BFO$ electrodes were subsequently submerged in a C1 solution (2 mM in methanol, containing triethylamine). Rinsing the electrons with MeOH and drying under N2, resulting (C1+PDI)@BFO.

C1@BFO was synthesized using the adsorption method. Specifically, BFO electrodes were immersed in a C1 solution (1.5 mM in methanol) for 45 minutes to produce C1@BFO. The electrodes were then rinsed with methanol and dried under a nitrogen atmosphere, resulting in the formation of C1@BFO. We have incorporated related discussions into the revised manuscript.

C1 and PDI amounts on the $BiFeO_3$ electrode

We've assessed the loading quantities of PDI and C1. The process involved submerging a (C1+PDI)@BFO film ($1 cm^2$ area) in a 5 mL methanol/water solution (5:1 v/v) containing NaOH, followed by ultrasonication for 30 minutes. This procedure desorbed molecules from the BFO film surface, allowing them to dissolve in the solution. The solution's absorbance was then analyzed using UV-vis spectroscopy. Utilizing the quantitative Lambert-Beer law, we determined the loading amount of PDI on the BFO film's surface to be 1.89×10^{-8} mol/cm^2. The loading quantity of C1 was ascertained through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), resulting in a value of 1.34×10^{-8} mol/cm^2.

PEC Measurements

The photocurrent densities were evaluated in a typical three-electrode cell with an Ag/AgCl reference electrode and a Pt mesh counter electrode. The simulated solar light of 100 mW cm^{-2} was obtained by an Oriel LCS-100 solar simulator (Newport) with an AM 1.5G filter. A 0.1 M Na_2SO_4 solution was used as the electrolyte. All the potential values were calculated to a reversible hydrogen

electrode (RHE) according to $E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + E_{(Ag/AgCl\ vs\ RHE)}$, where $E_{(Ag/AgCl\ vs\ RHE)}$ is 0.196 V.

The Faradaic efficiency (FE) of hydrogen evolution could be expressed by the following equation.

$$FE(\%) = \frac{2eN_A n_{H_2}}{Q} \times 100\%$$

equation S1

Where e is the elementary charge, N_A is the Avogadro constant, n_{H_2} is the amount of hydrogen determined by gas chromatography, and Q is the integrated charge passed through the photoelectrodes in 60 minutes. The cell was maintained at room temperature.

The Applied Bias Photon-to-current Efficiency (ABPE) of the photocathodes used in the test was calculated according to the following equation by converting the LSV curves.

$$ABPE(\%) = \frac{(0 - V_{RHE}) * (j_{light} - j_{dark})}{P_{light}} \times 100\%$$

equation S2

Where V_{RHE} is the applied potential versus RHE (V), j_{light} and j_{dark} are the measured photocurrent and dark current respectively, P_{light} (100 mW cm^{-2}) is the power density of AM 1.5G.

In order to quantitatively determine charge recombination behavior, a normalized parameter (D) was calculated using the following formula:

$$D = (I_t - I_{st})/(I_{in} - I_{st})$$

equation S3

where I_t, I_{st}, and I_{in} are the time-dependent, steady-state, and initial photocurrent, respectively. In $D = -1$ was defined as a transient time constant (T), which embodies the behavior and lifetime of charge carriers.[3]
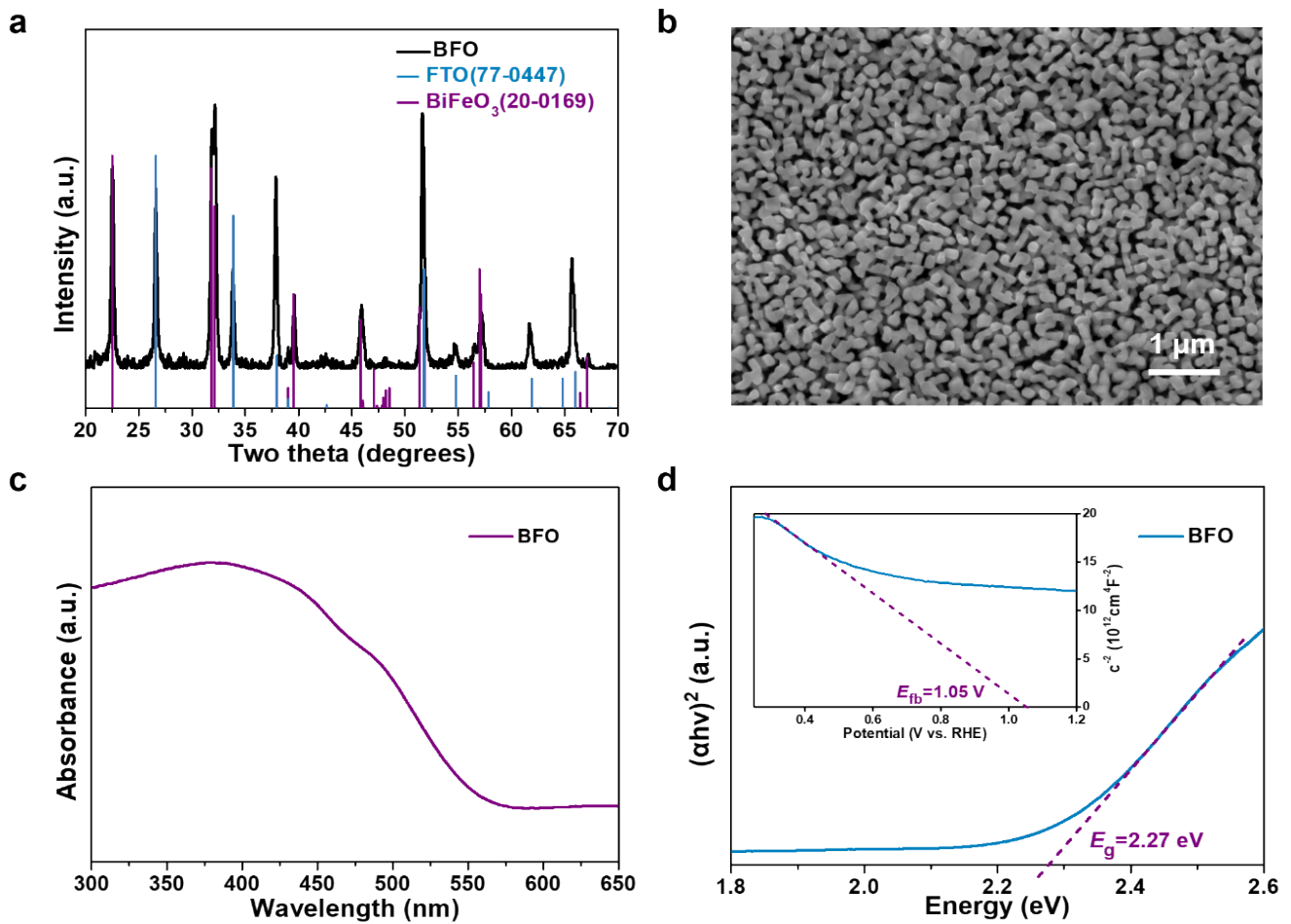
Figure S4. (a) XRD patterns of BFO. (b) SEM image of BFO. (c) UV–vis absorption spectrum of BFO. (d) Mott Schottky plots of BFO, measured in 0.1 M Na_2SO_4 solution, and the inset shows the corresponding Tauc plot.
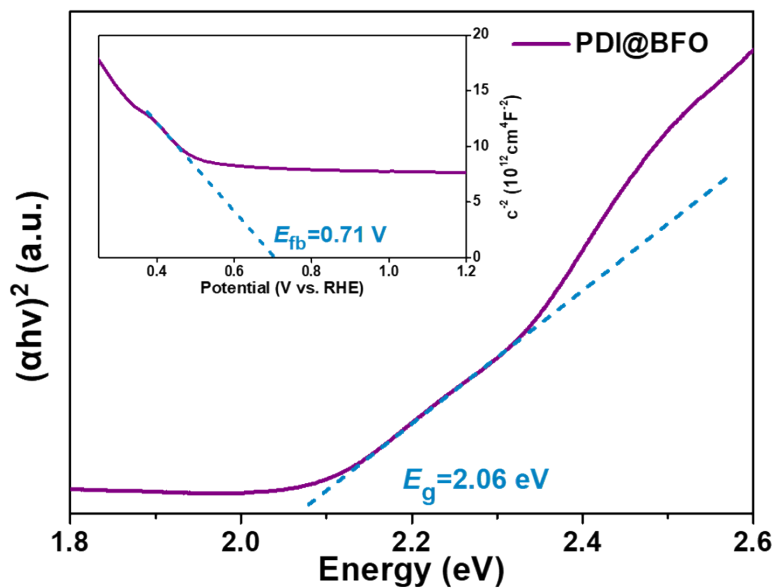

Figure S5. Mott Schottky plot of PDI@BFO, measured in 0.1 M Na_2SO_4 solution, and the inset shows the corresponding Tauc plot.
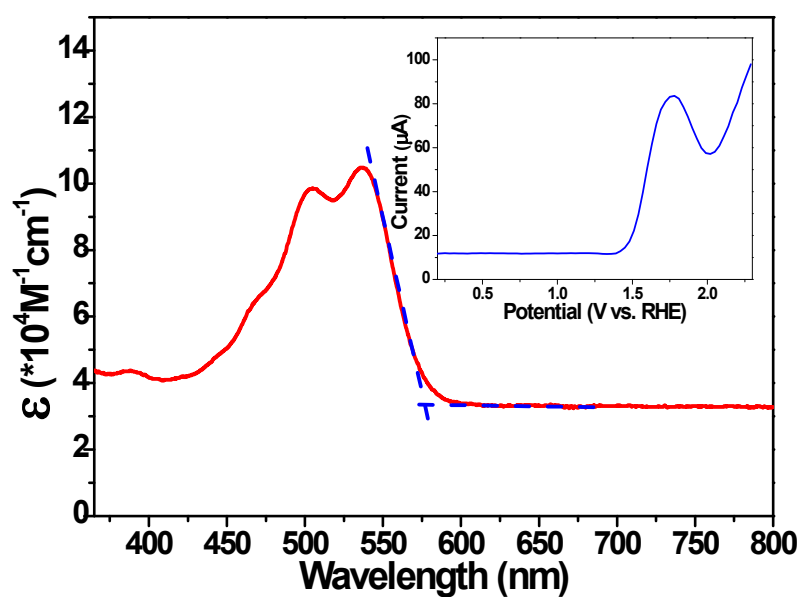
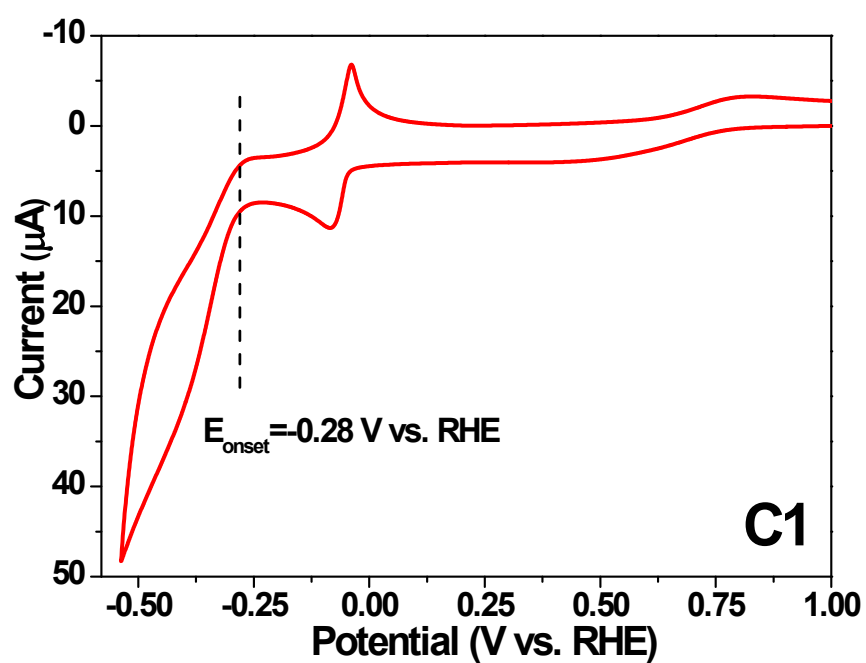**Figure S6.** (a) UV-vis absorption spectrum of PDI, and differential pulse voltammetry spectra (DPV, the insert).

Figure S7. The *J-V* plot to test the H$_2$ generation potential of C1 catalyst.
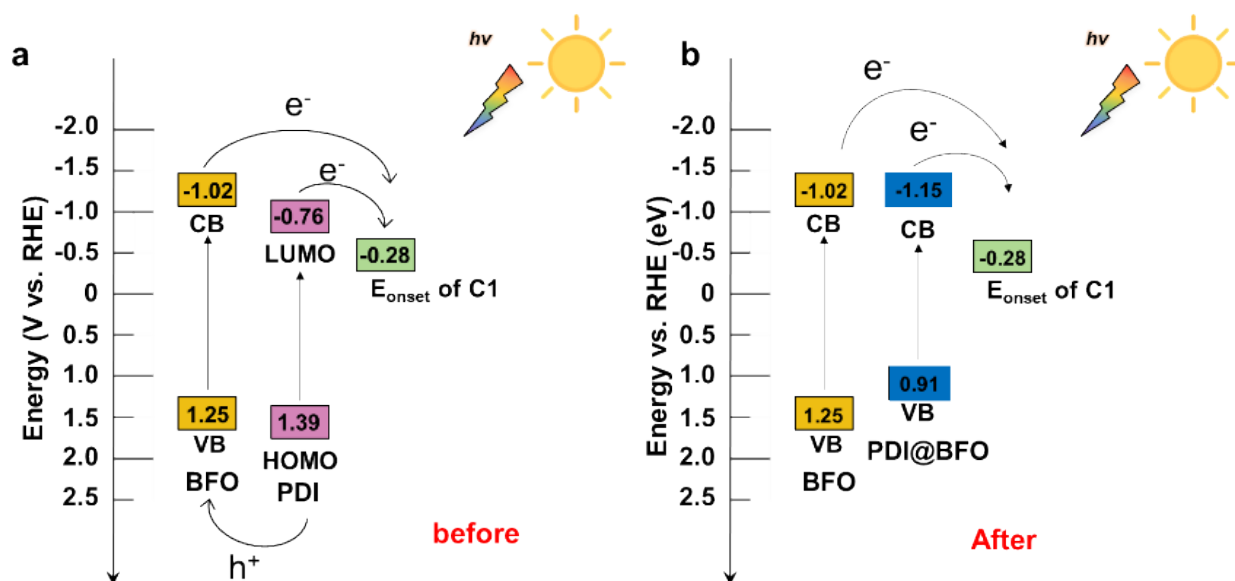
Figure S8. Energy diagram of (a) BFO, PDI, C1 before dye-sensitization, and (b) after dye-sensitization.
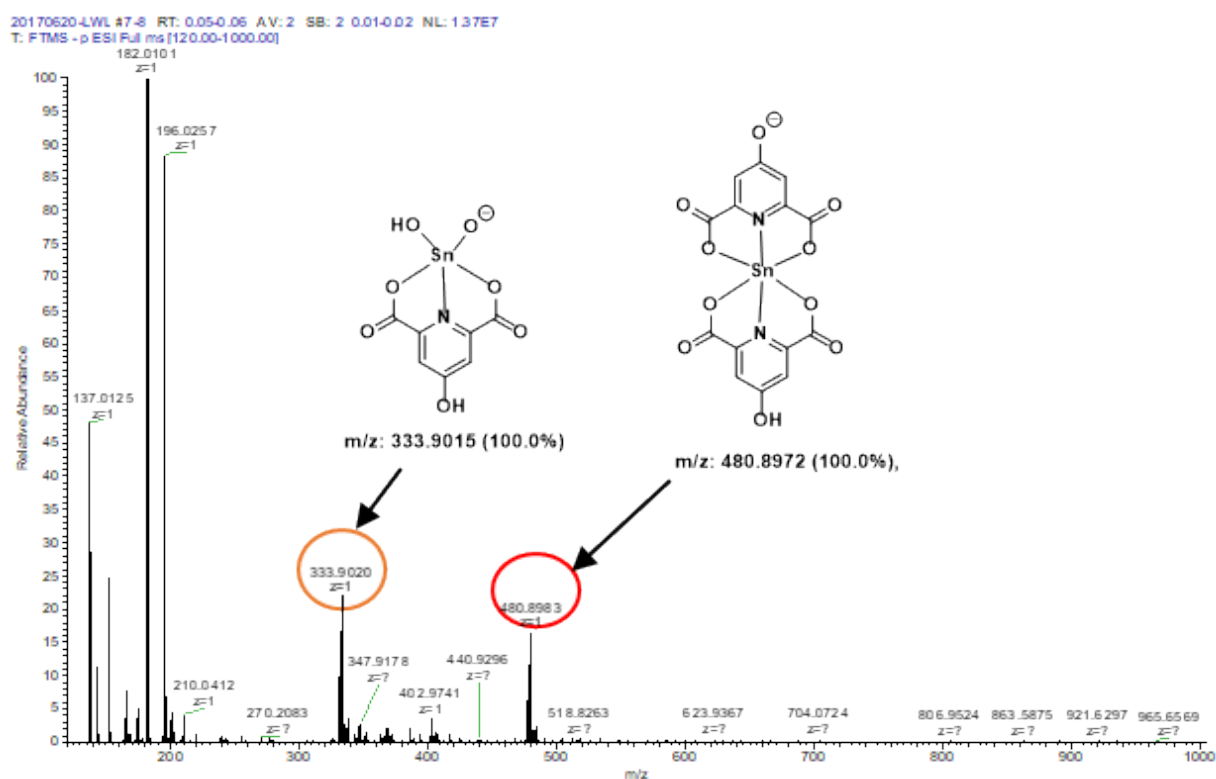
Figure S9. Mass spectrometry (MS) of the mixture of 4-hydroxypyridine-2,6-dicarboxylic acid and SnCl$_4$ in the solvent of methanol/triethylamine.
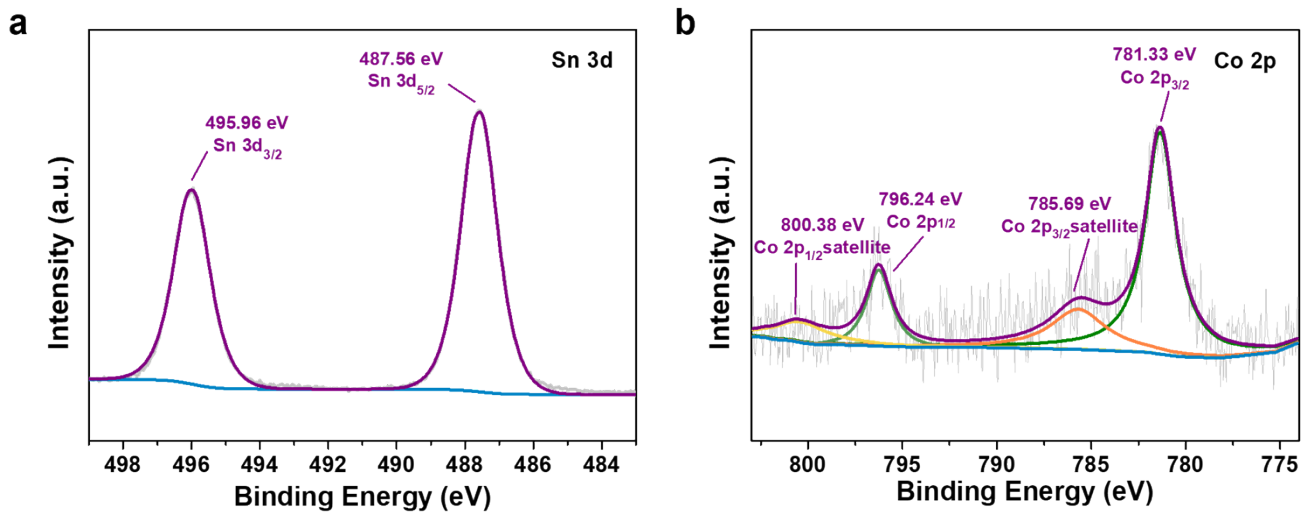
Figure S10. (a) X-ray photoelectron spectroscopy (XPS) survey spectrum specifically focused on Sn 3d orbitals. (b) Survey spectrum specifically focused on Co 2p orbitals.
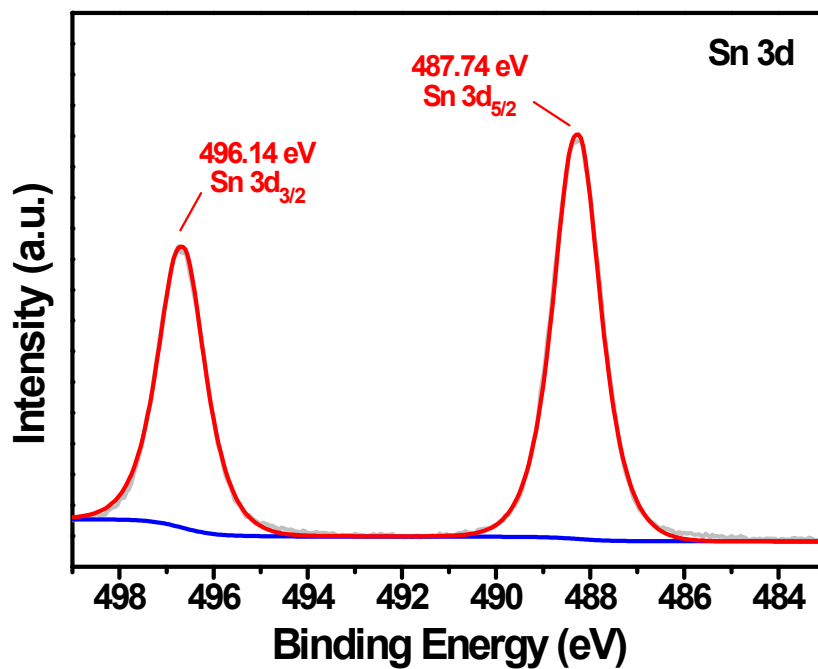

Figure S11. X-ray photoelectron spectroscopy (XPS) survey spectrum specifically focused on Sn 3d orbitals of (C1+PDI)@BFO photocathode after testing.
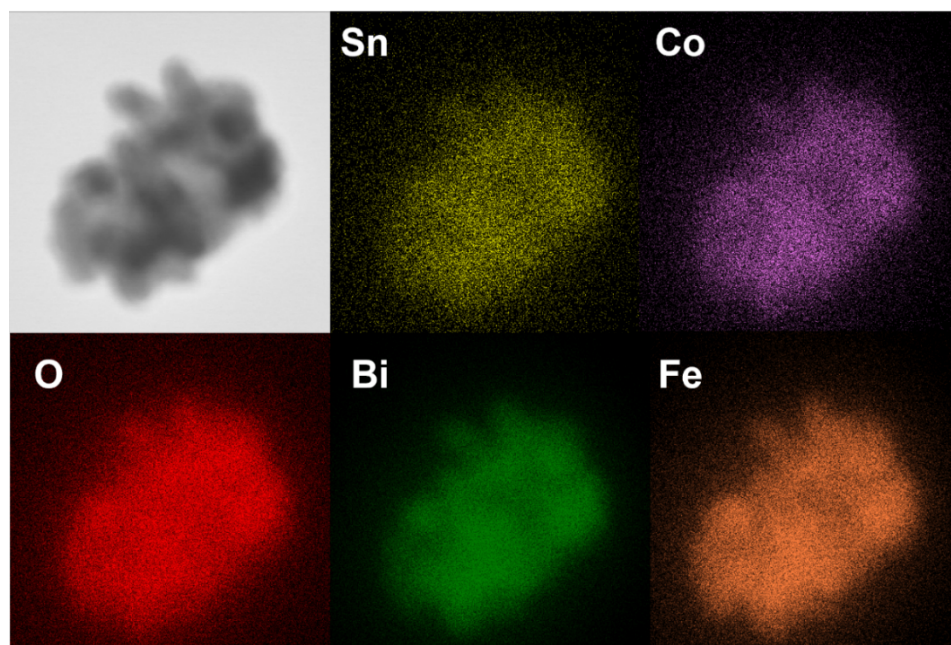
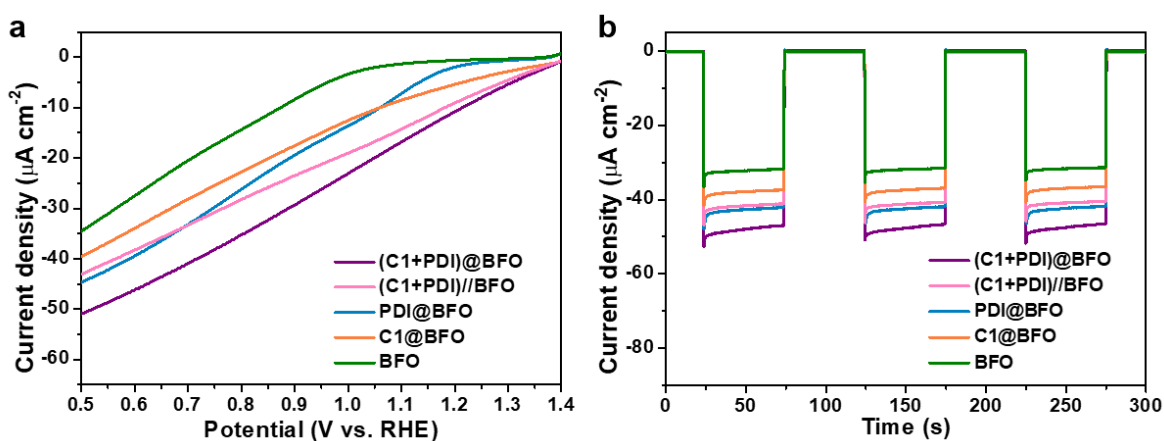**Figure S12.** The EDS elemental mapping images of (C1+PDI)@BFO.

Figure S13. (a) *I-V* plots and (b) *I-t* curves recorded at the potential of 0.5 V vs. RHE.

The PDI and C1 co-immobilized BFO photocathode (denoted as (C1+PDI)//BFO) was prepared by co-adsorbing method and the corresponding photoelectrochemical performance was measured. As shown in **Fig. S13**, the BFO photocathode with co-immobilized PDI and C1 exhibits a photocurrent comparable to that of PDI@BFO and demonstrated smaller photoelectrochemical performance compared to the Sn bridged (C1+PDI)@BFO photocathode under identical conditions.
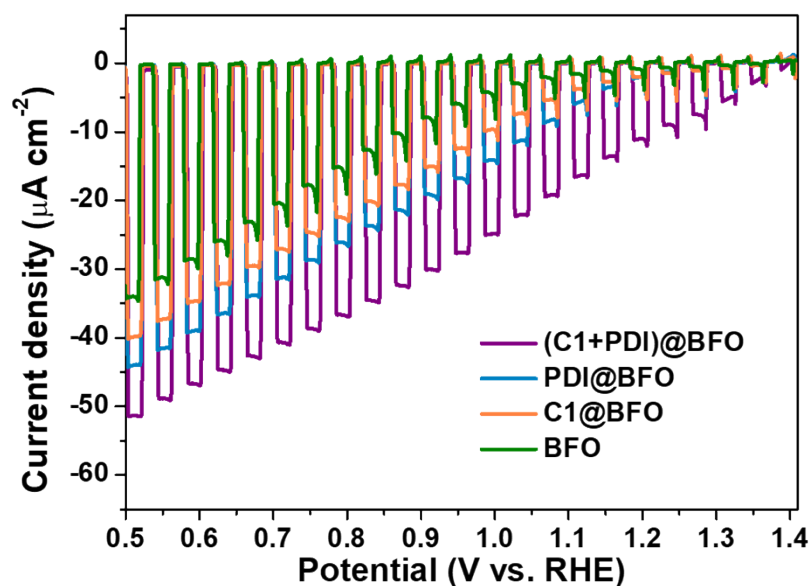
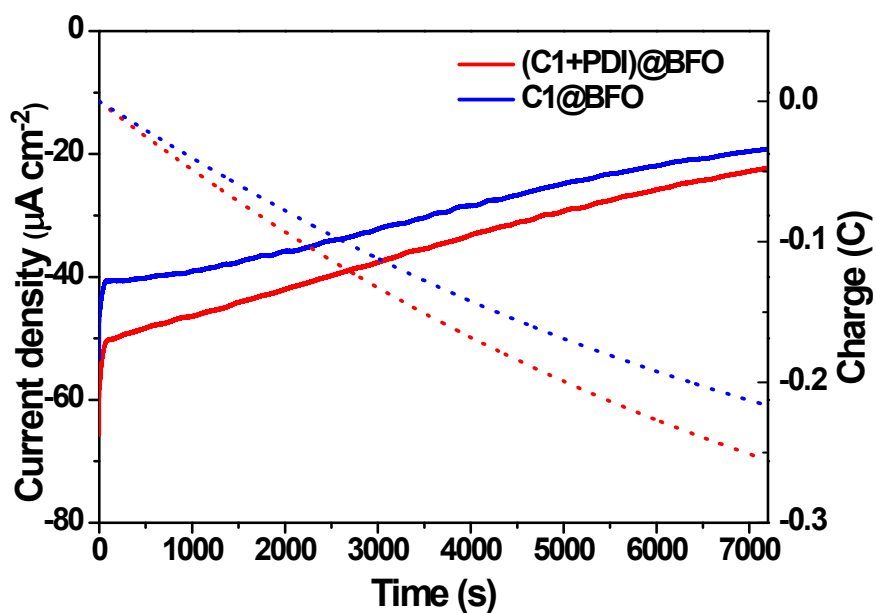**Figure S14.** The LSV response of the photocathodes under chopped illumination.

Figure S15. The controlled potential photo-electrolysis trace for 2 h of (C1+PDI)@BFO and C1@BFO held at 0.5V vs. RHE in Ar-saturated 0.1 M Na_2SO_4 solution under simulated solar light.

Table S1. The Faradaic efficiency of different photocathodes

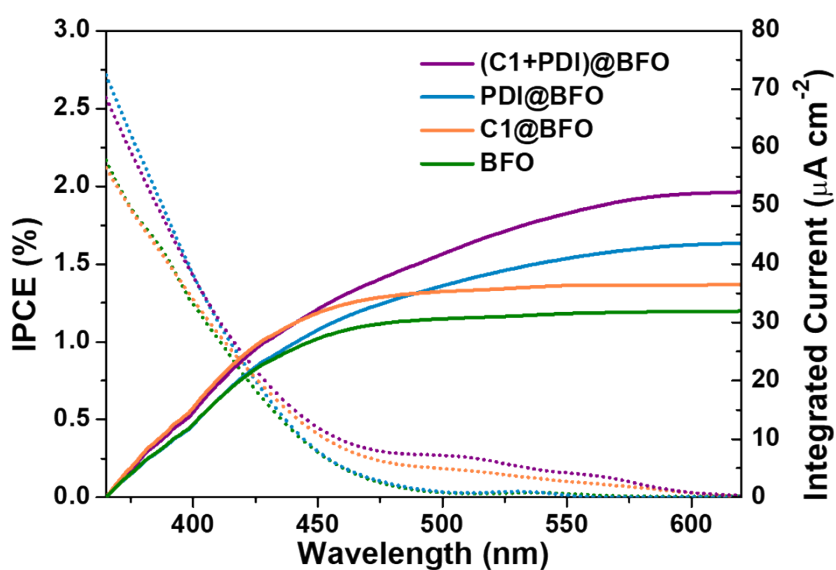|	C1 loading after testing (nmol cm^{-2})	Charge (mC cm^{-2})	H_2 production (μmol cm^{-2})	FE (%)
C1@BFO	5.8	217	0.275	53.4
(C1+PDI)@BFO	5.4	256	0.560	77.6

Figure S16 Incident photon-to-current efficiency (IPCE) curves under a monochromatic light at 0.5 V *vs.* RHE across varying wavelengths within a 0.1 M Na_2SO_4 solution.
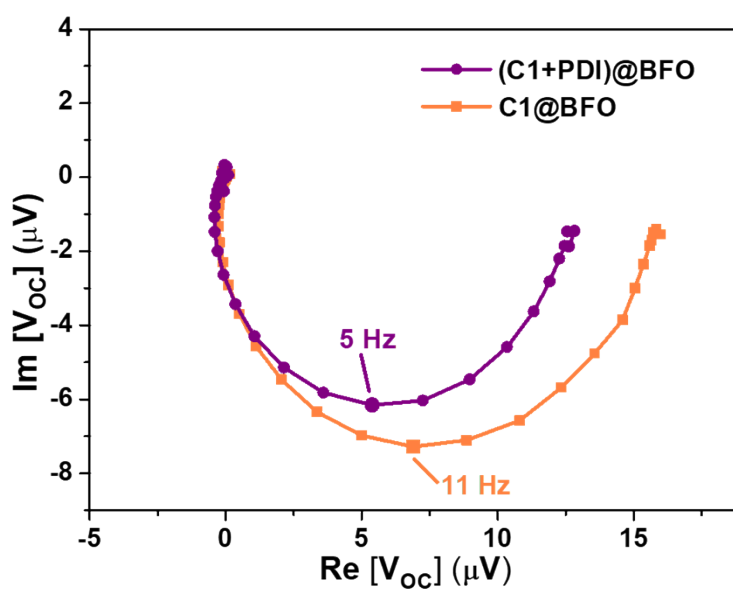

Figure S17 IMVS spectra of C1@BFO and (C1+PDI)@BFO photocathodes.

References

1.   C. Nie, W. Ni, L. Gong, J. Jiang, J. Wang and M. Wang, *J. Mater. Chem. A*, **2019**, *7*, 27432-27440.

2.   P. Yilmaz, D. Yeo, H. Chang, L. Loh and S. Dunn, *Nanotechnology*, **2016**, *27*, 345402.

3.   C. Liu, F. Li, L. Wang, Z. Li, Y. Zhao, Y. Li, W. Li, Z. Zhao, K. Fan, F. Li and L. Sun, *Fundamental Research*, **2022**, DOI: 10.1016/j.fmre.2022.03.013.