Supporting Information

Dye-sensitized $LaFeO_3$ Photocathode for Solar-Driven H_2 Generation

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Experimental details

Materials

Lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99.9%), iron nitrate nonahydrate ($Fe(NO_3)_3\ 9H_2O$, 99%), Ethyl cellulose (18-22 mPa.s), were purchased from Aladdin®. High purity water (18.2 $M\Omega \cdot cm^{-1}$) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments. Fluorine-doped tin oxide (FTO, NSG 10Ω 10 mm × 25 mm × 1.1 mm) substrates were purchased from local foreign trade company, before using, the FTO substrates were ultrasonically cleaned in deionized water, acetone and ethanol for

15 min, respectively. The Dubois-type $[Ni(P_2N_2)_2]^{2+}$ (NiP) catalyst was synthesized according to literatures.[1,2] The starting materials, **S1** [2,6-Pyridinedicarboxylic acid, 4-chloro-, 2,6-bis(1,1-dimethylethyl) ester], and **S2** [5,5'-(((4-bromophenyl)azanediyl)bis(4,1-phenylene))bis(thiophene-2-carbaldehyde)], were synthesized according to reported procedures.[3,4] All other related reagents were commercially available and used as received. Organic solvents were analytical reagent grade and used without further purification. All synthetic reactions were carried out under N_2 atmosphere with standard Schlenk techniques

Physical characterization methods

The morphology and composition of the fabricated films were characterized by field emission scan electron microscopy (FE-SEM, Carl Zeiss Supra 55, operated at 10 kV). X-ray diffraction (XRD) was measured by SmartLab (Rigaku™). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. ^{1}H-NMR spectra were obtained on a Bruker DRX-500 instrument at 298 K. High resolution mass spectrometry (HRMS) were obtained on MALDI micro MX instrument (Waters™). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was measured by Optima 2000 DV (PerkinElmer™).

Photoelectrochemical Measurements.

PEC measurements were carried out on a CHI 660e potentiostat (Shanghai Chenhua Instrument Co., LTD). All tests were performed at 25 °C in a three-electrode system. Linear sweep voltammetry curves were obtained at a scan rate of 5 mV s^{-1} with a Pt mesh as counter electrode, a HgO/Hg (1.0 M KOH) as the reference electrode, and a 1.0 M KOH solution (pH 13.6) saturated with O_2 as the electrolyte to evaluate the O_2 reduction activities of the electrode films. The recorded potential was converted against RHE using the Nernst equation ($E_{RHE} = E_{HgO/Hg} + 0.098$ V+ 0.059 pH). For H_2 generation, linear sweep voltammetry curves were obtained at a scan rate of 5 mV s^{-1} with a Pt mesh as counter electrode, Ag/AgCl (saturated KCl) as the reference electrode and a 0.5 M Na_2SO_4 solution (pH = 3) purged with Ar as the electrolyte. The recorded potential was converted against RHE using the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.194$ V + 0.059 pH). The simulated solar illumination was obtained by passing light from a 300 W Xenon arc lamp equipped with an AM 1.5G filter, and the power intensity of the incident light was calibrated to 100 mW cm^{-2} by a Newport OMM-6810B photometer (OMH-6742B, Silicon detector, 350-1100nm).

IPCE Measurements

The incident photon to current efficiency (IPCE) of each wavelength was determined using the illumination from a 300 W Xe arc lamp. The monochromatic light was produced using a monochromator (Sofn instruments). The light intensity (P_λ) at each wavelength (λ) was determined by Newport OMM-6810B photometer (OMH-6742B, Silicon detector, 350-1100 nm), J_{light} and J_{dark} are the measured photocurrent and dark current respectively, and the IPCE values were calculated using the following equation.

$$IPCE(\%) = \frac{1240 \times \left(J_{light} - J_{dark} \right)}{\lambda \times P_\lambda} \times 100\%$$

Synthesis

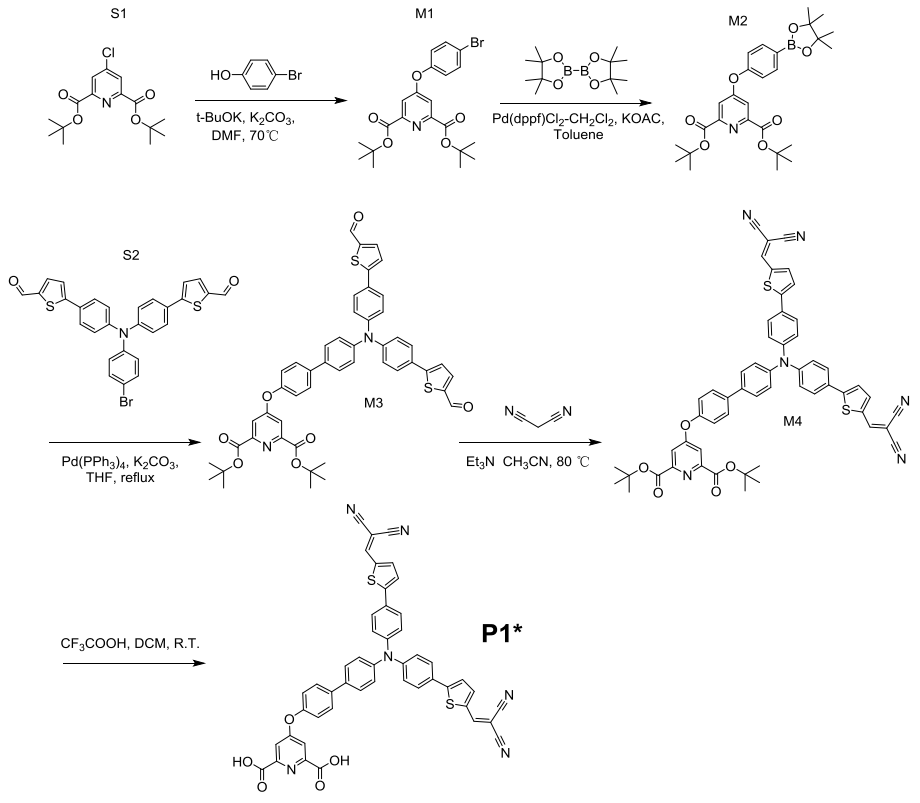

Figure S1. Synthetic routes of P1*

M1. A two-necked flask, 4-Bromophenol (520 mg, 3.0 mmol), **S1** (626 mg, 2.0 mmol), t-BuOK (336 mg, 3 mmol) and K_2CO_3 (140 mg, 1mmol) were dissolved in 11 mL DMF and the mixture was heated at 70℃ for 12 h under N_2 protection. After removal of solvent by a rotary evaporator, the residues were dispersed in brine, extracted with ethyl acetate 3 times, combined the organic phase and washed with brine. After dried with $MgSO_4$ and evaporated the solvent, yielding 700mg of **M1** (78%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.70 (s, 2H), 7.58 (d, *j*=8, 2H); 7.01 (d, *j*=8, 2H), 1.62 (s, 18H).

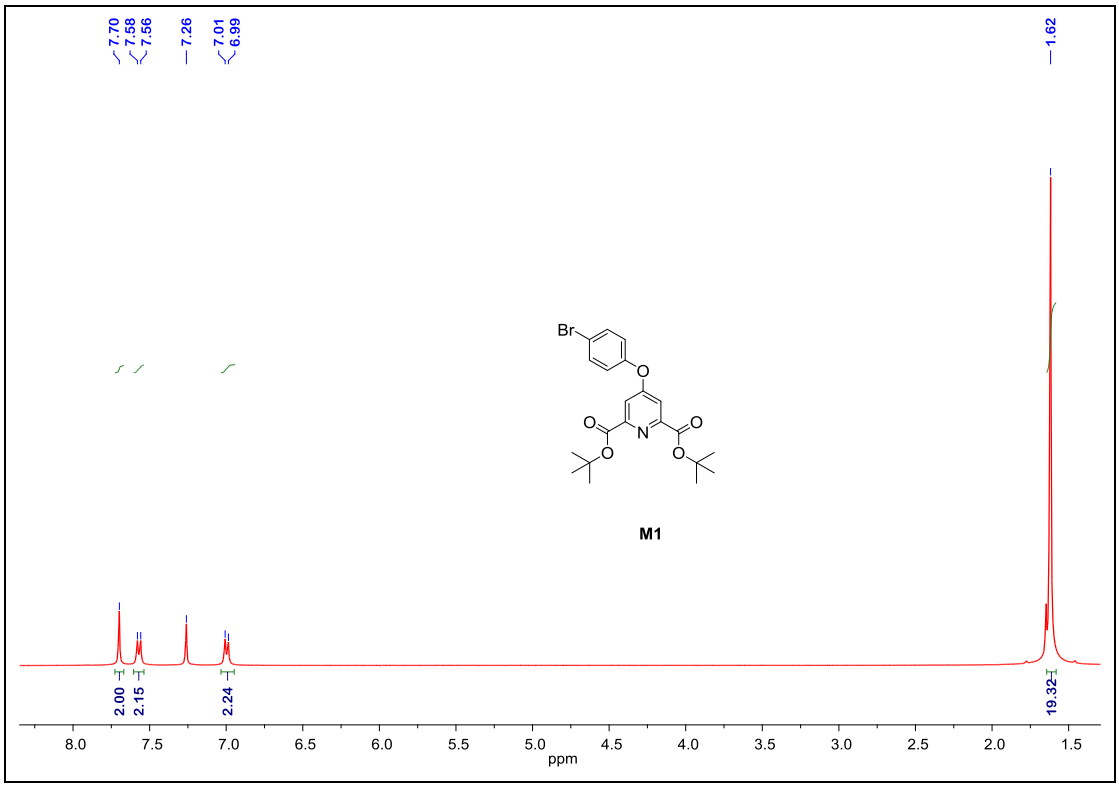

Figure S2. ^{1}H-NMR spectrum of compound **M1**

M2. Pd(dppf)Cl_2-CH_2Cl_2 (14 mg, 0.02 mmol), **M1** (450 mg, 1.0 mmol), bis(pinacolato)diboron (304.7 mg, 1.2 mmol) and CH_3COOK (196.3 mg, 2.0 mmol) were dissolved in 10 mL toluene. The reaction

mixture was heated at 80℃ for 2 hours in a microwave reactor (Biotage Initiator+). After removal of solvent by a rotary evaporator, the residues were purified by chromatography using a silica-gel column with CH_2Cl_2:Methanol (10:1) as a eluent, yielding 363 mg (73%) of **M2** as the desired product. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.90 (d, *j*=8, 2H), 7.71 (s, 2H); 7.09 (d, *j*=8, 2H), 1.61 (s, 18H), 1.36 (s, 12H).

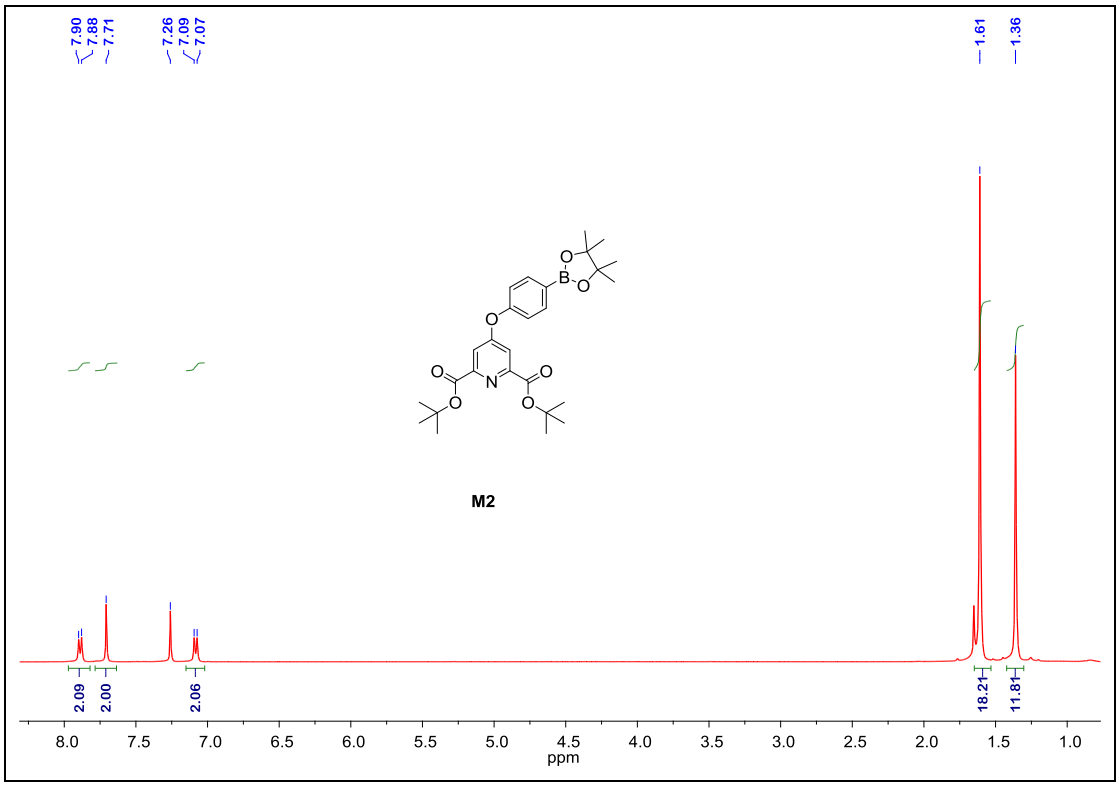

Figure S3. ^{1}H-NMR spectrum of compound **M2**

M3. $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), **M2** (100 mg, 0.2 mmol), **S2** (100 mg, 0.18 mmol) K_2CO_3 (138 mg, 1.0 mmol) and 0.5 mL H_2O were added in 15 mL of THF, the reaction mixture was refluxed for 12 h. After removal of solvent by a rotary evaporator, the residues were purified by chromatography using a silica-gel column with

CH_2Cl_2 as a eluent, 43 mg (~25%) of **M3** was isolated. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.88(s, 2H), 7.77 (s, 2H); 7.74 (d, *j*=4, 2H), 7.66 (d, *j*=8, 2H), 7.62 (d, *j*=8, 4H), 7.57 (d, *j*=13, 2H), 7.36 (d, *j*=4, 2H), 7.24 (m, 8H), 1.63 (s, 12H).

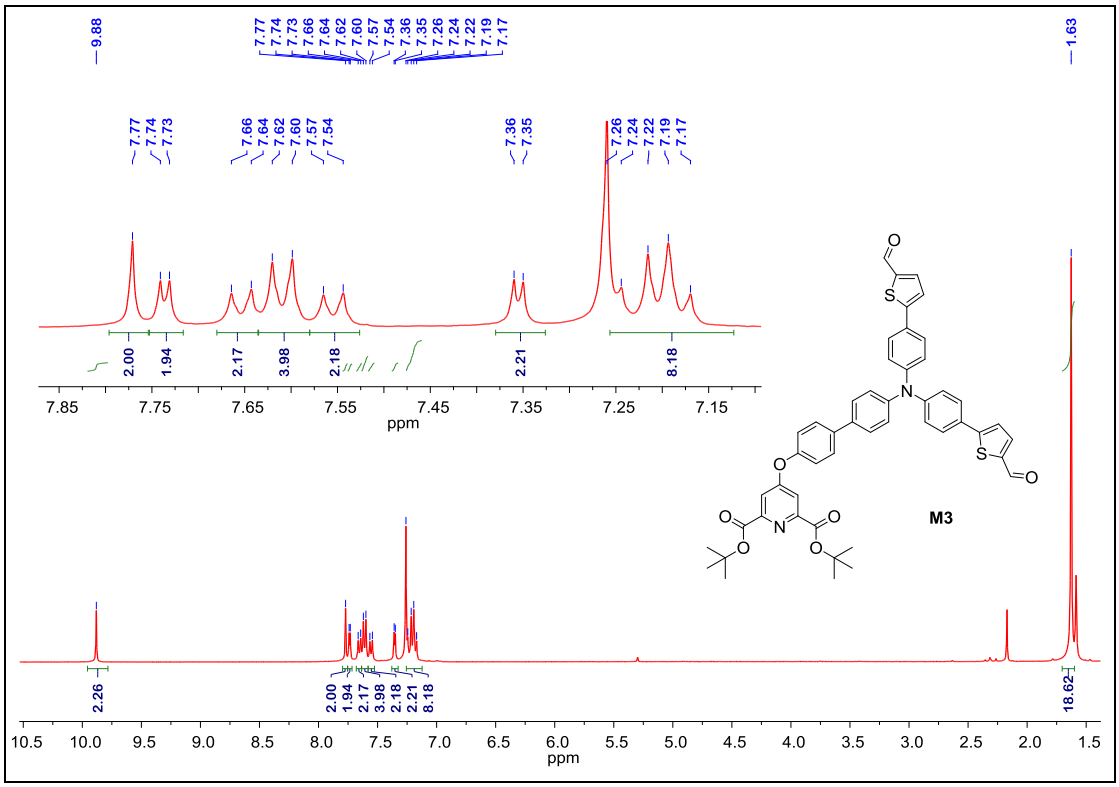

Figure S4. ^{1}H-NMR spectrum of compound **M3**

M4. **M3** (164 mg, 0.2 mmol), cyanoacetonitrile (164 mg, 2.5 mmol) and Et_3N (30 μL) were added in 15 mL of CH_3CN, the reaction mixture was heated to 80℃ for 12 h. After removal of solvent by a rotary evaporator, the residues were purified by chromatography using a silica-gel column with CH_2Cl_2:Methanol (100/1) as the eluent, 124 mg (68%) of **M4** was isolated. ^{1}H-NMR (400 MHz, CD_2Cl_2): 7.83 (s, 2H); 7.73 (m, 4H), 7.66 (m, 8H), 7.44 (d, *j*=4, 2H), 7.28 (d, *j*=8,

2H), 7.23 (m, 6H), 1.61 (s, 12H).

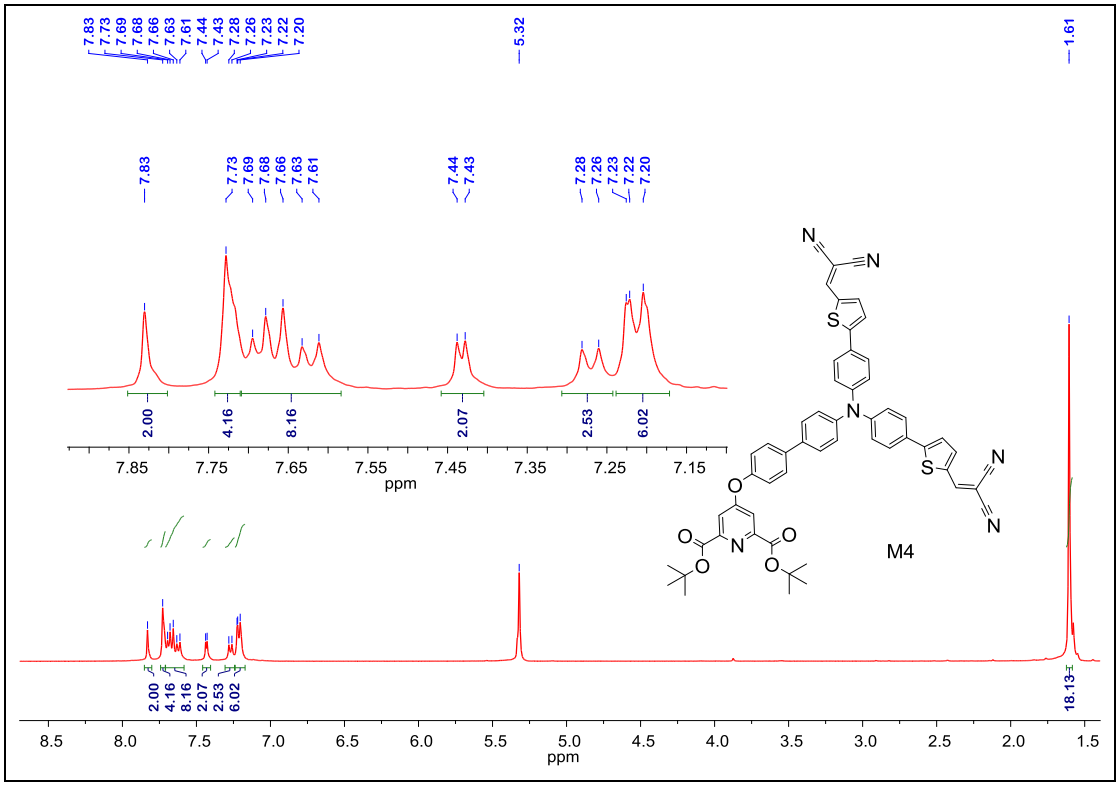

Figure S5. ^{1}H-NMR spectrum of compound **M4**

P1*: M4 (140 mg, 0.15 mmol) was dissolved in 4 mL CH_2Cl_2, after that, 2 mL Trifluoroacetate was added to the reaction mixture. The reaction was kept at room temperature for 5 h. After removed the solvents, the residues were recrystallized in acetone and petroleum ether, 110 mg (~90%) of **P1*** was isolated. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.96 (s, 2H); 7.83 (s, 2H), 7.73 (m, 4H), 7.64 (m, 6H), 7.44 (d, *j* = 5, 2H), 7.25 (m, 6H). FT-IR (υ cm^{-1}): 3411 (υ_{O-H}), 2221 ($\upsilon_{C\equiv N}$), 1729 ($\upsilon_{C=O}$), 1568 ($\upsilon_{C=C}$), 1488 ($\upsilon_{C=C}$), 1427 (υ_{CO2^-}), 1068(υ_{ring}), 804(υ_{ring}). HRMS $[M+H]^+$,calc. 819.1484, found 819.1505.

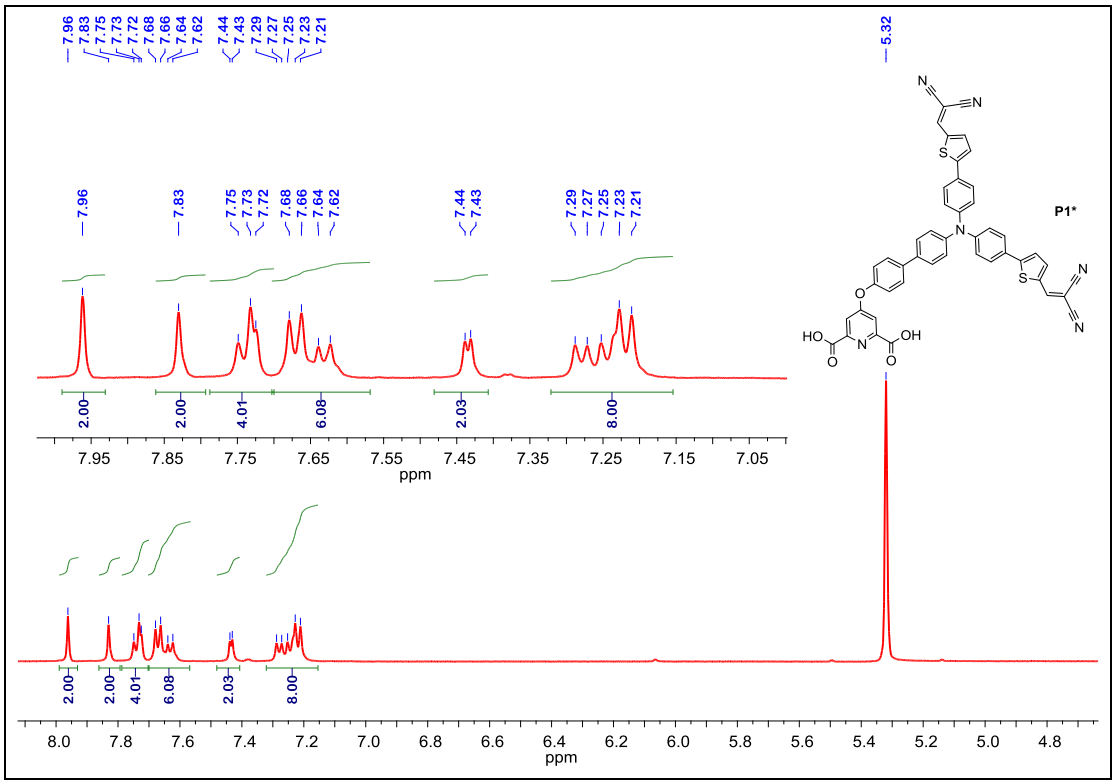

Figure S6. ^{1}H-NMR spectrum of compound **P1***

$LaFeO_3$ Film Preparation.

Mesoporous $LaFeO_3$ films were prepared by template spray pyrolysis method (the procedure was shown in ***Fig. 1***). In detail, FTO glasses were put on a hot plate at room temperature, subsequently, the temperature was slowly raised to 300℃. A solution containing ethanol (200 mL), $Fe(NO_3)_3$ $9H_2O$ (8.08 g, 20 mmol), $La(NO_3)_3$ $6H_2O$ (8.7 g, 20 mmol), acetylacetone (5 mL) and ethyl cellulose (1.0 g) was sprayed onto FTO at by a homemade electronic-controlled spraying device (***Fig. S7***).The distance between the spray gun and FTO was controlled as 8.0 cm, the

moving speed of the spray gun was controlled as 2.5 cm s^{-1}, and the pressure of air for driving the spray gun was controlled at 0.5 MPa. After 8-10 spraying cycles, high quality films can be obtained, which were further annealed in oven at 600℃ for 3 h to remove the ethyl cellulose template and obtain the mesoporous $LaFeO_3$ films.

Fabrication of P1*@$LaFeO_3$, NiP@$LaFeO_3$ and (NiP+P1*)@$LaFeO_3$.

The $LaFeO_3$ films were immersed into a solution of dye **P1*** (2 × 10^{-4} M in CH_2Cl_2) under dark for 1.5 h, and the sensitized $LaFeO_3$ electrodes were then rinsed with ethanol and dried in air, abbreviated as **P1***@$LaFeO_3$. To immobilize catalyst **NiP** on the surface of $LaFeO_3$ and **P1***@$LaFeO_3$, the corresponding films were immersed into a saturated solution of **NiP** in methanol for 12 h, rinsed with ethanol and dried in air, abbreviated as **NiP**@$LaFeO_3$ and (**NiP**+**P1***)@$LaFeO_3$, respectively.

To determine the loading amount of **P1*** and **NiP,** the film of (**NiP+P1***)@$LaFeO_3$ was dissolved in HNO_3 solution, then the loading amount of **P1*** was quantified by UV-Vis spectroscopy, 6.3 ± 0.8 × 10^{-10} mol cm^{-2} of **P1*** was adsorbed on the surface of $LaFeO_3$. The loading amount of **NiP** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). 4.3 ± 1.3 × 10^{-10} mol cm^{-2} of **NiP** was immobilized on the surface of $LaFeO_3$. The ratio

of dye to catalyst on the surface of LaFeO3 was calculated to be 1.5/1.

Figure S7. The homemade electronic-controlled spraying device

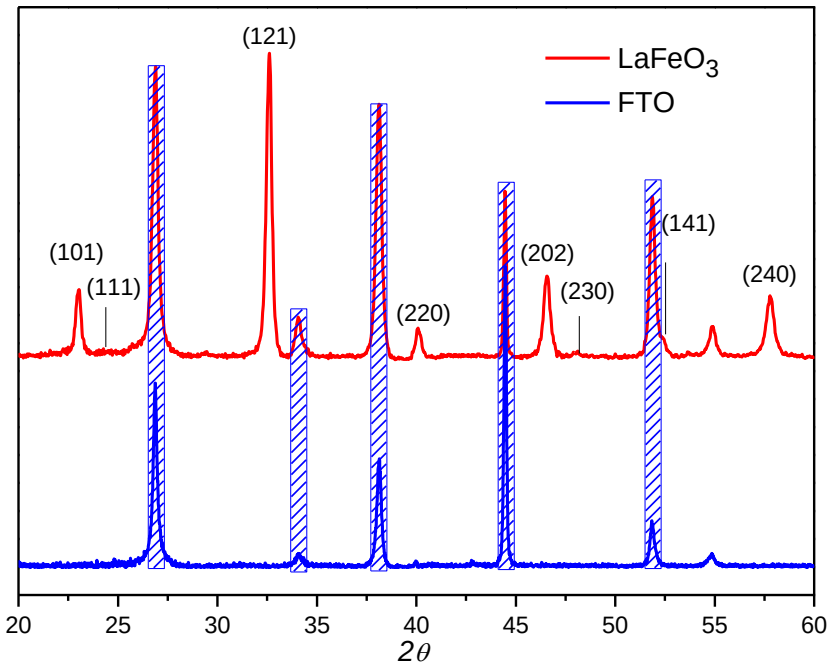

Figure S8. XRD patterns of the $LaFeO_3$ film (red) and FTO substrate (blue)

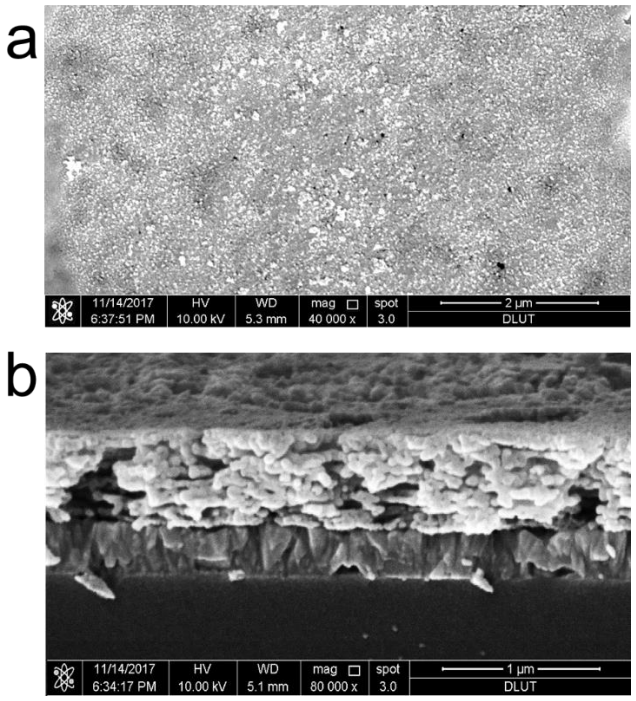

Figure S9. The SEM image of $LaFeO_3$, the top view (**a**) and the side view (**b**)

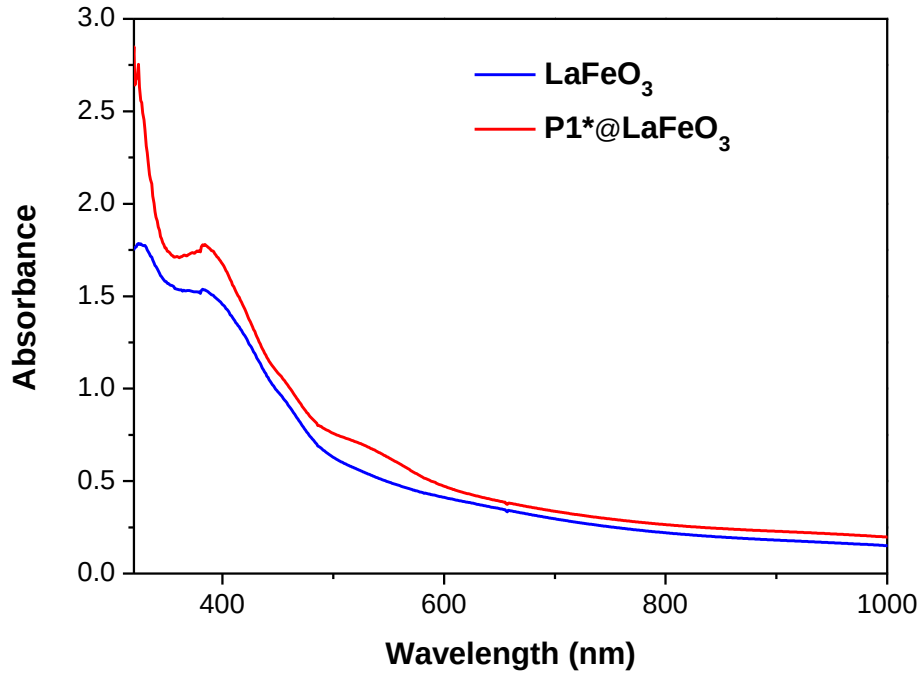

Figure S10. Absorption spectrum of the $LaFeO_3$ film and the corresponding absorption after adsorbing P1* on the surface.

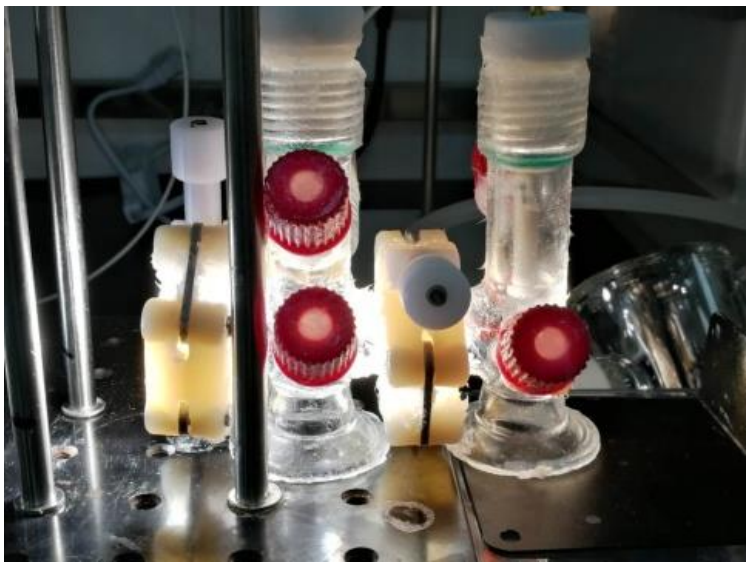

Figure S11. The two-compartment electrochemical cell setup separated by Nafion membrane for the photo-generated H_2 measurement.

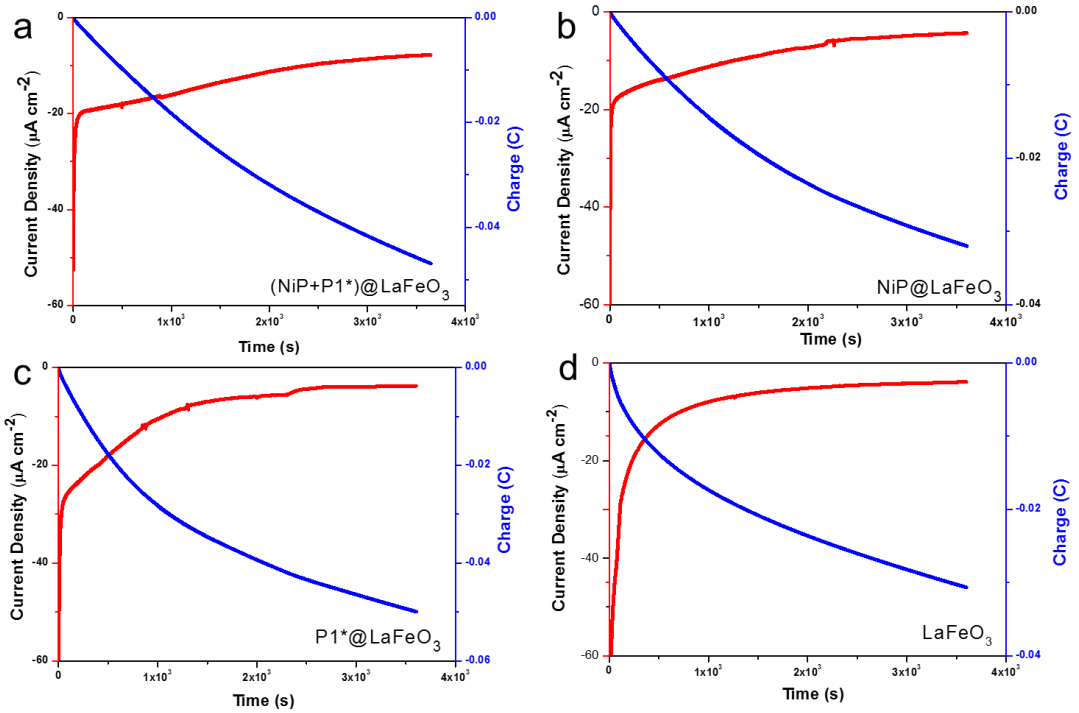

Figure S12. The controlled potential photoelectrolysis trace of (a) NiP+P1*@$LaFeO_3$, (b) NiP@$LaFeO_3$, (c) P1*@$LaFeO_3$ and (d) $LaFeO_3$ photo-electrodes held at +0.55 V vs. RHE in a 0.5 M

Na_2SO_4 solution adjusted to pH 3. The cell was maintained at room temperature. 0.0462 C of charge passed through the NiP+P1*@$LaFeO_3$ electrode, 0.107 μmol of H_2 was collected, resulting a Faraday Efficiency of 44.8%. 0.0319 C of charge passed through the $LaFeO_3$ electrode, 0.061 μmol of H_2 was collected, a Faraday Efficiency of 37% was obtained for NiP@$LaFeO_3$. 0.0499 C of charge passed through the P1*@$LaFeO_3$ electrode, 0.049 μmol of H_2 was collected, resulting a Faraday Efficiency of 19%. 0.0306 C of charge can produce 0.024 μmol, a Faraday Efficiency of 15% was obtained for $LaFeO_3$.

Table S1. The performance of recently published molecule based photocathodes for H_2 generation.

Photocathode	Electrolyte	Current density at bias	Faradaic efficiency	Reference
(NiP+P1*)@$LaFeO_3$	Na_2SO_4 (pH 3)	-20 μA cm^{-2} @0.6 V vs RHE	45%	This work
(NiP+DPP-P)@$CuCrO_2$	Na_2SO_4 (pH 3)	-15 μA cm^{-2} @0 V vs RHE	34%	5
(NiP+DPP-P)@NiO	Na_2SO_4 (pH 3)	-5.8 μA cm^{-2} @0 V vs RHE	34%	5
(NiP+Rudye)@NiO	Na_2SO_4 (pH 3)	-10 μA cm^{-2} @0.3 V vs RHE	8.6%	6
(Cobaloxime+RuP)@NiO	Phosphate (pH 7)	-13 μA cm^{-2} @0.2 V vs RHE	N. A.	7
(Co($dmgBF_2$)$_2$ +P1)@NiO	Phosphate (pH 7)	-35 μA cm^{-2} @0.4 V vs RHE	68%	8
(Cobaloxime+ CdSe)@NiO	Na_2SO_4 (pH 6.8)	-110 μA cm^{-2} @0.4 V vs RHE	81%	9

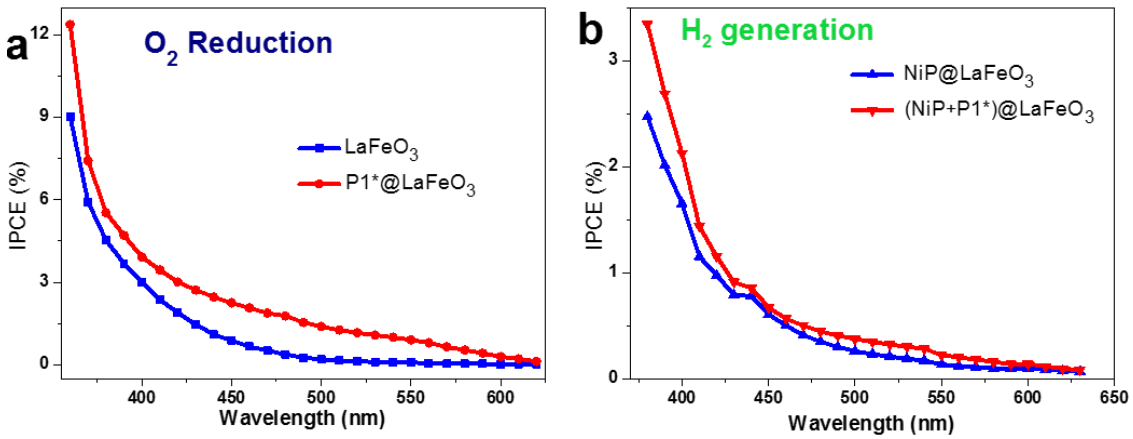

Figure S13. (a) IPCE of $LaFeO_3$ and **P1***@$LaFeO_3$ for O_2 reduction measured in 1.0 M KOH (pH = 13.6); data obtained at 0.75 V vs. RHE. (b) IPCE of **NiP**@$LaFeO_3$ and (**NiP**+**P1***)@$LaFeO_3$ for H_2 generation in 0.5 M Na_2SO_4 (pH = 3); data obtained at 0.55 V vs. RHE.

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