

Supporting Information for

Linear multiple-thiophene-containing conjugated polymer photocatalysts with narrow band gaps for achieving ultrahigh photocatalytic hydrogen evolution activity under visible light

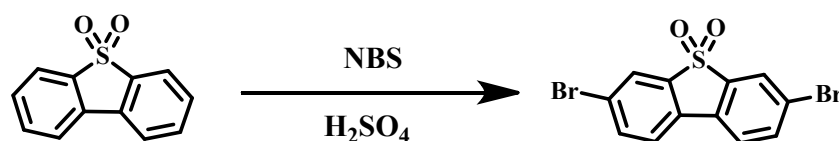
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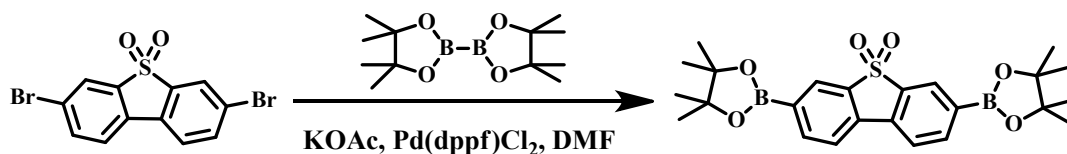
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Synthesis of 3,7-dibromodibenzothiophene-S,S-dioxide



M1 (6.05 g, 28.0 mmol) was dissolved in concentrated H₂SO₄ (150 mL) with strong stirring. NBS (12.46 g, 70.0 mmol) was slowly added into this solution in several portions at 0-5 °C. Then, the resulting mixture was stirred at room temperature for 24 h. Finally, the mixture was carefully poured into ice water. The white solid was obtained by filtration. The un-dissolved crude product was washed successively with 20% aqueous sodium hydrogen carbonate, water and methanol respectively. After drying in vacuum at 60 °C for 24 h, the product was further re-crystallized from chlorobenzene to gain 4.25 g white crystal in 41% yield. ¹H NMR (ppm, 400 MHz, CDCl₃): δ 7.94 (s, 2H), 7.76 (d, 2H), 7.65 (d, 2H).

Synthesis of M4



Under N₂ protection, 70 mL anhydrous DMF was added into a mixture of 3,7-dibromodibenzothiophene-S,S-dioxide (4.14 g, 11.0 mmol), bis(pinacolato)diboron (8.38 g, 33.0 mmol), CH₃COOK (6.25 g, 63.7 mmol) and Pd(dppf)Cl₂ (0.11 g, 0.13 mmol). The reaction solution was heated at 90 °C for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂. The organic phase was washed with water for three times, then the organic phase was collected and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then the residue was purified by column chromatography (petroleum ether/CH₂Cl₂ 1:1). After drying in vacuum at 60 °C for 24 h, the product was recrystallized from chloroform and methanol to gain 3.2 g white crystal in 62% yield. ¹H NMR (ppm, 400 MHz, CDCl₃): δ 8.30 (s, 2H), 8.03 (d, 2H), 7.78 (d, 2H), 1.36 (s, 24).

Characterization

Fourier-transform infrared (FT-IR) spectra were collected on a Vertex70 spectrometer (Bruker) using KBr disks. Solid-state ¹³C NMR spectra were obtained on a JEOL RESONANCE ECZ 400R NMR spectrometer at a MAS rate of 12 kHz. Powder X-ray diffraction (PXRD) measurement was performed by X-ray diffractometer (D/Max-3c). The morphology analysis was performed by using a field emission scanning electron microscope (SEM) (JSM-6700F). The UV-Vis reflectance spectra of the polymers were carried out by a scan UV-Vis spectrophotometer (UV-3600) using BaSO₄ as a reference sample. The fluorescent properties of the polymers were measured with a PerkinElmer FL-8500 fluorescence spectrophotometer by using excitation wavelength of 420 nm at room temperature. The surface photovoltage (SPV) spectra of the polymers were carried out by surface photovoltage spectrometer (CEL SPEC). N₂ adsorption isotherms were obtained using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. Samples were degassed at 100 °C for 15 h under vacuum (10⁻⁵ bar) before analysis. The surface areas were calculated from nitrogen adsorption data using Brunauer-Emmette-Teller (BET) method. The water adsorption isotherms were analyzed with a gravimetry vapor sorption analyser

BELSOPR-Max. The particle size was measured by the confocal laser scanning microscopy (CLSM) (OLYMPUS-FV1200). The measurement protocol of CLSM is presented as below. After the photocatalytic hydrogen production test, the photocatalytic reaction solution containing the polymer photocatalyst was dropped on a glass slide, on which the droplet was covered by another glass slide; then the above prepared sample was directly observed by the CLSM with a 520 nm excitation light in a dark room. The cyclic voltammetry (CV) measurement was carried out on a CHI660E (Chenhua, Shanghai) electrochemical workstation in a three-electrode system. Glassy carbon electrode with polymer photocatalyst was used as the working electrode. Hg/HgCl₂ electrode and platinum wire were used as the reference electrode and the counter electrode, respectively. The polymer was firstly mixed with 5 wt% Nafion in isopropanol, then the resulting mixture was dropped cast on the top of a glassy carbon working electrode. The working electrode was dried in a vacuum chamber for 60 min to remove the solvent. The CV measurement was carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (NBu₄PF₆) in acetonitrile with a scan rate of 100 mV s⁻¹. For the conversion from Hg/HgCl₂ redox couple to the Normal Hydrogen Electrode (NHE), the equation E_{NHE} = E_{SCE} + 0.241 V was applied. The photocurrent was also measured on CHI660E electrochemical workstation with a bias voltage of 0.02 V under UV-Vis light irradiation with 20 s light on-off cycles. The preparation of working electrode is in a manner similar to that of CV measurement. The prepared working electrode from the polymer catalyst and 5 wt% Nafion was immersed in 1.0 M Na₂SO₄ aqueous solution. For EIS, the frequency range was 10²-10⁶ Hz. The preparation of working electrode is in a manner similar to that of photocurrent measurement.

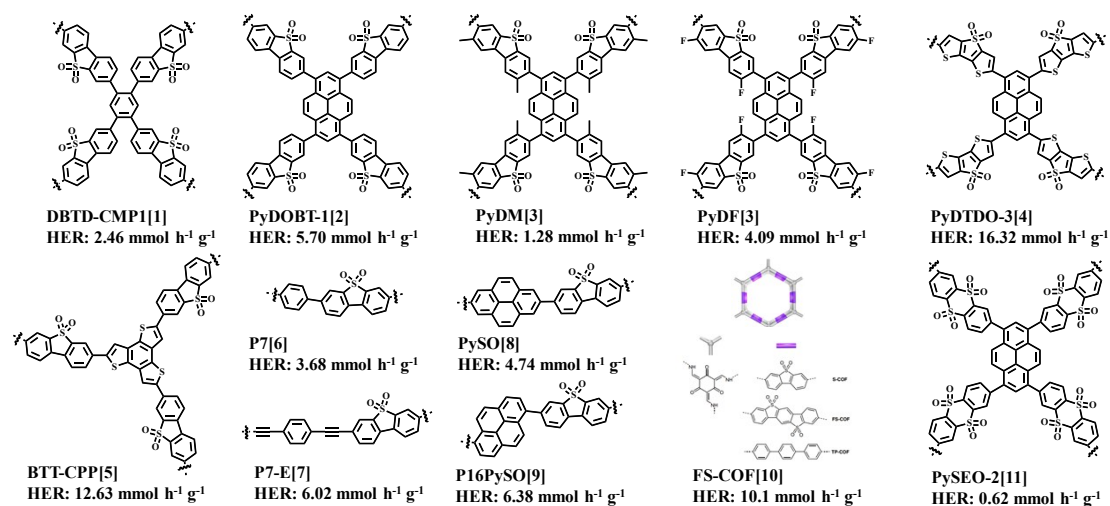
The apparent quantum yield measurement

The apparent quantum yield (AQY) for hydrogen evolution was measured with monochromatic light obtained by using band pass filter of 420, 450, 520, 550 and 600 nm. The AQY was calculated as below:

$$\eta = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where M is the amount of the produced H₂ (mol), N_A is Avogadro constant (6.022×10²³ /mol), h is the Planck constant (6.626×10⁻³⁴ J·s), c is the speed of light (3×10⁸ m/s), S is the irradiation area of the incident light (cm²), P is the intensity of

incident light (W/cm^2), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m). According to the equation, the apparent quantum yield is related to the intensity of incident light and the irradiation area. These parameters in different groups are possibly different, resulting in different apparent quantum yields.



Scheme S1. Molecular structures of the reported BTDO-based polymer photocatalysts and the corresponding HERs under visible light ($\lambda > 420$ nm).

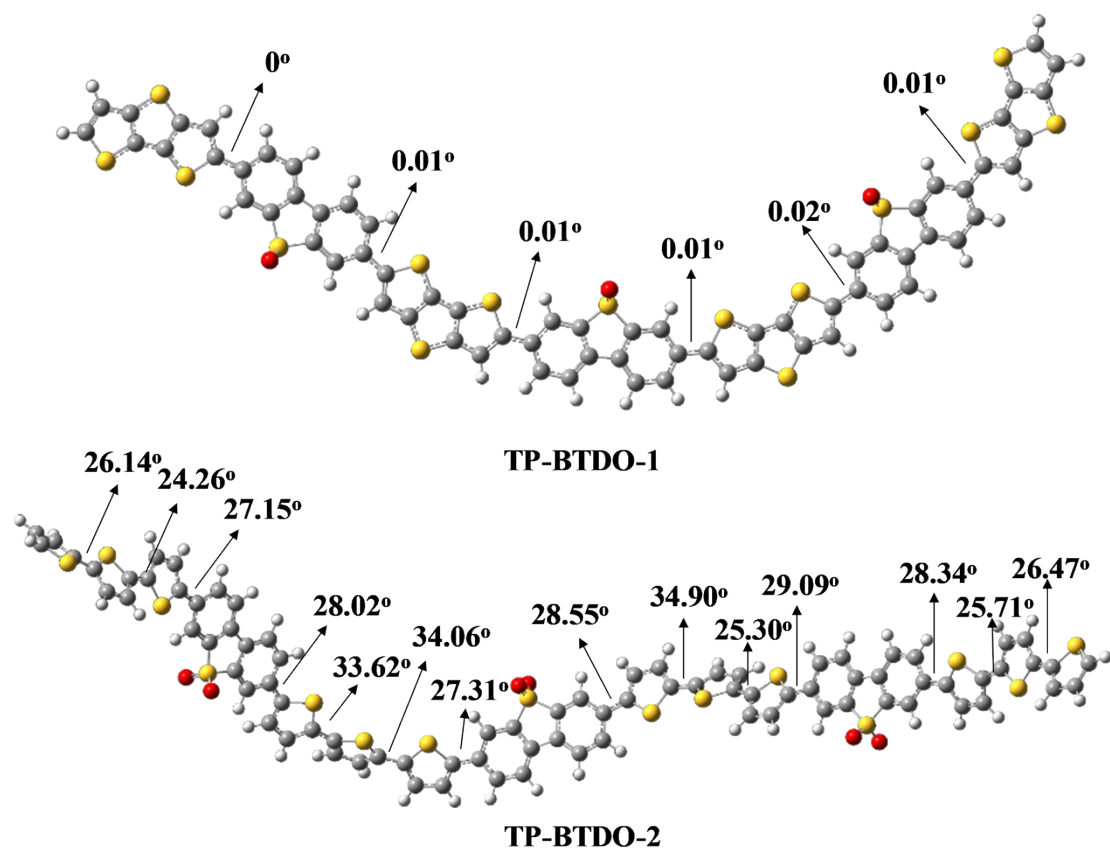


Fig. S1 The DFT geometry optimizations and the dihedral angles of the polymers.

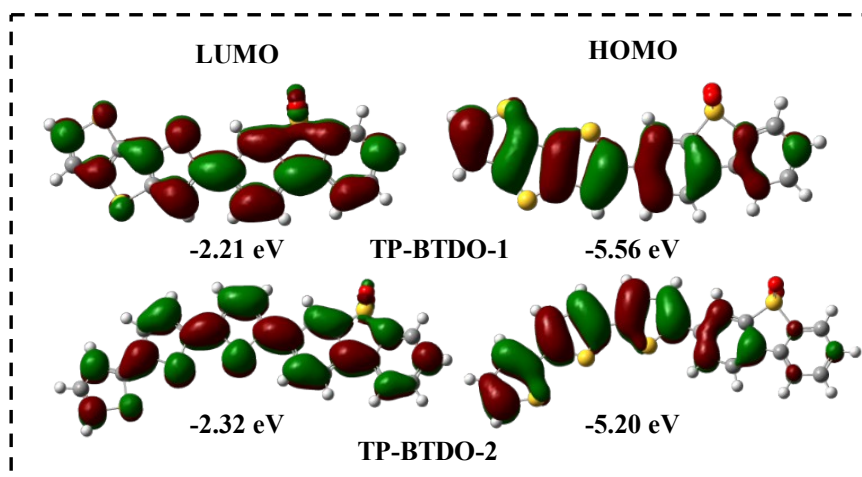


Fig. S2. HOMO and LUMO orbital distributions of the two polymers.

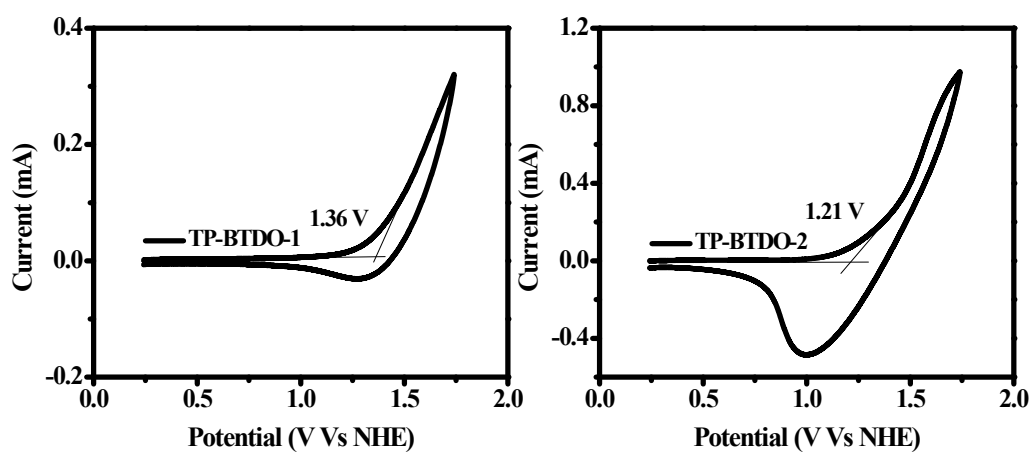


Fig. S3 The CV curves of the polymers vs NHE.

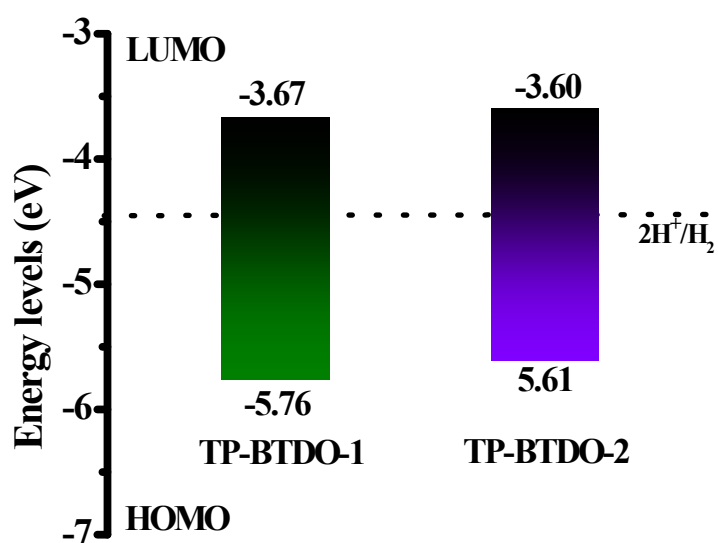


Fig. S4 Band structures of the two polymers identified by combining the results of cyclic voltammogram and UV/Vis absorption spectra.

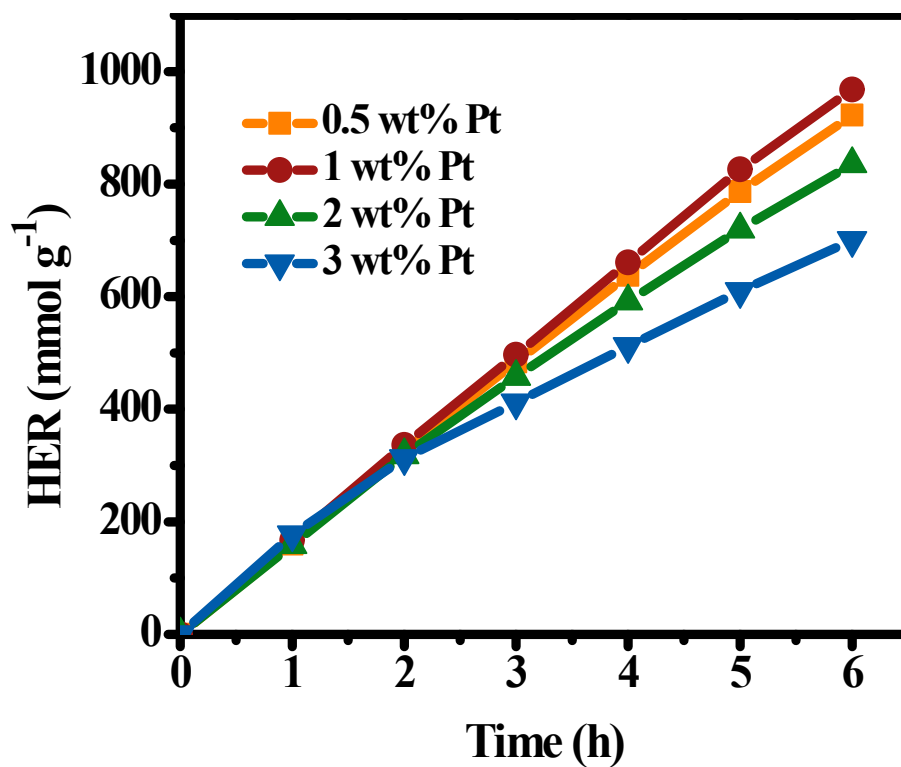


Fig. S5 The hydrogen evolution rates of TP-BTDO-2 with different Pt contents under UV/Vis light irradiation ($\lambda > 300$ nm).

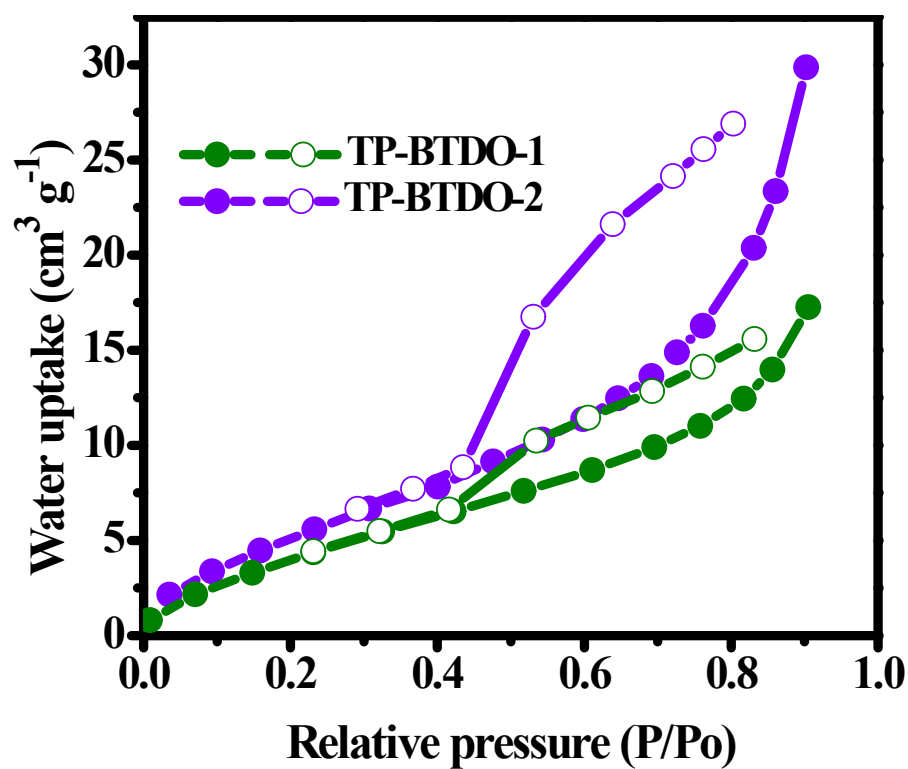


Fig. S6 The water vapor adsorption measurement of the polymers.

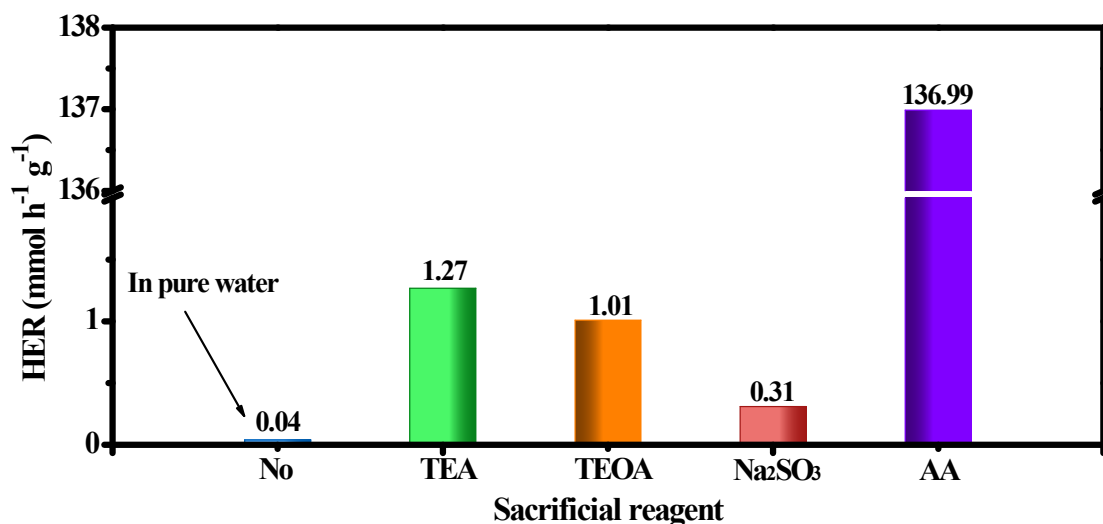


Fig. S7 The HERs of bare TP-BTDO-2 in pure water and using different sacrificial reagents under UV/Vis light irradiation ($\lambda > 300$ nm).

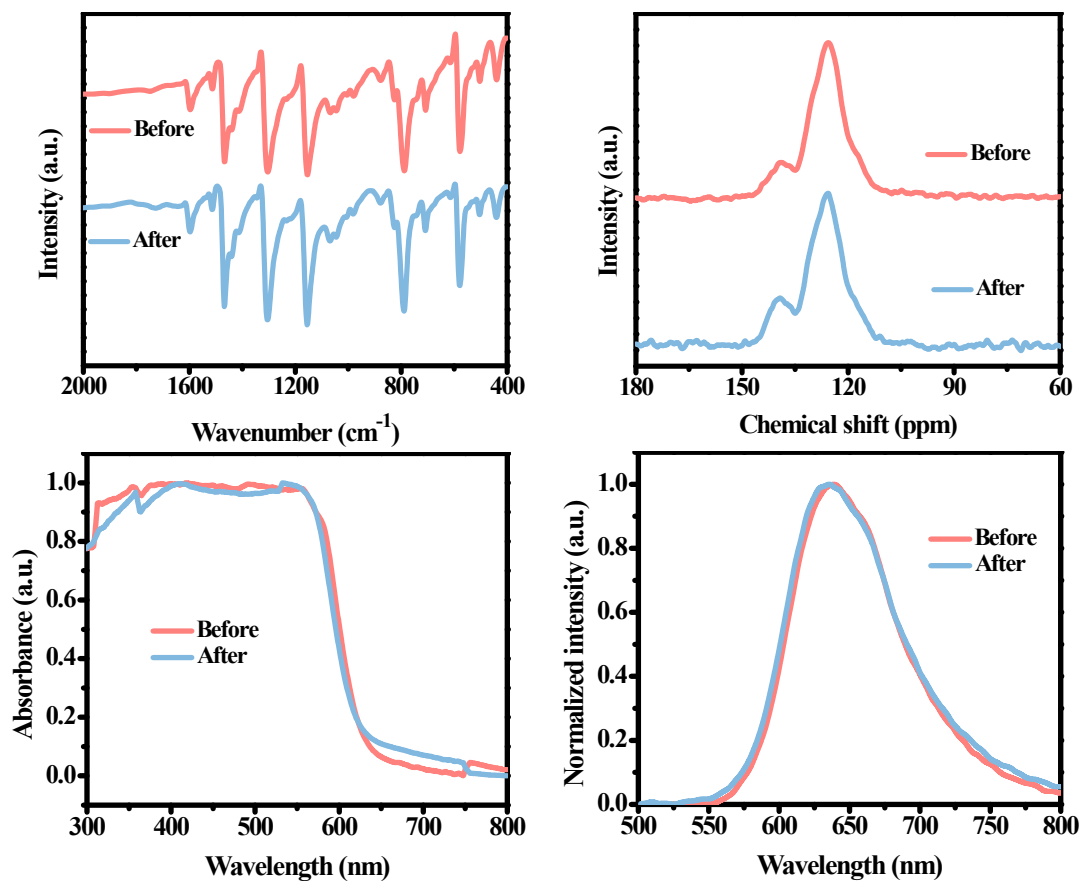


Fig. S8 The (a) FT-IR spectra, (b) solid-state ¹³C NMR spectra, (c) UV/Vis reflectance spectra and (d) PL spectra of TP-BTDO-2 before and after photocatalytic reaction in a AA/DMF/water mixture.

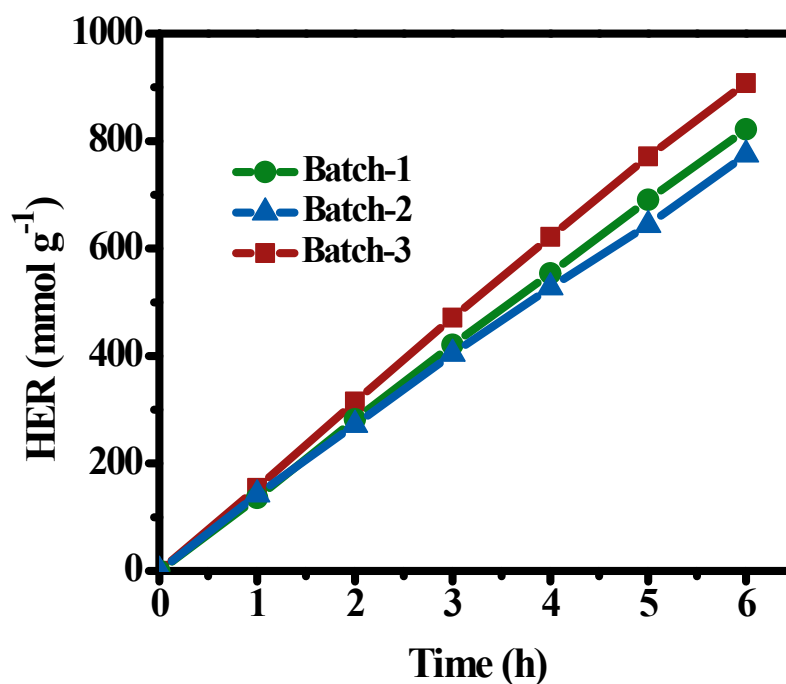


Fig. S9 The hydrogen evolution rates of TP-BTDO-2 produced from different batches under UV/Vis light irradiation ($\lambda > 300$ nm).

Table S1. The summary of the photocatalytic performances of polymeric photocatalysts for hydrogen evolution from water splitting ($\lambda > 420$ nm).

Photocatalysts	cocatalyst	sacrificial reagent	HER (mmol h ⁻¹ g ⁻¹)	Optical gap (eV)	AQY (%)	Ref.
TP-BTDO-2	No	AA	108.59	2.01	30.48 (10 mg@520 nm)	This work
PyBS-3	No	AA	36.0	2.54	29.30 (10 mg@420 nm)	[12]
Py-Tt	No	AA	45.8	2.02	--	[13]
P2	3 wt% Pt	TEA	20.3	2.22	7.04 (3.5 mg@500 nm)	[14]
PS-5	No	TEOA	7.5	2.12	15.3 (25 mg@420 nm)	[15]
CP1	0.5 wt% Pt	AA	16.0	1.98	1.62 (6 mg@550 nm)	[16]
PyDTDO-3	No	AA	16.3	1.81	3.93 (10 mg@550 nm)	[4]
BTT-CPP	No	AA	12.6	2.40	3.30 (6 mg@365 nm)	[5]
PyDOBT-1	3 wt% Pt	TEOA	8.5	2.37	6.10 (50 mg@400 nm)	[2]
DBTD-CMP1	3 wt% Pt	TEOA	4.6	2.53	<3.30 (50 mg@400 nm)	[1]
B-SO	3 wt% Pt	TEOA	0.78	3.41	0.34 (12.5 mg@420 nm)	[17]

B-FOBT-1,4-E	No	TEOA	13.3	2.18	5.70 (30 mg@420 nm)	[18]
PBT2	No	TEA	0.83	2.15	0.65 (50 mg@470 nm)	[19]
PySEO-1	3 wt% Pt	TEOA	6.02	1.90	4.10 (50 mg@400 nm)	[11]
P16PySO	No	TEOA	6.4	2.31	3.50 (50 mg@450 nm)	[9]
P-FSO	No	TEOA	8.0	2.31	8.50 (50 mg@420 nm)	[20]
PyDF	3 wt% Pt	TEOA	13.5	2.24	4.50(25 mg@420 nm)	[3]
Py-TPA-CMP	3 wt% Pt	AA	19.2	1.80	15.3 (3 mg@460 nm)	[21]
PCP10	No	TEA	8.6	--	1.05 (12 mg@400 nm)	[22]
PySO	No	TEA	4.74	2.58	3.28 (10 mg@420 nm)	[8]
S-CMP3	No	TEA	3.1	2.56	13.20 (30 mg@420 nm)	[23]
CNSO-20	No	TEOA	5.02	2.18	10.16 (50 mg@420 nm)	[24]
TEBN11	3 wt% Pt	TEA	1.89	--	2.7 (25 mg@420 nm)	[25]
P7-E	No	TEOA	6.02	2.79	4.20 (30 mg@420 nm)	[7]
CTF-N	2 wt% Pt	TEOA	10.8	2.17	4.07 (50 mg@420 nm)	[26]
CTF-BT/Th-1	3 wt% Pt	TEOA	6.6	--	7.30 (50 mg@420 nm)	[27]
Triazine-Ph-CPP	No	TEOA	3.5	2.83	61.5 (32 mg@365 nm)	[28]
CTF-0-M ₂	3 wt% Pt	TEOA	1.0	2.07	11.0 (100 mg@365 nm)	[29]
CTF-15	3 wt% Pt	TEA	2.9	2.58	15.90 (25 mg@420 nm)	[30]
Cl-ECF	3 wt% Pt	LA	1.3	2.23	0.68 (20 mg@420 nm)	[31]
FS-COF	8 wt% Pt	AA	10.1	1.85	3.2 (5 mg@420 nm)	[10]
g-C ₁₈ N ₃ -COF	3 wt% Pt	AA	0.2	2.42	1.06 (50 mg@420 nm)	[32]
Cd-COF (90:10)	0.5 wt% Pt	LA	3.7	--	4.20 (30 mg@420 nm)	[33]
NKCOF-108	5wt% Pt	AA	8.0	1.82	2.96 (15 mg@520 nm)	[34]

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