Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Donor-Acceptor Engineering in Conjugated Polymer Photocatalysts: Thieno[3, 2-b]thiophene-Dibenzothiophene Sulfone Copolymers for Noble-Metal-Free Visible-Light Hydrogen Evolution

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Experimental Section

Synthesis of M1

Add 8.42 g of S, S-dioxy-dibenzothiophene and 150 mL of concentrated sulfuric acid to a 500 mL three-necked flask. Stir the mixture until the S, S-dioxy-dibenzothiophene completely dissolves in the sulfuric acid. Then, add 14.0 g of N-bromosuccinimide (NBS) to the three-necked flask in batches. Allow the reaction to proceed for 6 hours under an ice bath. After the reaction, pour the mixture into ice water, resulting in the precipitation of a large amount of white solid. Collect the solid by suction filtration and wash the filter cake alternately several times with deionized water and ethanol until the pH of the washings reaches 7. Dry the solid. The dried product is then recrystallized using dichloromethane to obtain colorless needle-like crystals.

Synthesis of M2

Under N_2 protection, 100 mL of anhydrous DMF was added into a mixture of 3,7-Dibromodibenzothiophene 5,5-Dioxide (5.795 g), Bis(pinacolato)diboron (9.46 g), CH_3COOK (8.76 g) and Pd(dppf)Cl_2 (0.154 g). The reaction solution was heated to 100 °C for 24 h. After cooling down to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic phase was collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 = 1:5). After drying in vacuum at 60 °C for 24 h, the product was re-crystallized from chloroform and methanol to gain 3.41 g white crystal in 60% yield. The synthetic paths of the above monomers M1 and M2 are shown in **Fig. S1**. They were also characterized to verify their purity, and the ^{1}H NMR results are shown in **Fig. S2** and **Fig. S3**.

Photocatalytic Experiment

In the hydrogen evolution experiments of this work, a LabSolar 6A reaction system (Beijing PerfectLight Technology Co., Ltd.) was employed. A 300 W Xe lamp equipped with a 420 nm cutoff filter served as the simulated visible light source. The evolved hydrogen was quantified using a GC-7806 gas chromatograph (Beijing Shiwei Puxin Analytical Instrument Co., Ltd.), which was equipped with a chromatographic column and a flame ionization detector (FID), via the external standard method to evaluate the hydrogen evolution performance of the polymers. Specifically, 10 mg of the polymer powder sample was added to a mixed solvent consisting of 10 mL of DMF and 90 mL of ascorbic acid and stirred for 30 min. The hydrogen evolution simulation experiments were performed using a 6A all-glass automatic recirculation analysis system. A 300 W xenon lamp was used as a visible light source, and the UV light was filtered using a UV cutoff filter of λ 420 nm. The dissolved temperature of the test mixture was held at 10 C by circulating the coolant. The hydrogen production rate of the polymer was analyzed using an on-line chromatograph.

Photocatalysis test under natural light illumination

The polymer powder (40 mg) was sonicated in 40 mL DMF and 360 mL of ascorbic acid water-soluble leaf mixture, stirred and dispersed for 30 mins. The outdoor photocatalytic test was conducted on the roof of Wuhan Institute of Technology (longitude 114.25 E, latitude 30.28 N). The Weather conditions, including solar intensity and temperature, are recorded regularly. The photoreactor consisted of a 500 mL round bottom flask connected to an ascending graduated cylinder to estimate hydrogen production. The volume of hydrogen produced was measured every half hour in Wuhan, People’s Republic of China, on July 24, 2024.

Characterization

Thermogravimetric analysis (TGA) measurement was performed by using a differential thermal analysis instrument (HITACHI STA200) over the temperature range from 25 to 800 °C under an air atmosphere with a heating rate of 5 °C min^{-1}. Fourier transform infrared spectroscopy (FT-IR) was carried out with a NICOLET 5700 FT-IR spectrometer. The samples for FT-IR study were prepared as KBr pellets. Solid-state ^{13}C NMR spectra were obtained on a Bruker Advance Neo 400WB NMR spectrometer at a MAS rate of 12 kHz. Powder X-ray diffraction (PXRD) measurement was performed by X-ray diffractometer (D8 ADVANCE). XPS analysis was performed using an X-ray photoelectron spectrometer (Escalab 250XI) to determine the elemental composition and chemical states on the sample surface. The obtained results were calibrated against the C 1s peak of carbon at 284.8 eV. In situ XPS measurements were conducted under illumination using the aforementioned conditions. The morphology analysis was performed by using a field emission scanning electron microscope (SEM) (GeminiSEM 300). Uv-Vis absorption spectra of the as-obtained materials were measured on a U-3900 Uv-Vis spectrometer by measuring the reflectance of powders in the solid state. The scan was arranged from 200 to 800 nm and $BaSO_4$ was chosen as a reflectance standard. Photoluminescence (PL) spectroscopy was recorded via Edinburgh FLS1000 spectrofluorometer at room temperature. The excitation wavelength was 350 nm. The measurements were carried out using a Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure N_2 and He gases. Before the adsorption measurements, powdered samples were placed under reduced pressure (<10^{-5} bar) at 120 °C for 12 h. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K. The residual Pd content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The photocurrent, Mott-Schottky analysis and electrochemical impedance spectra (EIS) were measured using a CHI 600 electrochemical workstation (Shanghai, China). A homogeneous suspension of samples was prepared by dispersing 5 mg sample in 270 μL ethanol and 30 μL Nafion (10 wt% Nafion in ethanal) was added as an additive and the mixture were mechanically grounded/ sonicated for 10 min. The working electrode was prepared by applying 50 μL of the uniform suspension to the surface of the graphite working electrode and then forming a film in a vacuum oven at 50 ºC. The EIS measurement was performed in a home-made three-electrode quartz cell employing electrolyte solution (the concentration of $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl were all 0.1 M). The photocurrent and Mott-Schottky curves were performed in a home-made three-electrode quartz cell employing 0.1 M Na_2SO_4 as electrolyte solution, the difference was using 300 W xenon lamp (PLS-SXE 300) as the light source for the photocurrent. The femtosecond transient absorption (fs-TA) experiments were performed using a regenerative amplified Ti: sapphire laser system (Coherent Inc.; 800 nm, 85 fs, 7 mJ per pulse, 1 kHz repetition rate) as the light source, in conjunction with a Helios spectrometer (Ultrafast Systems LLC). The instrument response function (IRF) for this setup was measured to be approximately 120 fs. The theoretical calculations were performed via the Gaussian 16 suite of programs. The structure of the studied molecules was fully optimized at the B3LYP-D3BJ/6-31g (d, p) level of theory. The vibrational frequencies of the optimized structures were carried out at the same level. The structure was characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The electrostatic potentials of molecule has been calculated and analyzed using the Multiwfn software, and the isosurfaces have been visualized using the Visual Molecular Dynamics (VMD) program.

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, 475, 520 nm and 600 nm. The AQY was calculated as below:

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

Where M is the amount of the produced H_2 (mol), N_A is Avogadro constant (6.022×10^{23}/mol), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^{8} m/s), S is the irradiation area of the incident light (cm^2), 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. For the AQY measurement, the dosage of polymer photocatalyst is 10 mg. The photoreaction time and irradiation area are t=3600 s, S=3.14 cm^2, respectively. The incident light intensity at wavelengths of 420 nm, 475 nm, 520 nm, and 600 nm was 2699 nW, 306 nW, 340 nW, 313 nW.

Fluorescence life test

The fluorescence lifetime of the polymers was analyzed by time-resolved photoluminescence spectroscopy with the following formula. The parameters are all the data in the fitting process, as shown in **Table S2**.

$$\tau_{ave} = \frac{A_1T_1^2 + A_2T_2^2}{A_1T_1 + A_2T_2}$$

Table S1

Table S1 Feed composition and resulting polymer designations

TPA (mol)	T (mol)	DT (mol)	TT (mol)	M1 (mol)	M2 (mol)	CPs
1	3			15	16	TPA-T-BTDO
1		3		15	16	TPA-DT-BTDO
1			3	15	16	TPA-TT-BTDO
1				15	16	TPA-BTDO
				1	1	PDBTSO

Table S2

Table S2 Pore structure characteristic parameters of the polymers

Samples	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3. g^{-1})	Average pore width (nm)
TPA-T-BTDO	137.78	0.30	8.68
TPA-DT-BTDO	84.03	0.25	6.35
TPA-TT-BTDO	72.17	0.058	3.24

Table S3

Table S3 Calculated fluorescence lifetimes for the polymers

CPs	A_1	τ_1	A_2	τ_2	τ_{ave} (ns)	R^2
TPA-T-BTDO	1.08717	0.98585	0.03449	20.3737	8.66	98982
TPA-DT-BTDO	1.08622	1.1762	0.0512	13.96473	5.77	0.99067
TPA-TT-BTDO	1.0858	1.00487	0.0528	19.30515	9.84	0.99003

Table S4

Table S4 Hydrogen production rate of the TPA-TT-BTDO under natural light conditions

Time	illumination intensity (W cm^{-2})	H_2 capacity (mL)	HER (mmol h^{-1} g^{-1})
10:00-10:30	32	41	67
10:30-11:00	41	40	89
11:00-11:30	38	34	76
11:30-12:00	76	56	125
12:00-12:30	67	46	102
12:30-13:00	70	46	102
13:00-13:30	49	36	80

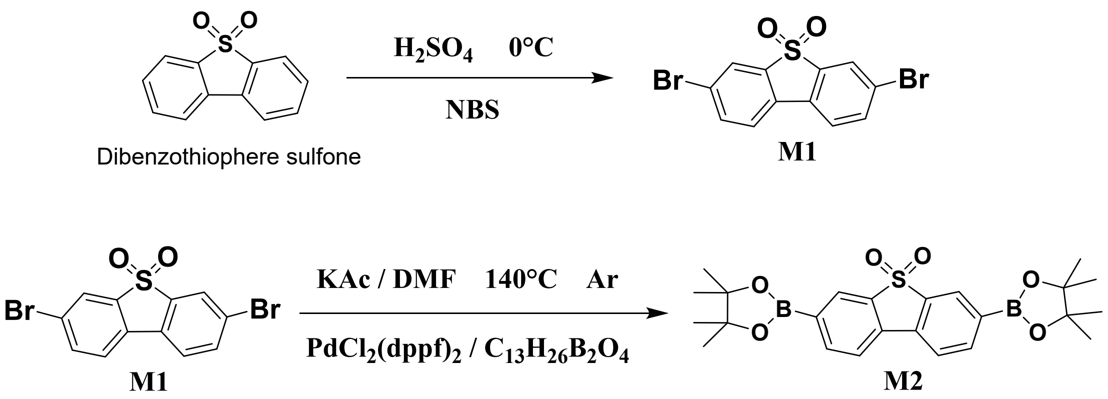


Fig. S1 Methods for the synthesis of the M1 and M2 monomers

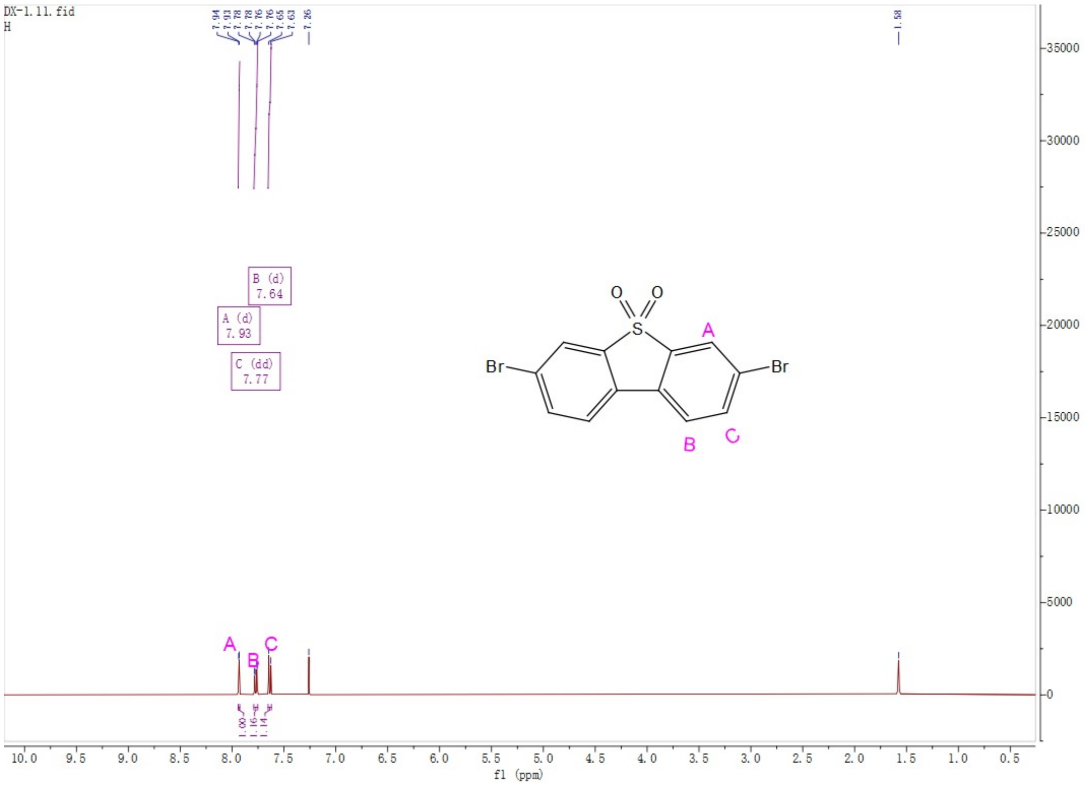


Fig. S2 The ^{1}H NMR spectrum of M1

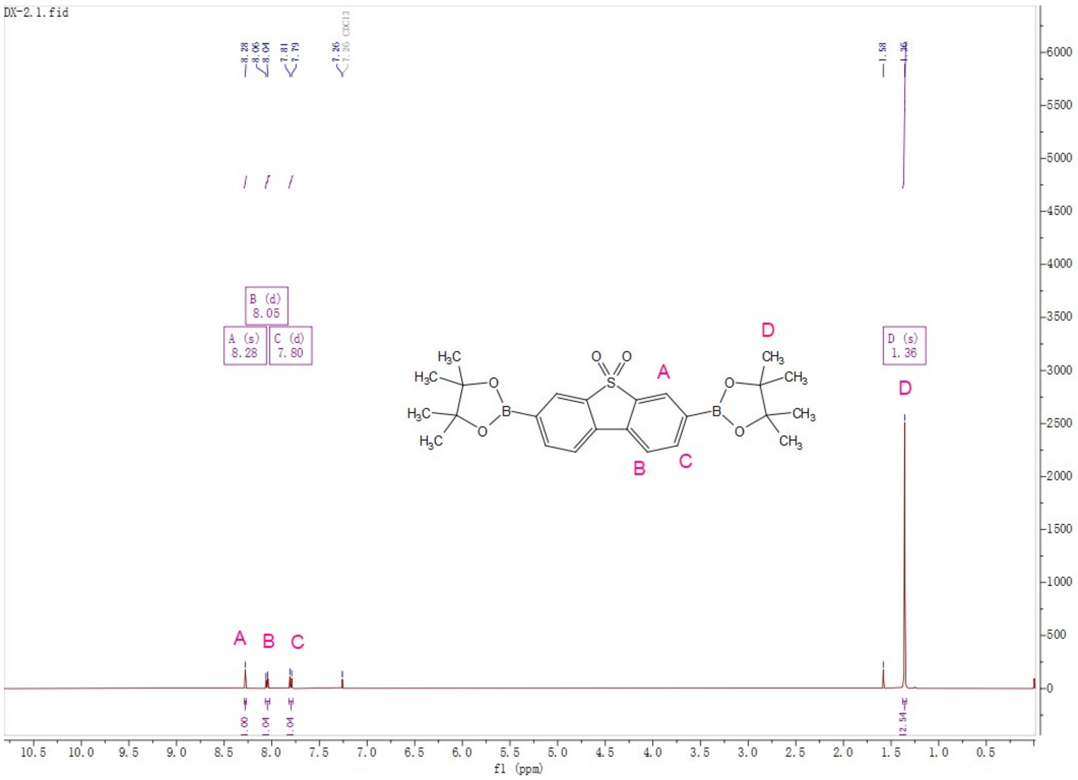


Fig. S3 The ^1H NMR spectrum of M2

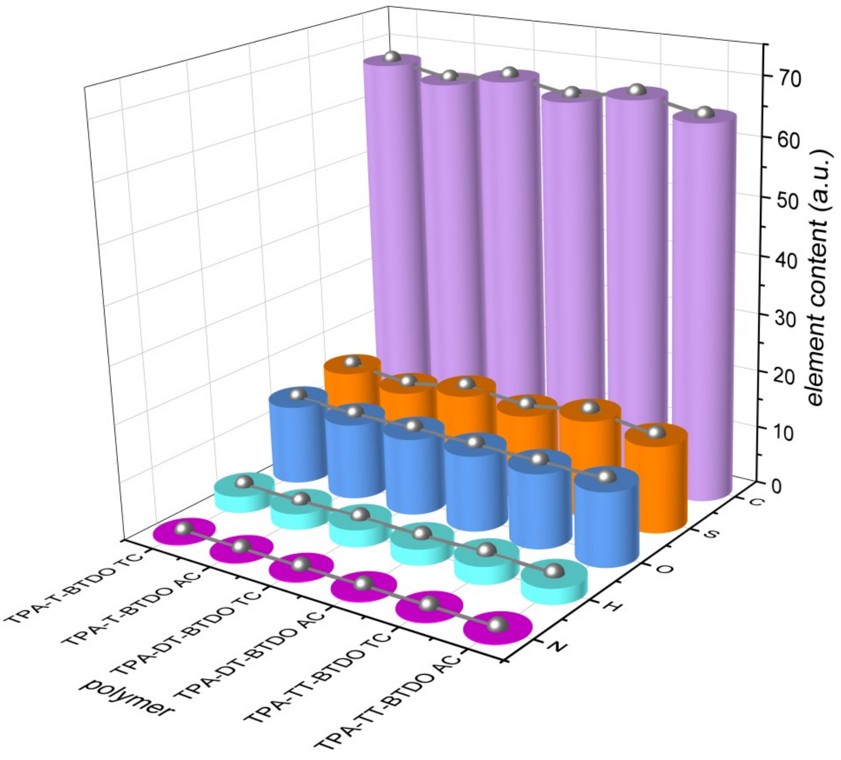


Fig. S4 Comparative analysis chart of organic element contents between prepared polymers and their theoretical values

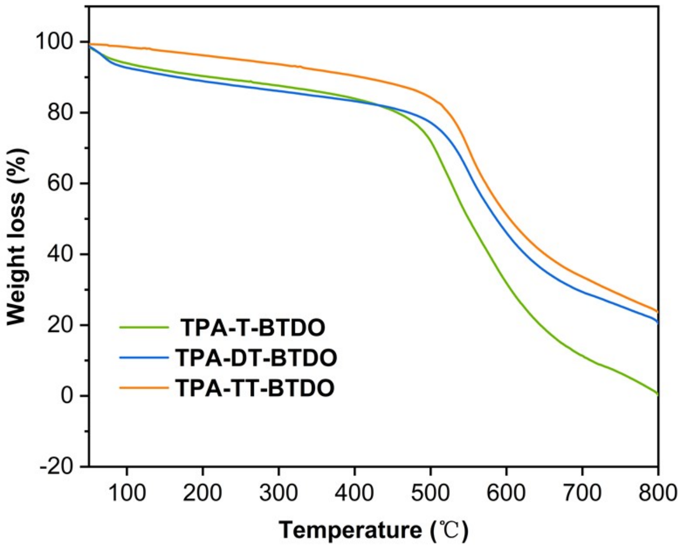


Fig. S5 TGA curve of polymers under nitrogen atmosphere

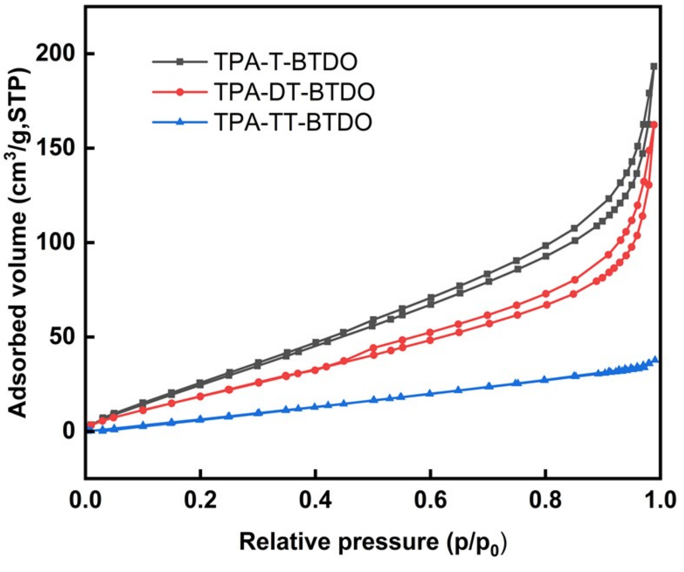


Fig. S6 N_2 adsorption-desorption isotherms of the synthesized TPA-T-BTDO, TPA-DT-BTDO and TPA-TT-BTDO polymers.

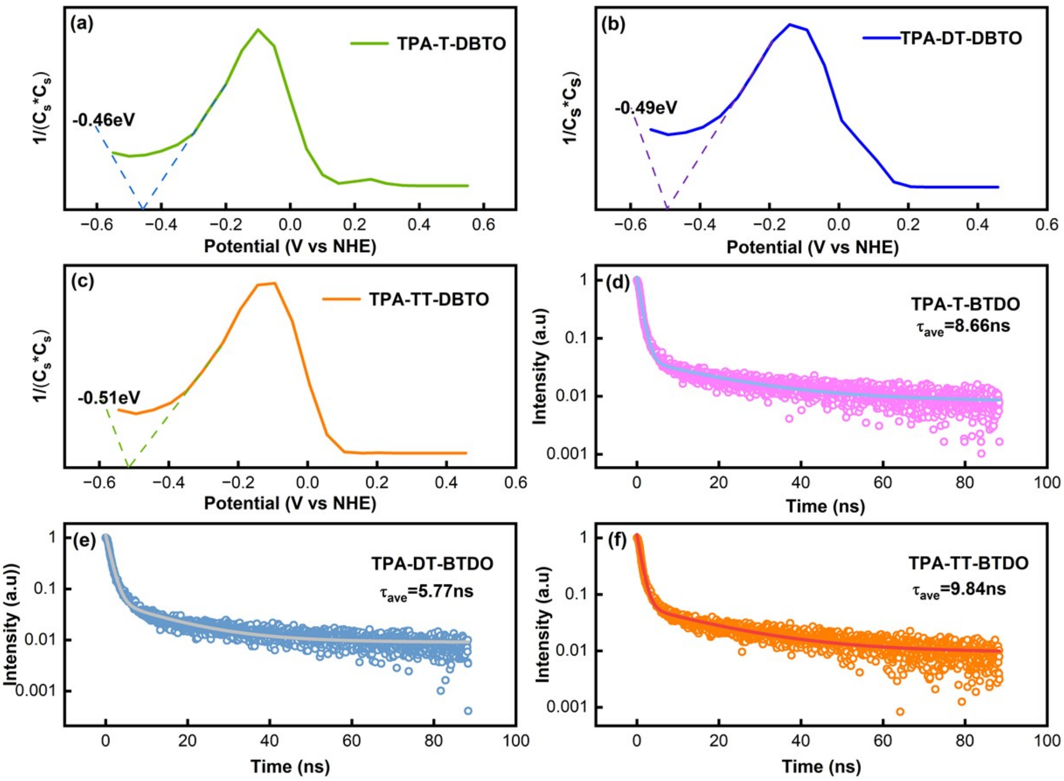
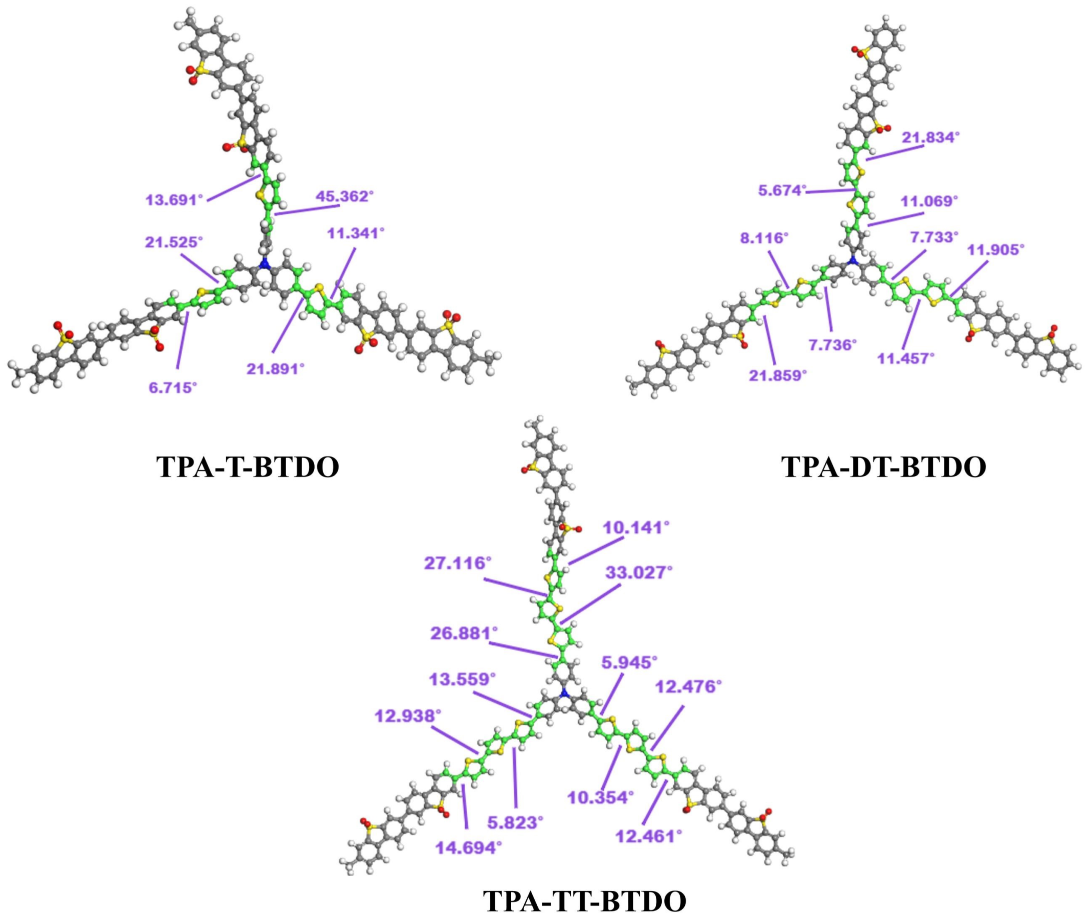


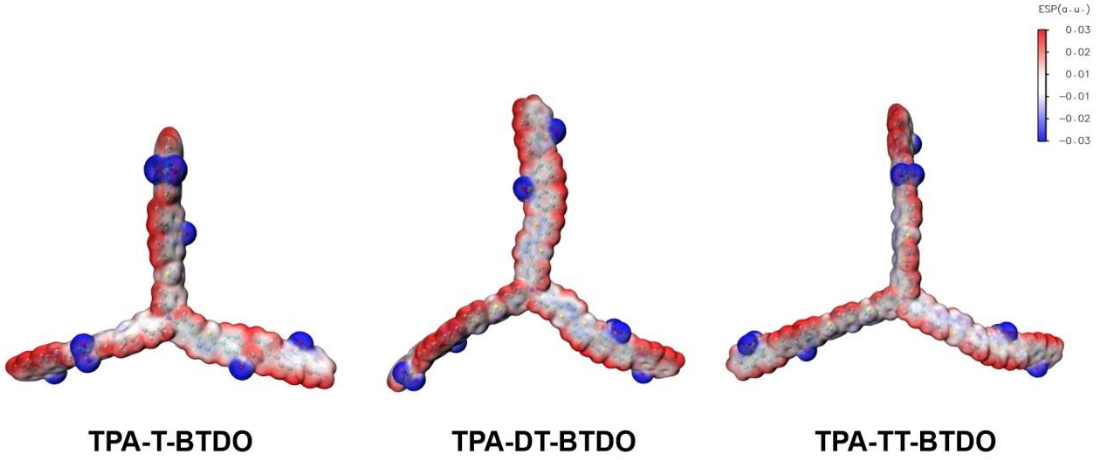
Fig. S7 Mott Schottky curve (a-c) and Fluorescence lifetime of the TPA-T-BTDO, TPA-DT-BTDO, TPA-TT-BTDO polymers (d-f)



TPA-T-BTDO **TPA-DT-BTDO**

TPA-TT-BTDO

Fig. S8 Torsion angle distribution of three polymers



TPA-T-BTDO **TPA-DT-BTDO** **TPA-TT-BTDO**

Fig. S9 The electrostatic potential (ESP) maps of TPA-T-BTDO, TPA-DT-BTDO, and TPA-TT-BTDO

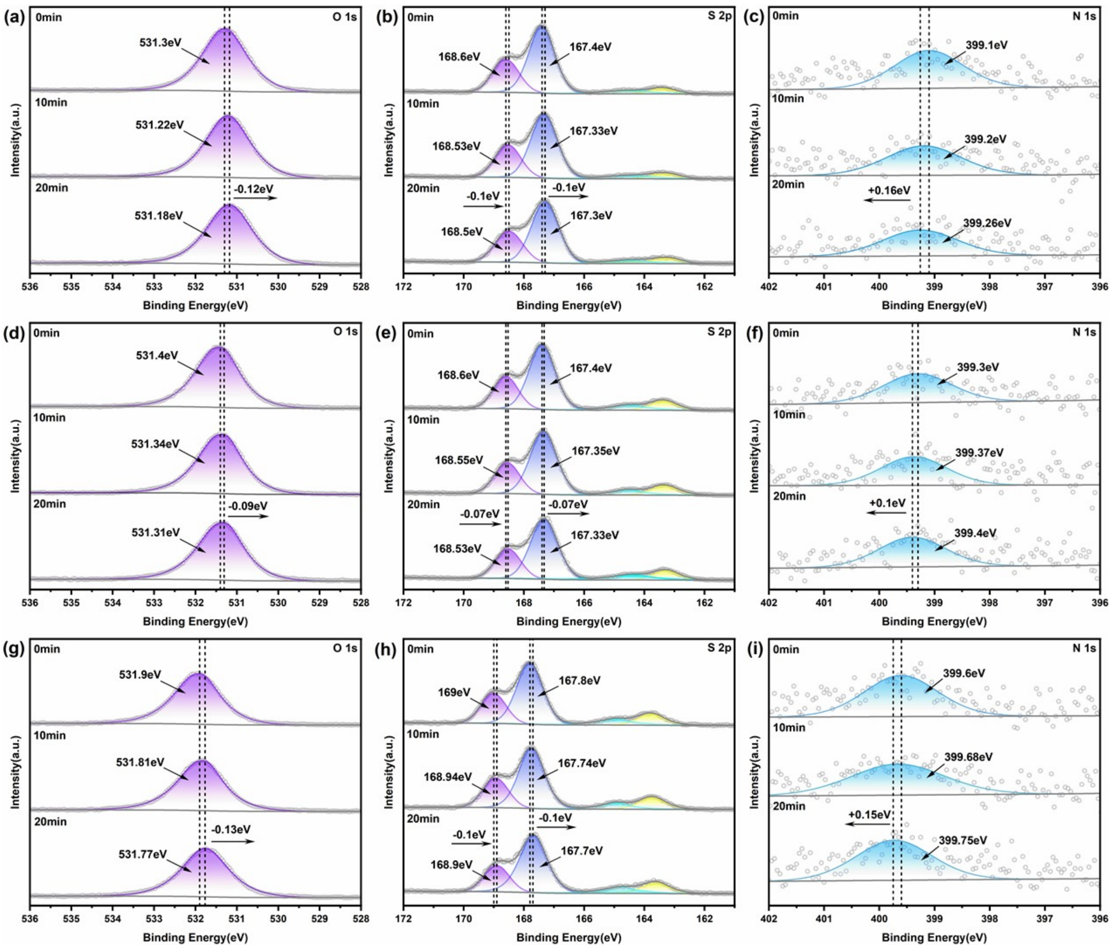


Fig. S10 (a-c) Near in-situ XPS spectra of TPA-T-BTDO: (a) O 1s, (b) S 2p, (c) N 1s, (d-f) Near in-situ XPS spectra of TPA-DT-BTDO: (d) O 1s, (e) S 2p, (f) N 1s, (g-i) Near in-situ XPS spectra of TPA-TT-BTDO: (g) O 1s, (h) S 2p, (i) N 1s.

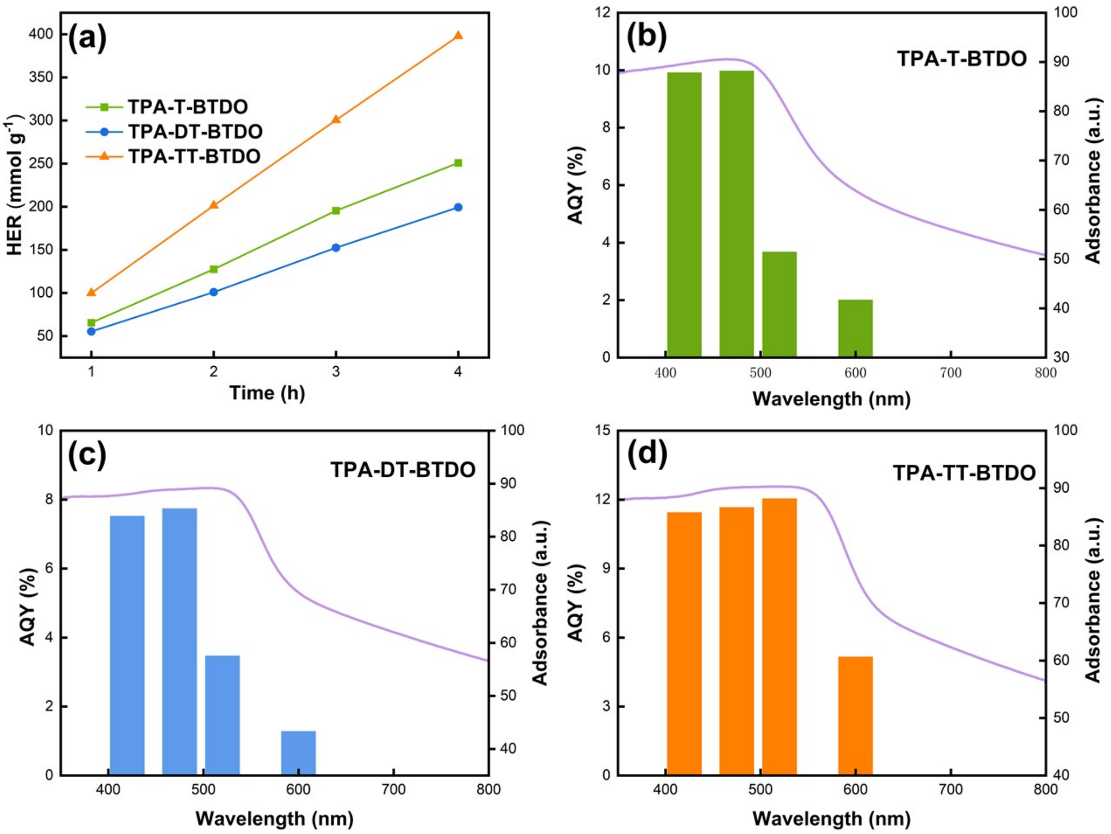


Fig. S11 (a) HERs of TPA-T-BTDO, TPA-DT-BTDO, and TPA-TT-BTDO; (b) AQY of TPA-T-BTDO; (c) AQY of TPA-DT-BTDO; (d) AQY of TPA-TT-BTDO

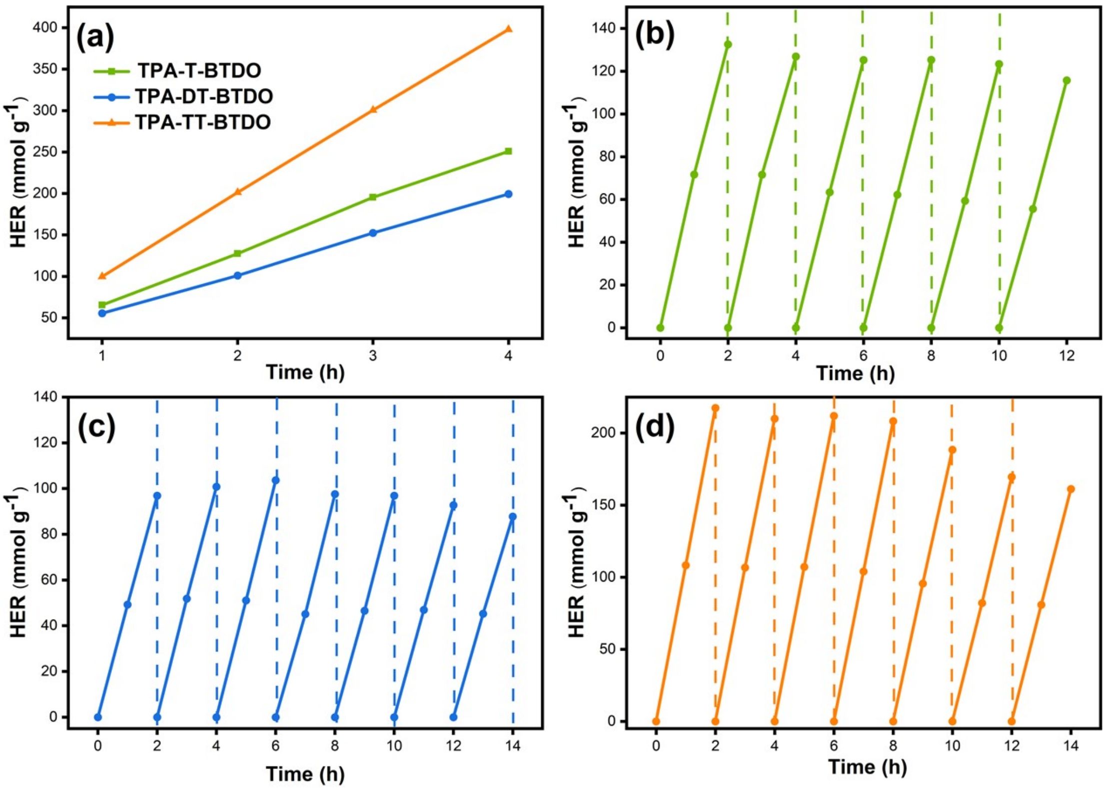


Fig. S12 Cyclic performance of the polymers: (a) HER activity, cycling stability of (b) TPA-T-BTDO, (c) TPA-DT-BTDO, (d) TPA-TT-BTDO

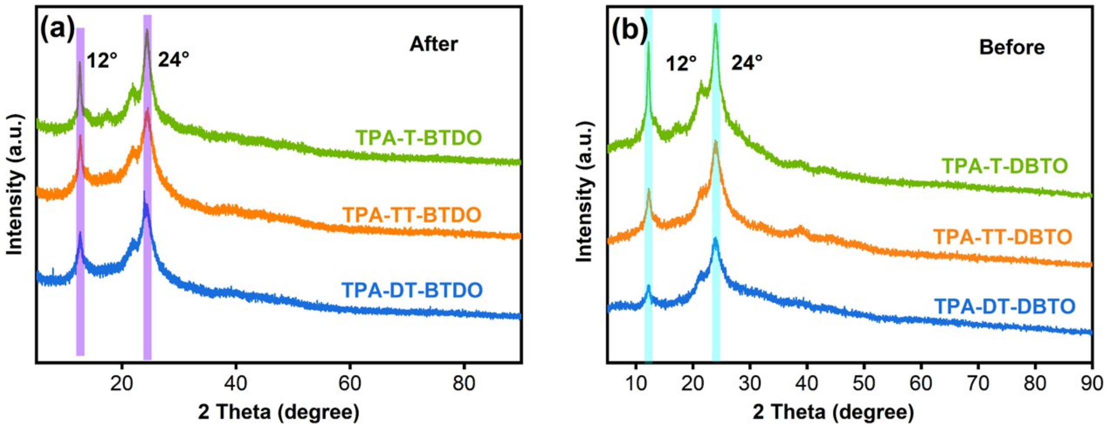


Fig. S13 Structural characterization of polymer (b) before and (a) after hydrogenation.

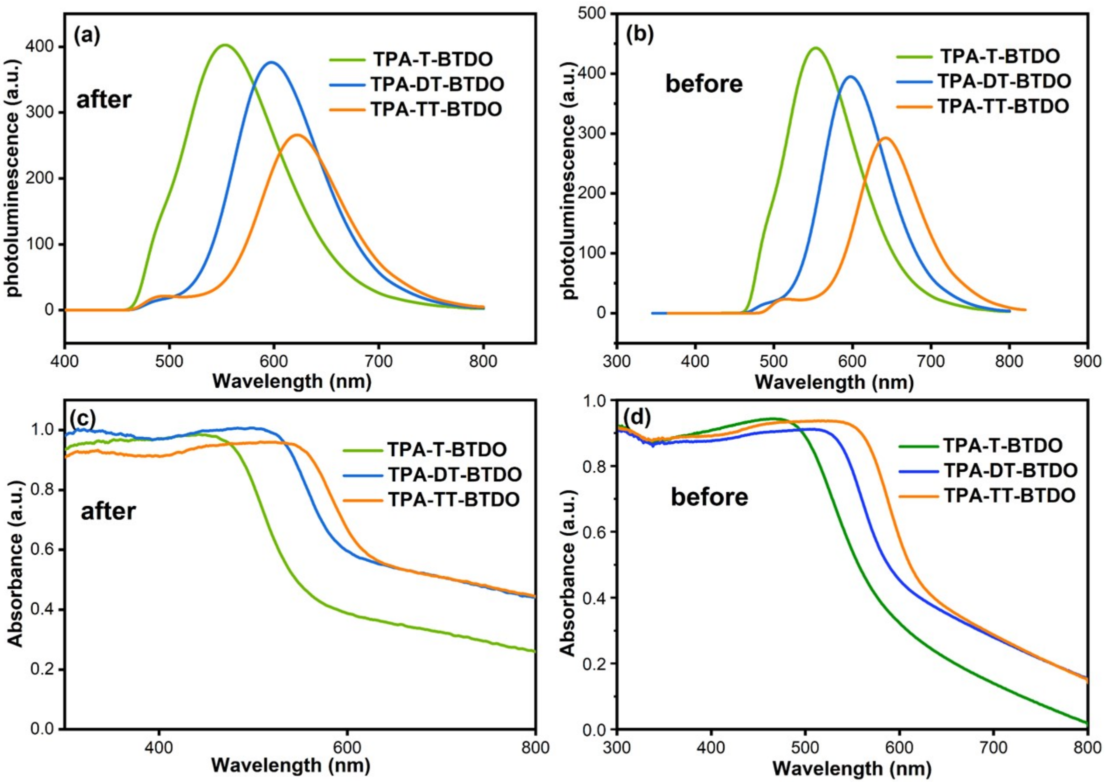


Fig. S14 Repeated performance testing of polymer catalyst: (a) PL spectra of catalysts after H_2 production; (b) PL spectra of catalysts before H_2 production; (c) Uv-Vis spectra of catalysts after H_2 production; (d) Uv-Vis spectra of catalysts before H_2 production.

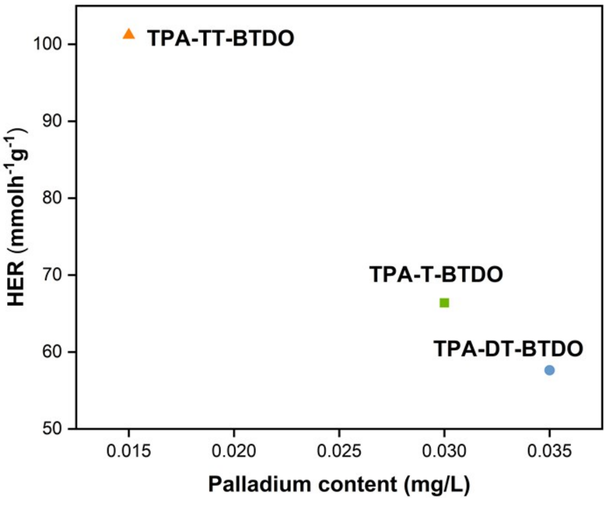


Fig. S15 Residual Pd content in polymers as determined by ICP