

Supporting Information for

Realizing high hydrogen evolution activity under visible light by narrow band gap organic photocatalysts

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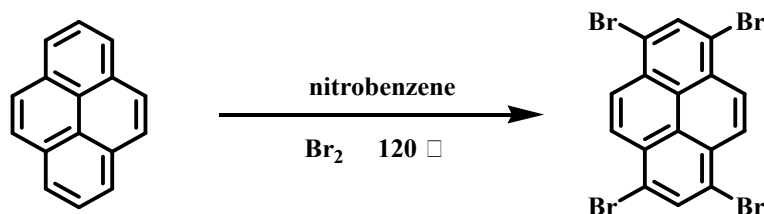
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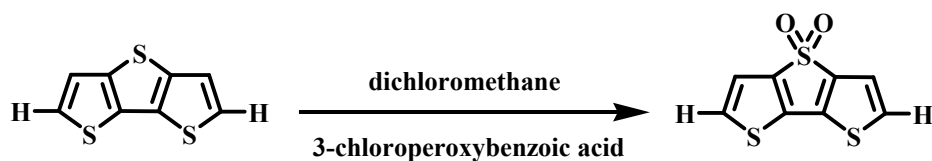
Experimental Section

Synthesis of 1,3,6,8-tetrabromopyrene



At room temperature, pyrene (10.0 g, 50.0 mmol) and about 150 mL nitrobenzene solution was added into a two-necked flask with strong stirring. About 13 mL liquid bromine was slowly added into the mixture solution after pyrene is completely dissolved. Then, the reaction solution was heated to 120 °C and stirred for 6 h. The mixture was poured into 150 mL deionized water and the crude product was obtained by filtration when the reaction solution was cooled to room temperature. The undissolved crude product was washed successively with deionized water, dichloromethane, acetone and tetrahydrofuran, respectively. After drying in vacuum at 60 °C for 24 h, the pure 1,3,6,8-tetrabromopyrene was obtained as white solid (23.6 g, 91% yield).

Synthesis of dithieno[3,2-b:2',3'-d]thiophene-S,S-dioxide



At room temperature, dithieno[3,2-b:2',3'-d]thiophene (0.98g, 5.0 mmol) and 5 mL anhydrous dichloromethane was added into a 100 mL reaction flask, 3-chloroperoxybenzoic acid (2.59g, 15.0 mmol) was dissolved in 30 mL anhydrous dichloromethane. Then, the 3-chloroperoxybenzoic acid solution in anhydrous dichloromethane was slowly added into the reaction flask, and the reaction solution was stirred for 24 h at room temperature. Then, the mixture was washed with sodium carbonate aqueous solution and extracted with dichloromethane, the collected organic phase was dried by MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (petroleum ether/dichloromethane = 2:1 vol/vol). After drying at 50 °C under vacuum for 24 h, the product was obtained as yellow solid (1.06 g, 93%). ¹H NMR (ppm, 400 MHz; CDCl₃): δ 7.35 (d, J = 5.2 Hz, 2H), 7.22 (d, J = 7.6 Hz, 2H). ¹³C NMR (ppm, 300 MHz; CDCl₃): δ 143.48, 136.16, 129.65, 120.42. GC-MS: calculated: C₈H₄O₂S₃, 228.31, found: 227.87.

Characterization

Elemental composition was measured by EURO EA3000 Elemental Analyzer. Thermogravimetric analysis (TGA) measurement was performed by using a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 25 to 750 °C under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. Fourier-transform infrared (FT-IR) spectra were collected on a Tensor 27 FT-IR 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 measurement (PXRD) 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-Lambda 950, PerkinElmer, US) using BaSO₄ as a reference sample. The fluorescence properties of the polymers were measured with a Shimadzu F-7000 PC fluorescence spectrometer by using excitation wavelength of 380 nm at room temperature. 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-Emmett-Teller (BET) method. The residual Pd content was determined by inductively coupled plasma mass spectrometry (ICP-MS). Pd and other elements content were obtained by energy dispersive X-ray spectroscopy (EDX). 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 $E_{\text{NHE}} = E_{\text{SCE}} + 0.241 \text{ V}$ 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 for CV measurement. The prepared working electrode from the polymer catalyst and 5 wt% Nafion was immersed in 1.0 M Na₂SO₄ aqueous solution.

Photocatalytic hydrogen generation experiment

The photocatalytic hydrogen generation experiments of the photocatalysts were performed on a set of photocatalytic equipment (Beijing Perfect Light Co.). First of all, the as-synthesized polymer of 10 mg was ultrasonically dispersed in a mixed solution containing 80 mL water and 20 mL TEA or TEOA as a sacrificial electron donor to form a well-dispersed polymer suspension. After the photocatalytic system was degassed to remove the dissolved air, the suspension was irradiated with a 300 W Xe lamp under vacuum with stirring. Circulating cooling water was used to keep the photocatalytic reaction temperature at 6 °C. A 420 nm filter was used to filter off ultraviolet light to obtain the simulated visible light irradiation ($\lambda > 420$ nm). The produced hydrogen was measured online by using a gas chromatograph.

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, 500, 550, 600 and 650 nm. The irradiation area was controlled as 6.25 cm². The AQY was calculated as below:^[1]

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

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/cm²), 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. In addition, the mass loading of the polymer photocatalyst could significantly affect the apparent quantum yield since different mass loading of photocatalyst will lead to different amount of the produced H₂ (M). For example, much higher external quantum efficiency of ~ 6.9% was obtained by using 25 mg PyDTDO-3 than 10 mg used in this work. It seems that there is no a unified standard at present since different research groups employed different mass loading of photocatalyst to test the external quantum efficiency/apparent quantum yield (Table S2). In this work, the total amount of the produced H₂ (M mol) is from 10 mg in 6 h. The photoreaction time and irradiation area are t = 3600 s, S = 6.25 cm², respectively. The produced H₂ amount M are 26.44, 27.76, 25.25, 35.15, 23.77, 13.85 μmol h⁻¹ (10 mg) under 420, 450, 500, 550, 600, 650 nm with the intensity of incident light of 18.1, 17.6, 14.6, 17.3, 19.7 and 21.6 mW cm⁻², respectively.

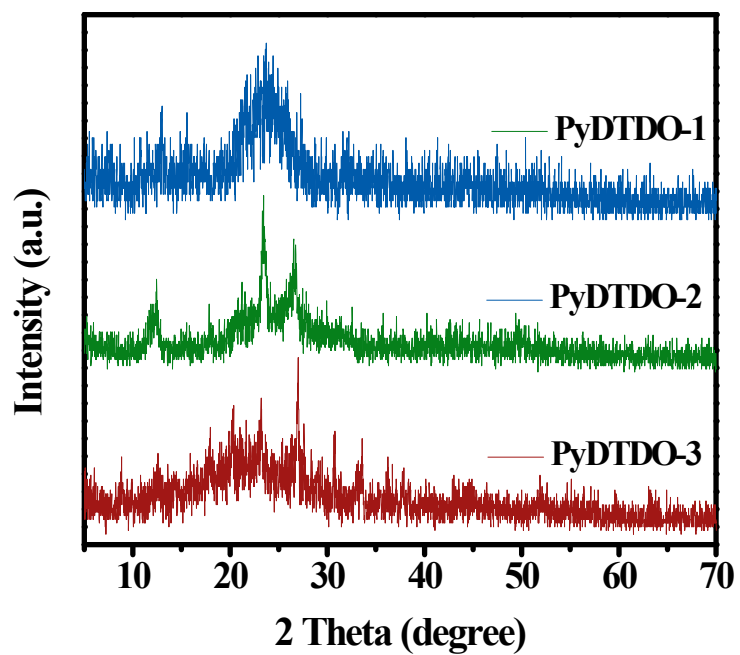


Fig. S1. Powder XRD patterns of PyDTDO-1, PyDTDO-2 and PyDTDO-3.

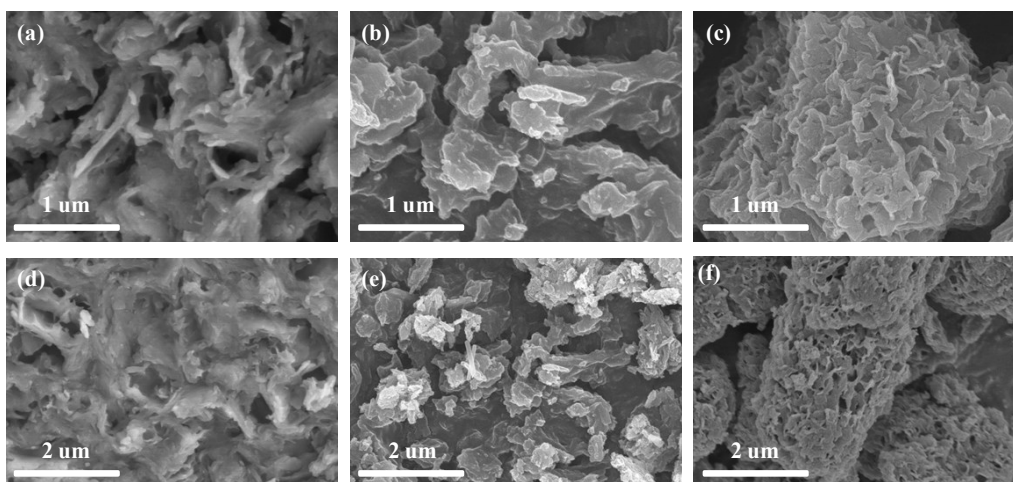


Fig. S2. Scanning electron microscope images of PyDTDO-1 (a & d), PyDTDO-2 (b & e) and PyDTDO-3 (c & f).

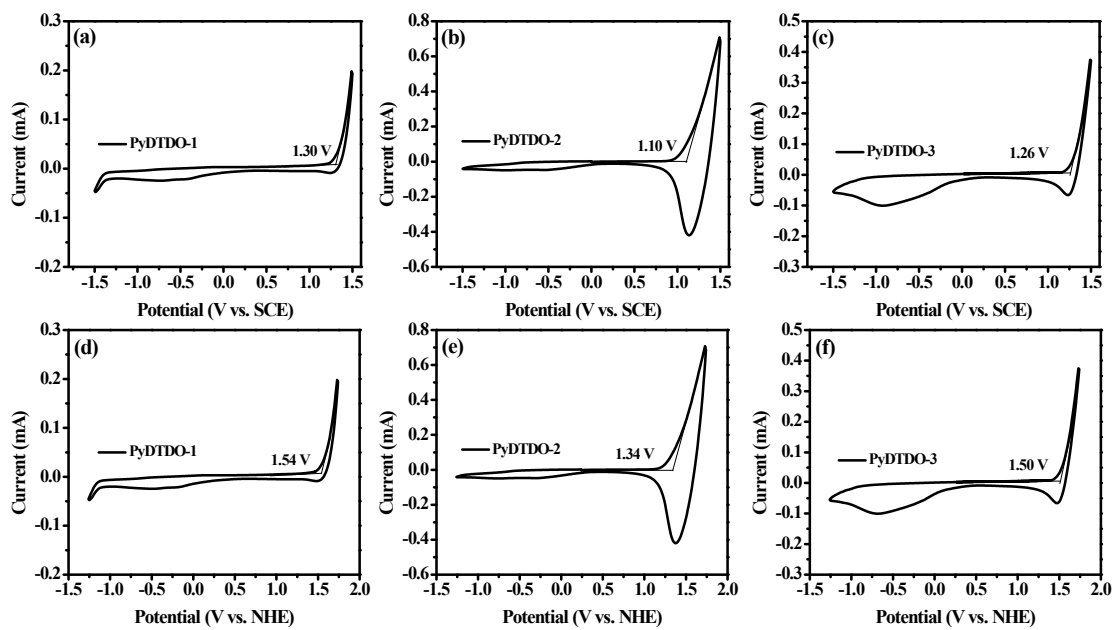


Fig. S3. The CV curves of the polymers vs SCE (a-c) and NHE (d-f).

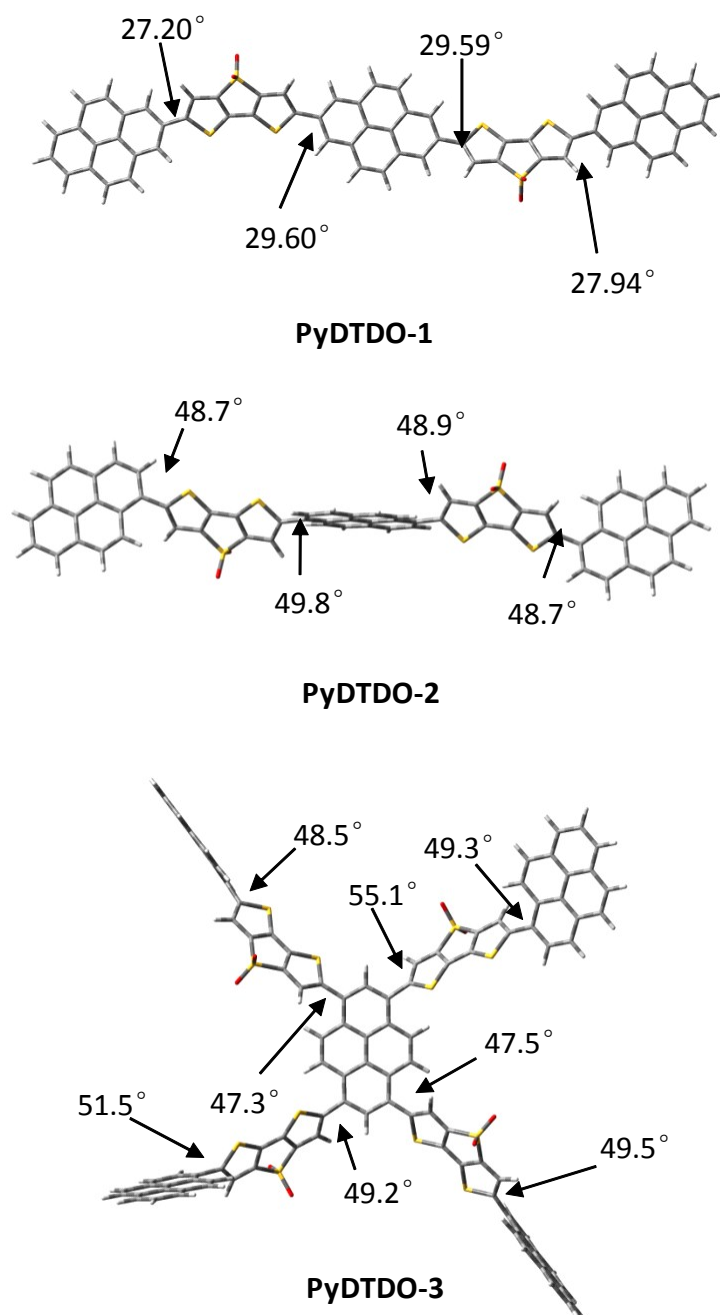


Fig. S4. The DFT geometry optimizations and the dihedral angles of the polymers.

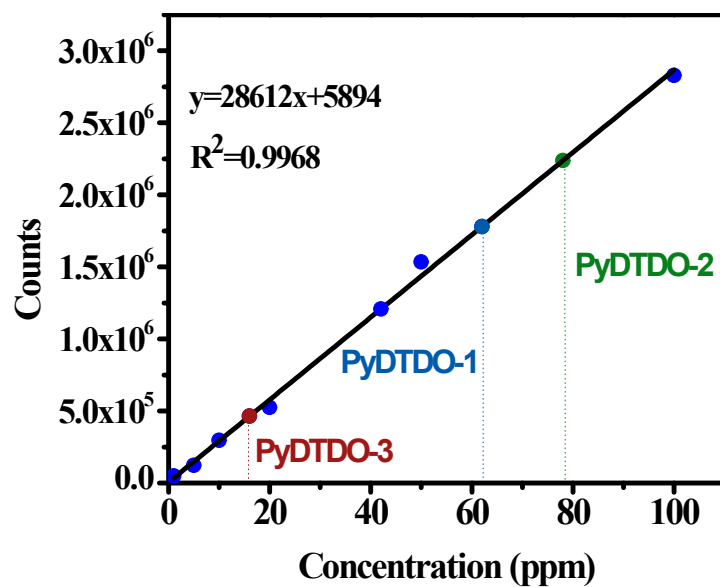


Fig. S5. The residual Pd contents in PyDTDO-1, PyDTDO-2 and PyDTDO-3 measured by ICP-MS.

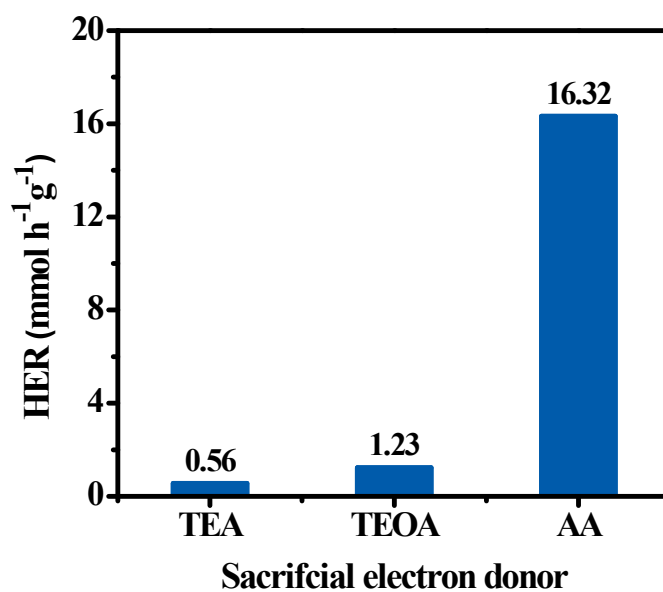


Fig. S6. The comparison of hydrogen evolution rate of PyDTDO-3 in aqueous solution containing different sacrificial reagents under visible light.

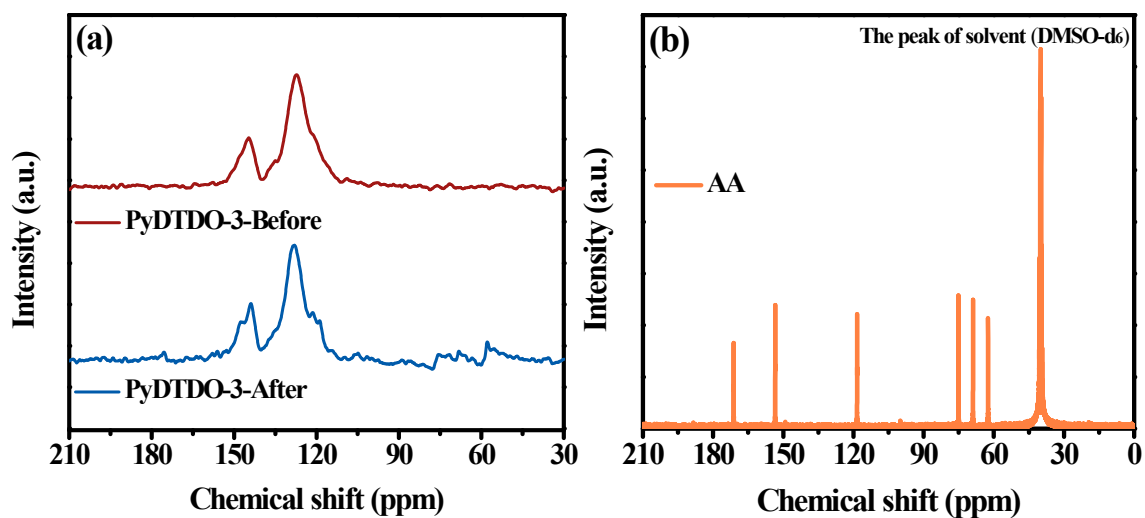


Fig. S7. (a) The solid-state ^{13}C CP-MAS NMR spectra of the polymer PyDTDO-3 before and after photocatalytic reaction under visible light ($\lambda > 420$ nm) for 24 h in a AA/DMF/water mixture. (b) the liquid-state ^{13}C NMR spectrum of AA.

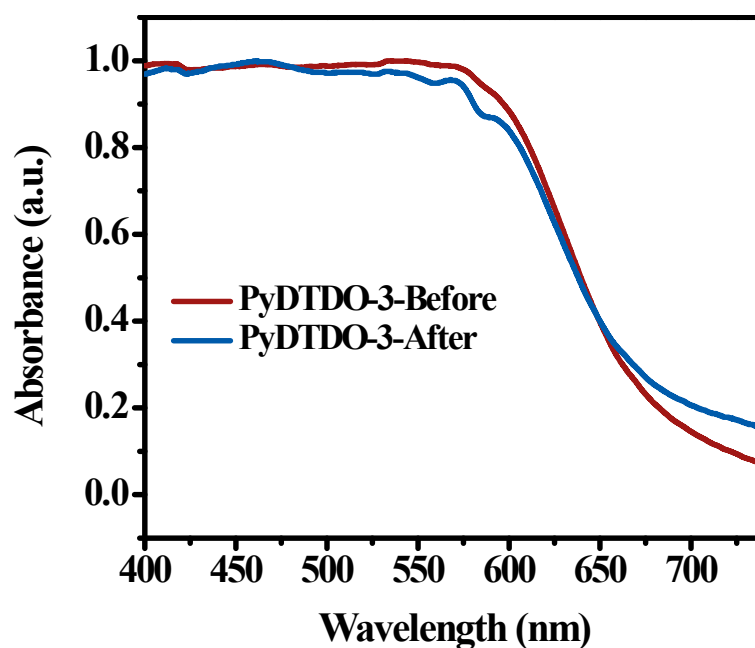


Fig. S8. UV-Vis absorption spectra for the polymer PyDTDO-3 before and after photocatalytic reaction under visible light ($\lambda > 420$ nm) for 24 h in a AA/water/DMF mixture.

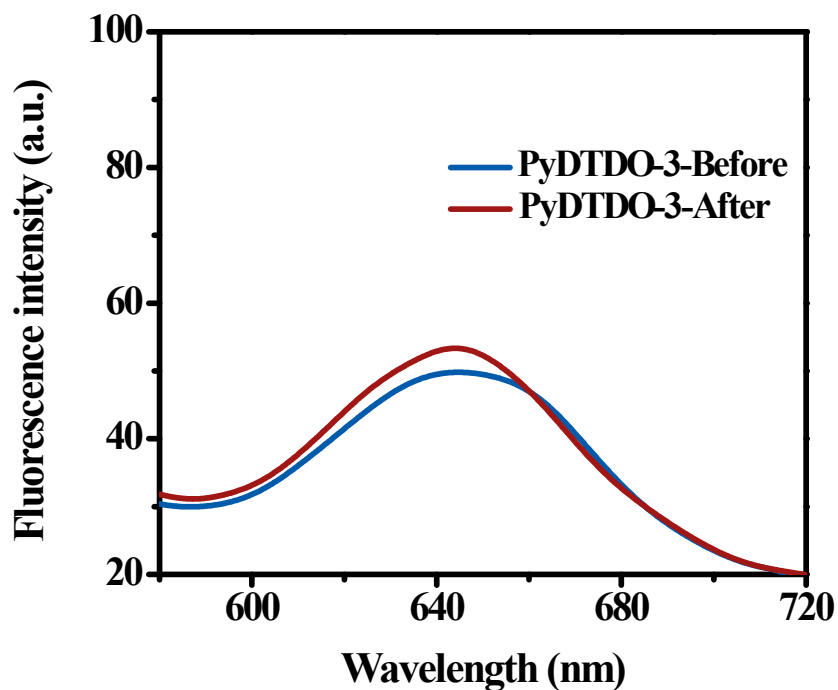


Fig. S9. Photoluminescence spectra of the polymer PyDTDO-3 before and after photocatalytic reaction under visible light ($\lambda > 420$ nm) for 24 h in a mixture of AA/water/DMF.

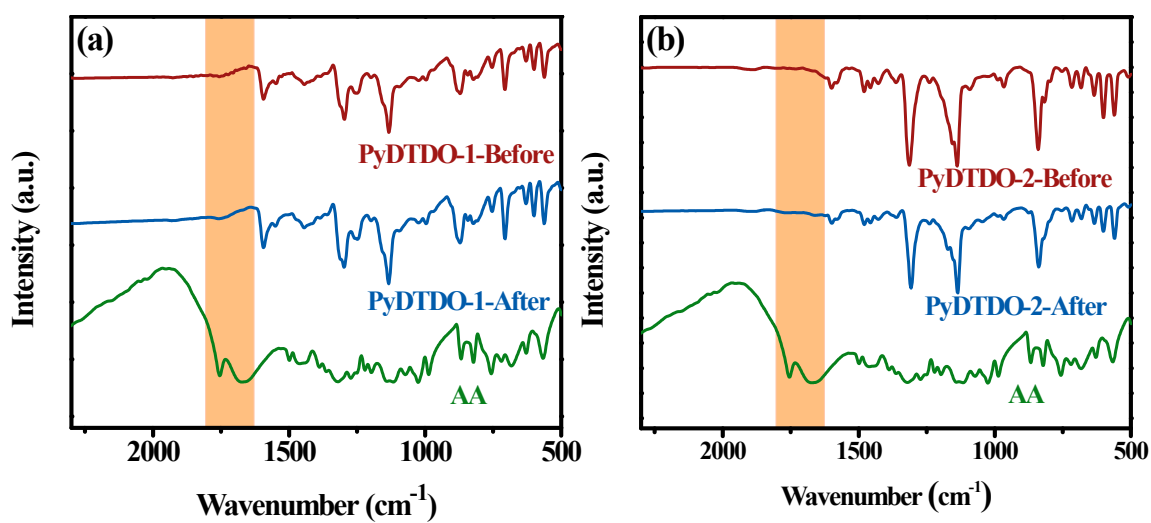


Fig. S10. FT-IR spectra of PyDTDO-1 (a), PyDTDO-2 (b) before and after photocatalytic reaction under visible light for 24 h in a mixture of AA/DMF/water.

Table S1. Fitted decay time of the polymers

Polymer	$\tau 1$ (ns)	$\tau 2$ (ns)
PyDTDO-1	0.8449	2.4861
PyDTDO-2	0.9851	/
PyDTDO-3	0.6912	/

Table S2. The summary of the photocatalytic performances of polymeric photocatalysts for hydrogen evolution from water splitting ($\lambda > 420$ nm).

Photocatalysts	cocatalyst	sacrificial reagent	HER (mmol $\text{h}^{-1} \text{g}^{-1}$)	Optical gap (eV)	AQY (%)	Ref.
					3.70 (10 mg@420 nm)	
PyDTDO-3	No	AA	16.32	1.81	3.93 (10 mg@550 nm)	This work
					6.87 (25 mg@550 nm)	
PyDOBT-1	3 wt% Pt	TEOA	8.52	2.37	6.10 (50 mg@400 nm)	[2]
DBTD-CMP1	3 wt% Pt	TEOA	4.60	2.53	3.30 (50 mg@400 nm)	[3]
B-FOBT-1,4-E	No	TEOA	13.3	2.18	5.70 (30 mg@420 nm)	[4]
PySEO-1	3 wt% Pt	TEOA	6.01	1.90	4.10 (50 mg@400 nm)	[5]
P16PySO	No	TEOA	6.38	2.31	3.50 (50 mg@450 nm)	[6]
P-FSO	No	TEOA	8.00	2.31	8.50 (50 mg@420 nm)	[7]
PCP10	No	TEA	8.63	--	1.05 (12 mg@400 nm)	[8]
PySO	No	TEA	4.74	2.58	3.28 (10 mg@420 nm)	[9]
S-CMP3	No	TEA	3.10	2.56	13.2 (30 mg@420 nm)	[10]
PrCMP-1	3 wt% Pt	TEOA	0.005	1.74	--	[11]
CP-CMP-10	No	TEA	0.17	2.33	--	[12]

SP-CMP	No	TEA	0.12	2.84	0.23 (25 mg@420 nm)	[13]
F _{0.5} -CMP	No	Na ₂ S/Na ₂ SO ₃	0.66	2.30	5.8 (5 mg@400 nm)	[14]
P7-E	No	TEOA	6.02	2.79	4.20 (30 mg@420 nm)	[15]
CTF-N	2 wt% Pt	TEOA	10.76	2.17	4.07 (50 mg@420 nm)	[16]
CTF-BT/Th	3 wt% Pt	TEOA	6.60	--	7.30 (50 mg@420 nm)	[17]
Triazine-Ph-CPP	No	TEOA	3.50	2.83	61.5 (32 mg@365 nm)	[18]
CTF-HUST-C1	3 wt% Pt	TEOA	5.10	--	--	[19]
CTF-0-M ₂	3 wt% Pt	TEOA	1.03	2.07	11.0 (100mg@365 nm)	[20]
CTF-15	3 wt% Pt	TEA	2.94	2.58	15.90 (25mg@420 nm)	[21]
Cl-ECF	3 wt% Pt	LA	1.30	2.23	0.68 (20 mg@420 nm)	[22]
g-C ₁₈ N ₃ -COF	3 wt% Pt	AA	0.29	2.42	1.06 (50 mg@420 nm)	[23]
N ₃ -COF	Pt	TEOA	1.70	--	0.44 (5 mg@450 nm)	[24]
Cd-COF (90:10)	0.5 wt% Pt	LA	3.68	--	4.20 (30 mg@420 nm)	[25]
TTR-COF	Au	TEOA	0.43	2.71	--	[26]
TpPa-COF-(CH ₃) ₂	3 wt% Pt	SA	8.33	2.06	--	[27]

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