Supporting Information

Sulfide Oxidation Tuning in 4,8-di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene Based Dual Acceptor Copolymers for Highly Efficient Photocatalytic Hydrogen Evolution

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Keywords: dual acceptor copolymer; benzodithiophene derivatives; different number of sulfonyl group; photocatalytic hydrogen evolution

Experimental Section

General methods

All reagents were acquired from commercial suppliers and used without further purification. 2,6-dibromo-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene and 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide were synthesized according to previously reported procedures.[1] UV–vis transmittance spectra of the polymers were performed using a Hitachi U-3300 spectrophotometer. UV–vis diffuse reflectance spectroscopy was performed on a jasco v650. The HOMO levels of polymers were determined by a Riken Keiki AC-2 photoelectron spectrometer with a UV source. Fluorescence spectra of the polymers were measured using a Hitachi F-7000 spectrophotometer. TGA of the polymers was performed under nitrogen using a TA Q600 instrument over the temperature range of 30–800 °C. X-ray photoelectron spectra were collected using a ULVAC-PHI PHI 5000 Versaprobe II chemical analysis electron spectrometer (ESCA). ^{1}H NMR ^{13}C NMR spectra were measured using a Bruker Avance 500 MHz NMR spectrometer. Solid state ^{13}C NMR spectra were measured using a Bruker Avance III 400 MHz Solid NMR. Mass spectra were performed on JEOL JMS700 HRMS. Time-resolved transient PL spectra of the polymer were measured on a spectrometer (FLS980, Edinburgh Instruments) with a gated photomultiplier tube. Solid ^{13}C NMR spectra were measured using BRUKER AVANCE III 400MHz. Images of contact angle were captured with an upright epifluorescence microscope (E600, Nikon, Japan). Residue palladium of the polymers were performed using a iCAP 7000 Series ICP spectrometer. The molecular geometries of the polymers were optimized, and their orbital energies and charge distributions computed using DFT at the and B3LYP/6-31G** (H, C, O, P) levels. Fluorescence microscope were collected using a Nikon ECLIPSE Ti-U.

General polymerization procedure

A mixture of monomers, Na_2CO_3, $Pd(PPh_3)_4$, tetra-n-butylammonium bromide, water and toluene were evacuated and degassed by nitrogen for 30 min and then refluxed for 72 h. Furthermore, the reaction mixture was poured into methanol and washed with methanol, hexane, chloroform, water to remove by-products and reactants. Finally, the polymer was collected and dried under vacuum.

Poly{2,6-dibromo-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-alt dibenzo[b,d]thiophene 5,5-dioxide} (PBDTTS)

Monomer BDTTBr (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene, 736 mg, 1.0 mmol), BSO (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide, 468 mg, 1.0 mmol), Na_2CO_3 (2544 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization.

Poly{2,6-dibromo-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide -alt-dibenzo[b,d]thiophene 5,5-dioxide} (PBDTTS-1SO)

Monomer BDTTBr-1SO (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide, 692 mg, 0.9 mmol), BSO (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide, 421 mg, 0.9 mmol), Na_2CO_3 (2289 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 11.7 mg, 0.036 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), toluene (35 mL), and water (9 mL) were used for polymerization.

Poly{2,6-dibromo-8-(5-(2-ethylhexyl)-1,1-dioxidothiophen-2-yl)-4-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide -alt-dibenzo[b,d]thiophene 5,5-dioxide} (PBDTTS-2SO)

Monomer BDTTBr-2SO (8-(5-(2-ethylhexyl)-1,1-dioxidothiophen-2-yl)-4-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide, 320 mg, 0.4

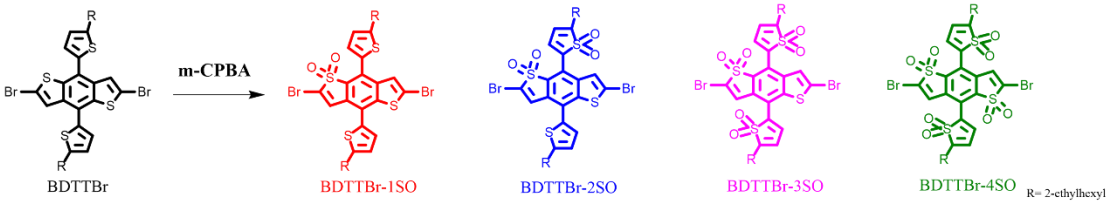
mmol), BSO (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide, 187 mg, 0.4 mmol), Na_2CO_3 (1017 mg, 9.6 mmol), tetra-n-butylammonium bromide (TBAB, 5.2 mg, 0.016 mmol), $Pd(PPh_3)_4$ (22 mg, 0.019 mmol), toluene (15 mL), and water (4 mL) were used for polymerization.

Poly{2,6-dibromo-4,8-bis(5-(2-ethylhexyl)-1,1-dioxidothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide -alt-dibenzo[b,d]thiophene 5,5-dioxide} (PBDTTS-3SO)

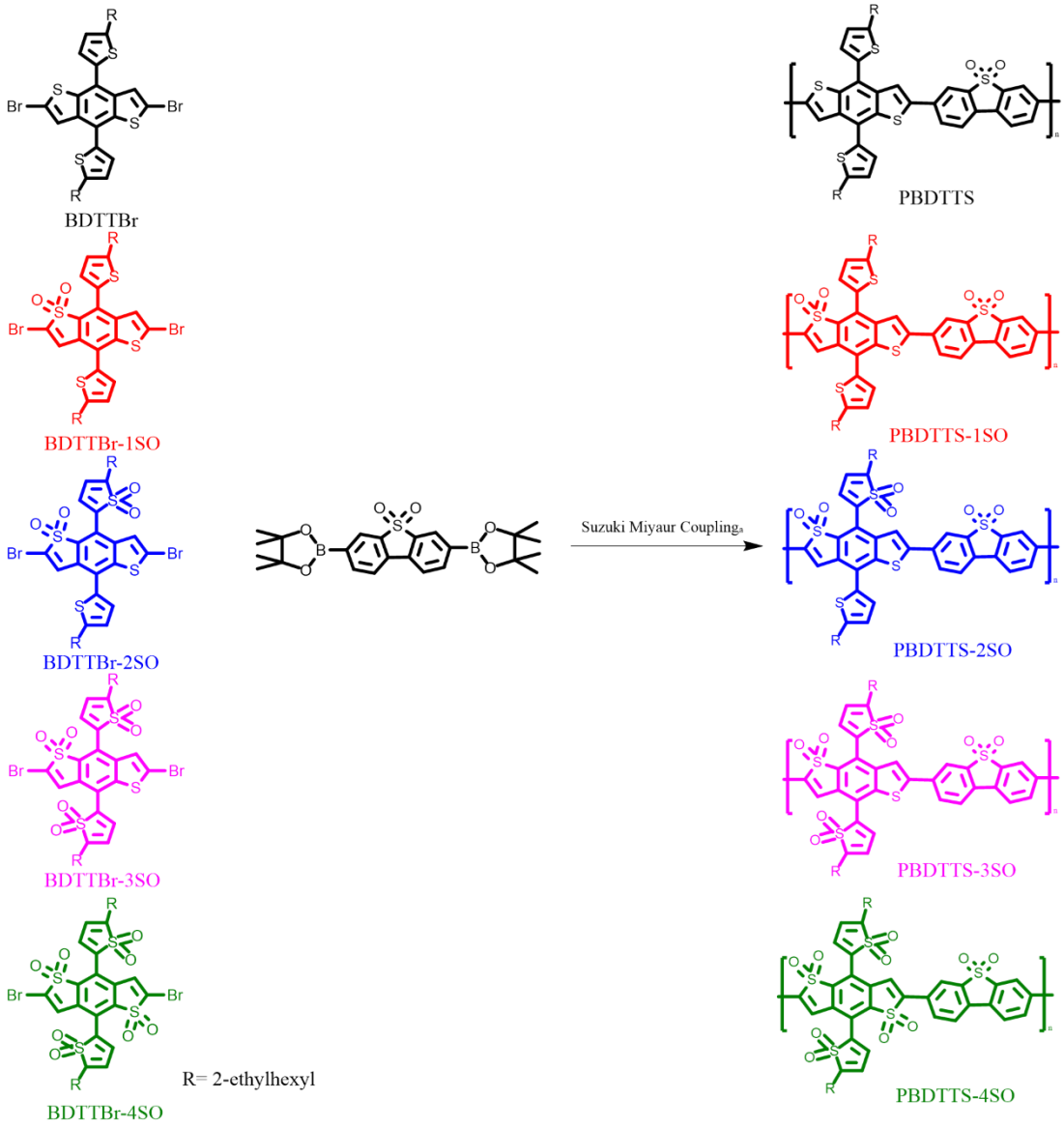
Monomer BDTTBr-3SO (4,8-bis(5-(2-ethylhexyl)-1,1-dioxidothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide, 208 mg, 0.25 mmol), BSO (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide, 117 mg, 0.25 mmol), Na_2CO_3 (636 mg, 6 mmol), tetra-n-butylammonium bromide (TBAB, 3.2 mg, 0.01 mmol), $Pd(PPh_3)_4$ (16 mg, 0.012 mmol), toluene (10 mL), and water (2.5 mL) were used for polymerization.

Poly{2,6-dibromo-4,8-bis(5-(2-ethylhexyl)-1,1-dioxidothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1,5,5-tetraoxide -alt-dibenzo[b,d]thiophene 5,5-dioxide } (PBDTTS-4SO)

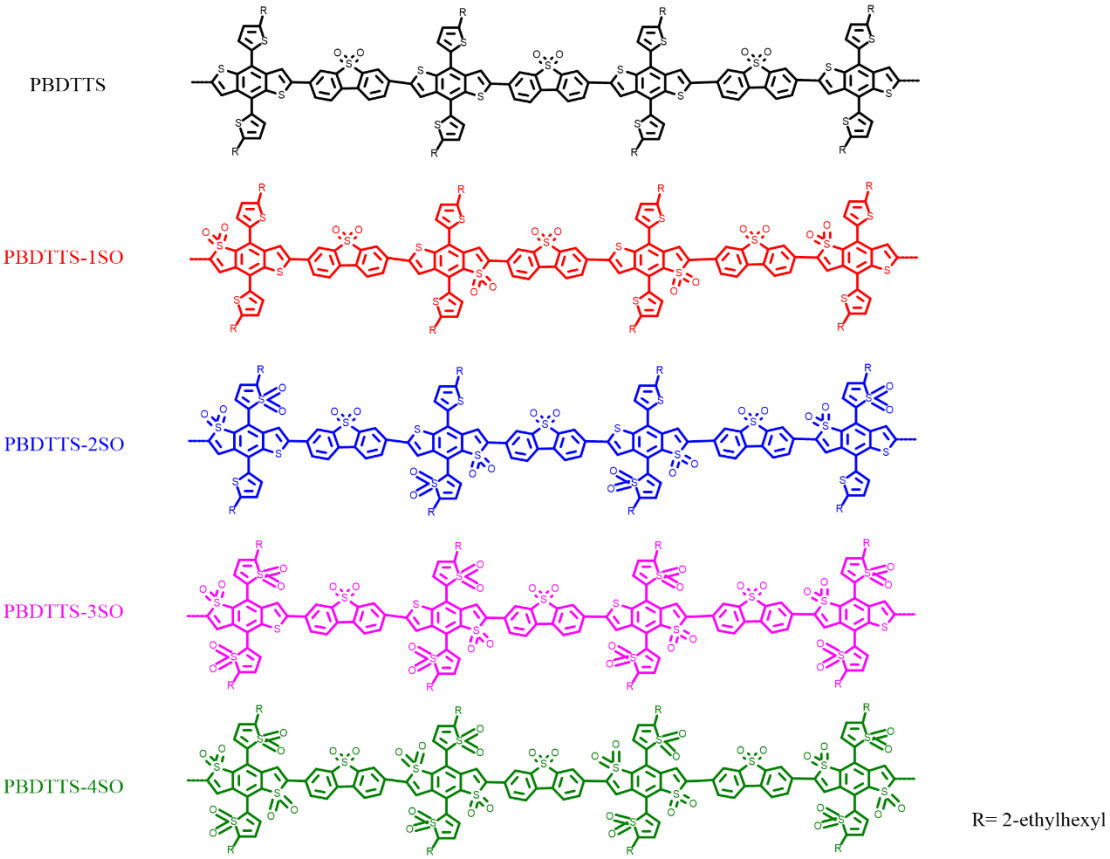
Monomer BDTTBr-1SO (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene 1,1-dioxide, 778 mg, 0.9 mmol), BSO (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide, 421 mg, 0.9 mmol), Na_2CO_3 (2289 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 11.7 mg, 0.036 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), toluene (35 mL), and water (9 mL) were used for polymerization.



Scheme S1. Synthetic diagram of BDTTBr derivatives.



Scheme S2. Synthetic diagram of conjugated polymers.



Scheme S3. Molecular structures of conjugated polymers.

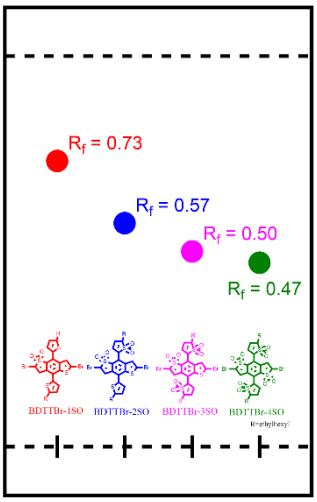


Figure S1. Thin layer chromatography for BDTTBr derivatives.

Table S1. Synthetic conditions of BDTTBr derivatives.

	Solvent	Time (h)	Temperature (°C)	mCPBA (eq)	R_f [a)]	Yield (%)
BDTTBr-1SO	DCM	4	40	4	0.73	57.6
BDTTBr-2SO	DCM	16	40	9	0.57	8.3
BDTTBr-3SO	DCM	16	40	9	0.50	13.3
BDTTBr-4SO	Chloroform	24	60	18	0.47	37.5

[a)] Obtained from thin-layer chromatography (DCM:Hexane = 1:1).

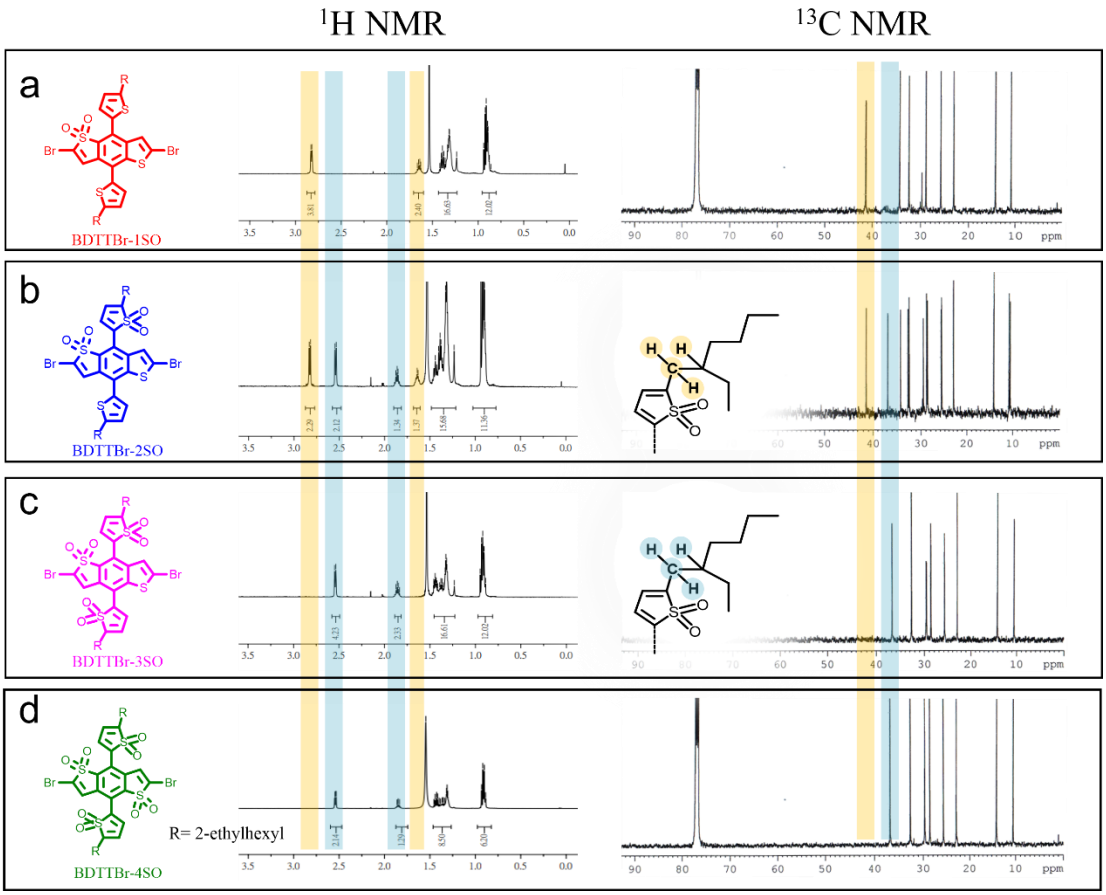


Figure S2. ^{1}H NMR, ^{13}C NMR, HRMS of (a) BDTTBr-1SO, (b) BDTTBr-2SO, (c) BDTTBr-3SO, and (d) BDTTBr-4SO.

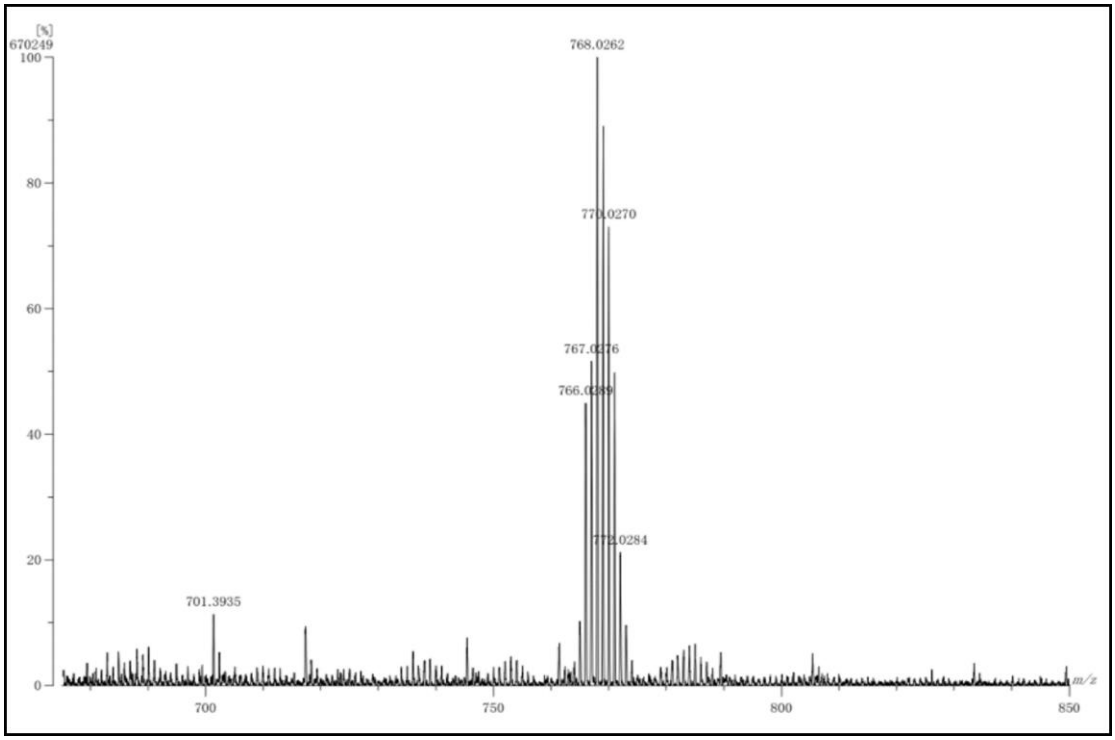


Figure S3. Mass spectra of BDTTBr-1SO.

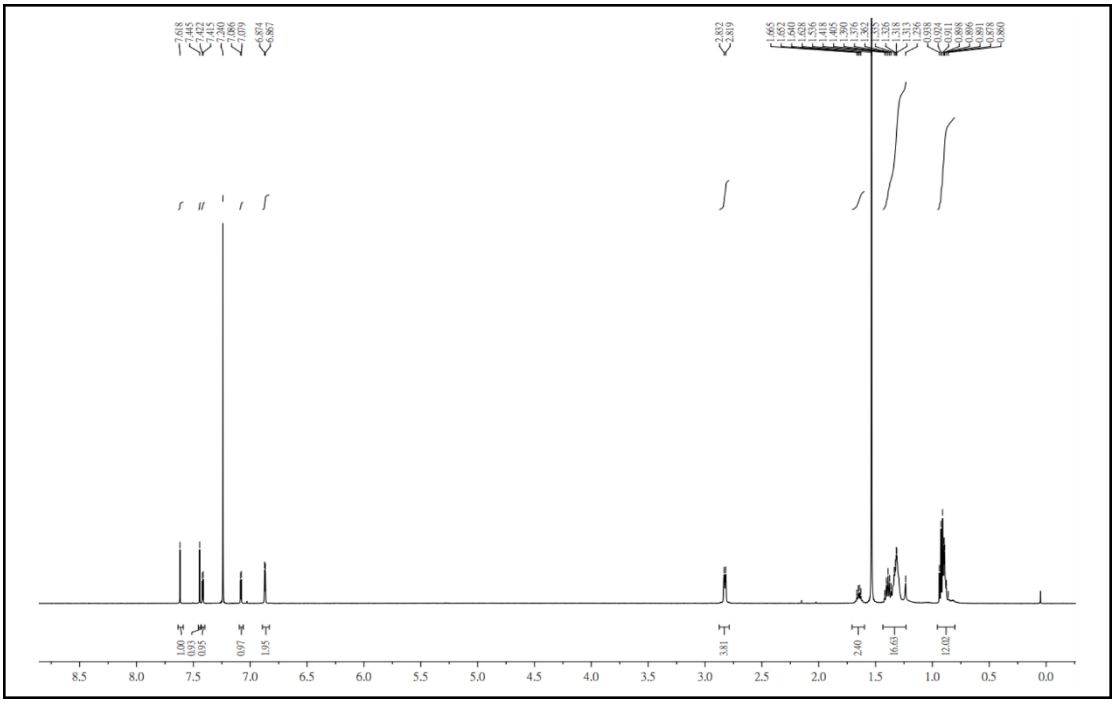


Figure S4. ^{1}H NMR spectra of BDTTBr-1SO.

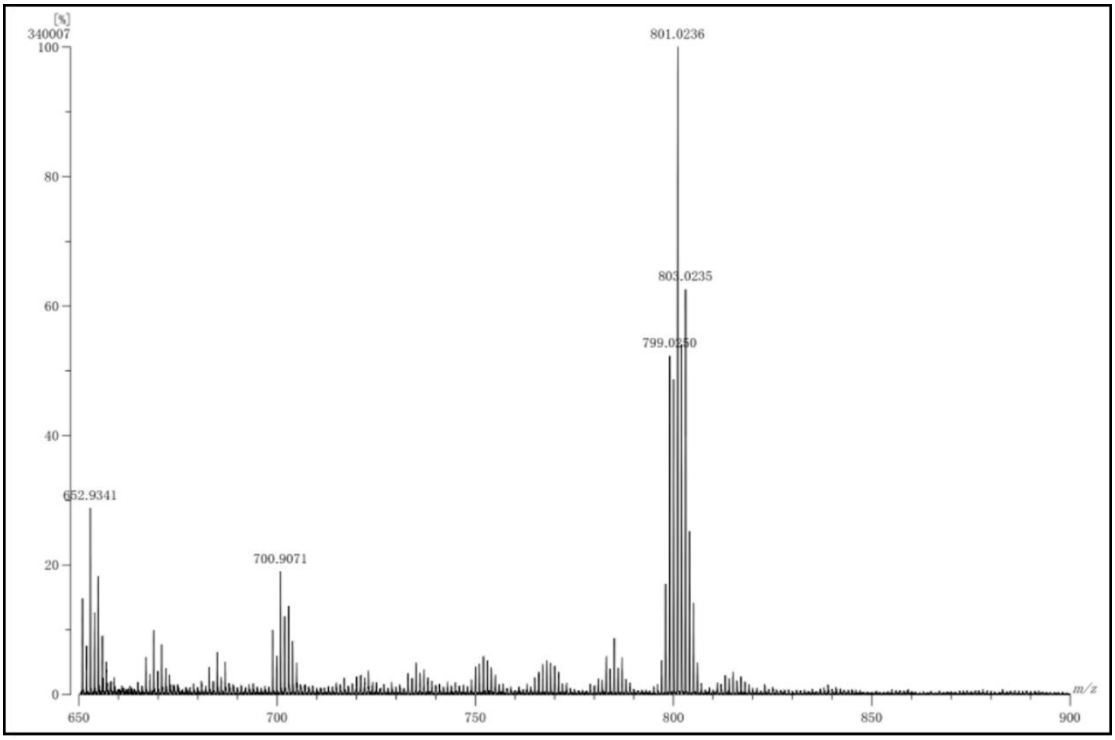


Figure S5. Mass spectra of BDTTBr-2SO..

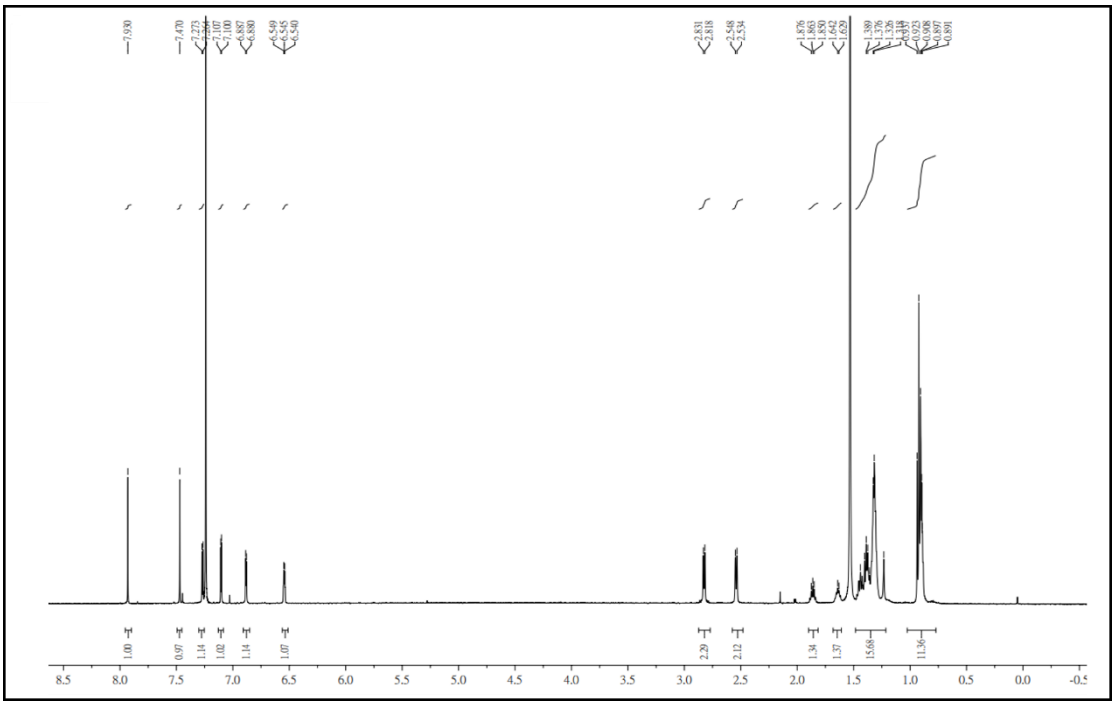


Figure S6. ^{1}H NMR spectra of BDTTBr-2SO.

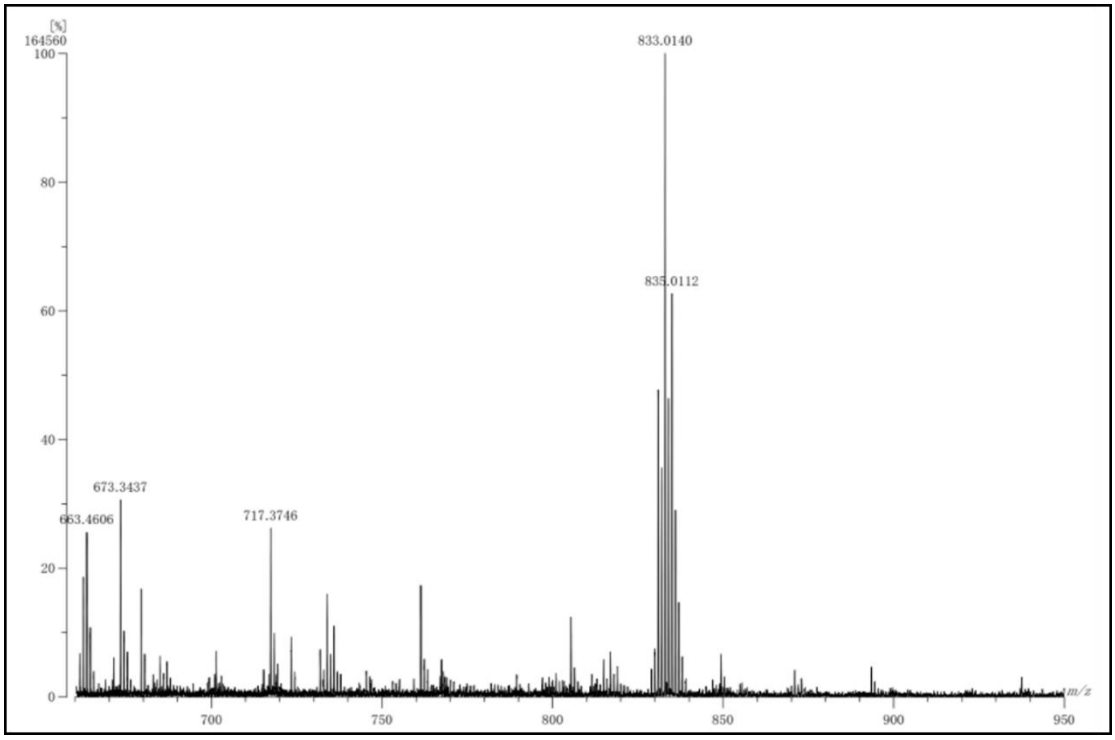


Figure S7. Mass spectra of BDTTBr-3SO.

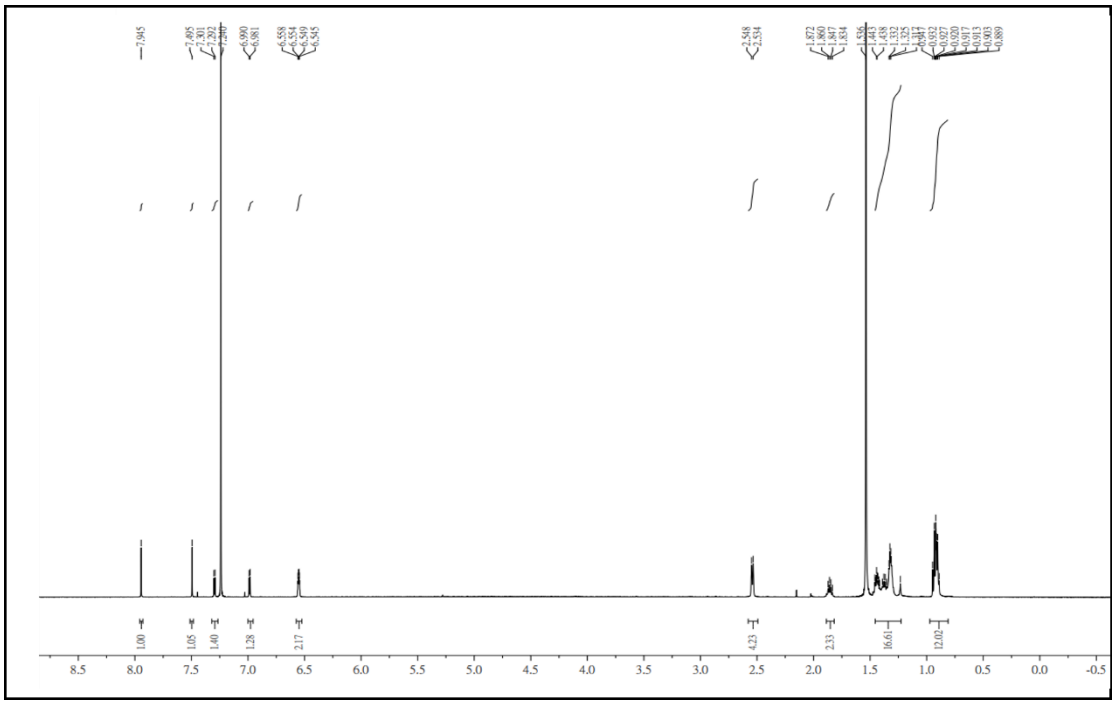


Figure S8. ^{1}H NMR spectra of BDTTBr-3SO.

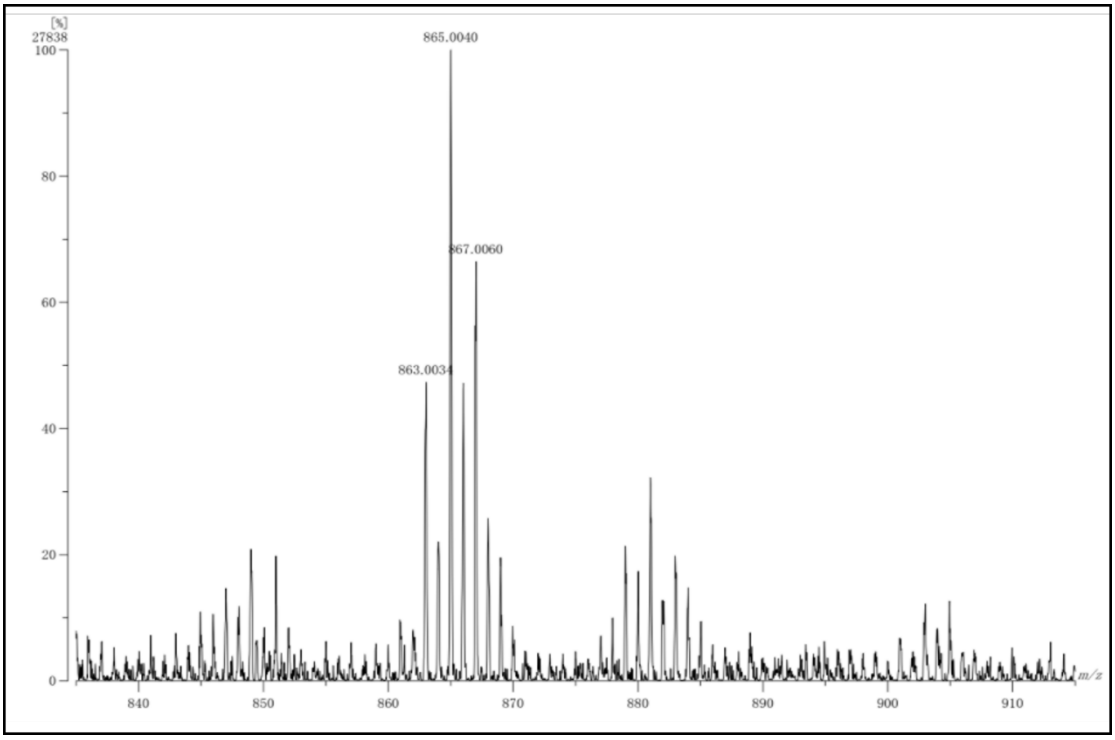


Figure S9. Mass spectra of BDTTBr-4SO.

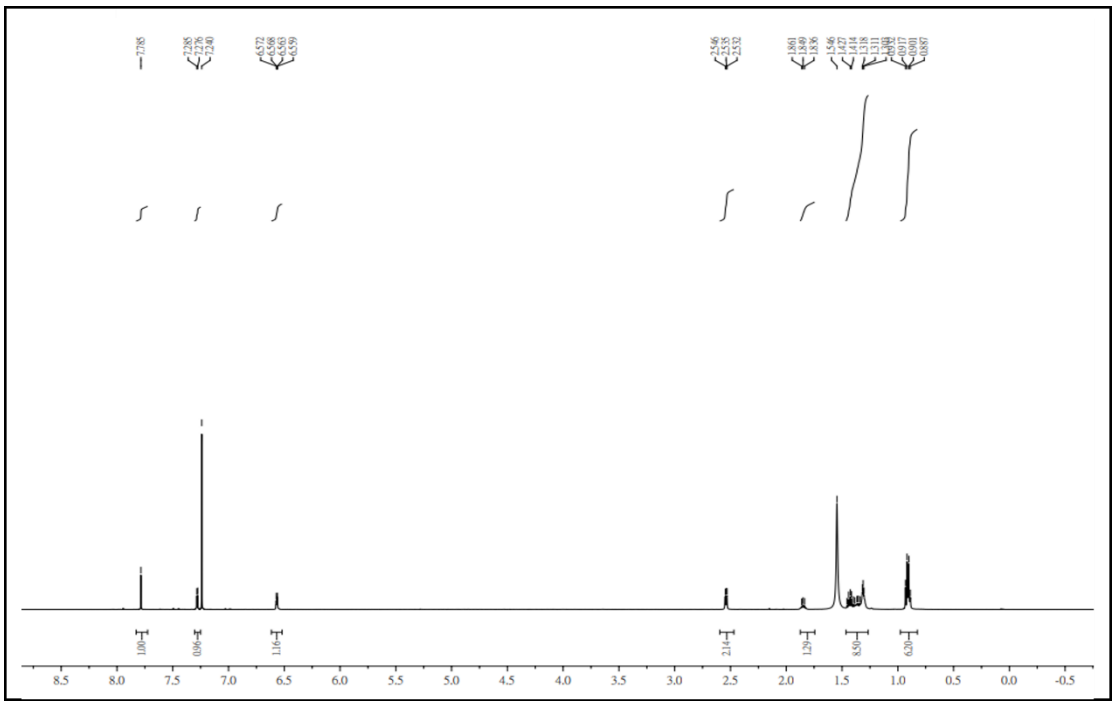


Figure S10. ^{1}H NMR spectra of BDTTBr-4SO.

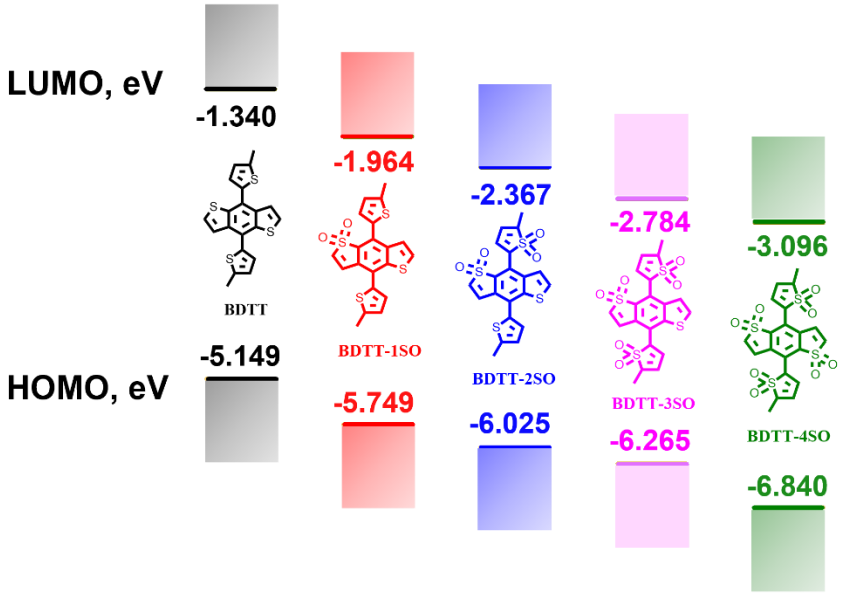


Figure S11. Calculated LUMO and HOMO energy levels and optical energy gaps of the BDTT derivatives.

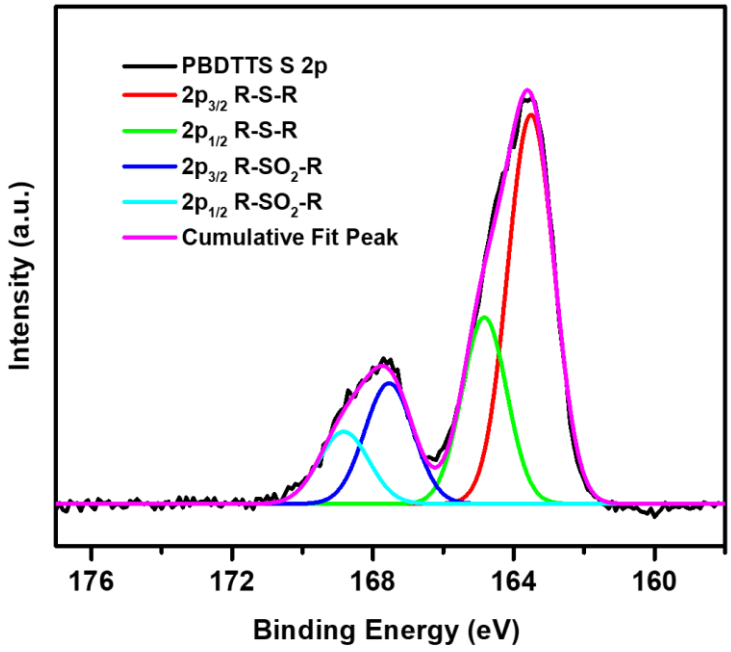


Figure S12. XPS S 2p of PBDTTS.

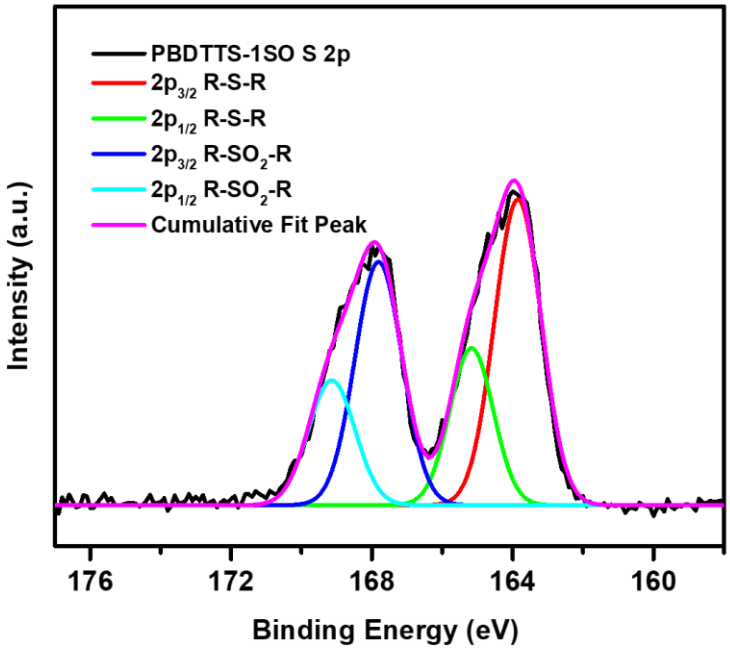


Figure S13. XPS S 2p of PBDTTS-1SO.

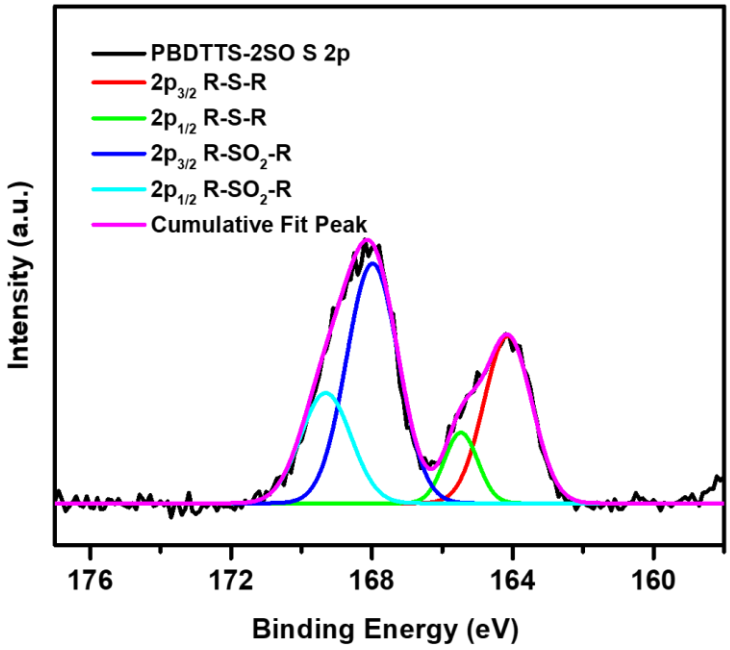


Figure S14. XPS S 2p of PBDTTS-2SO.

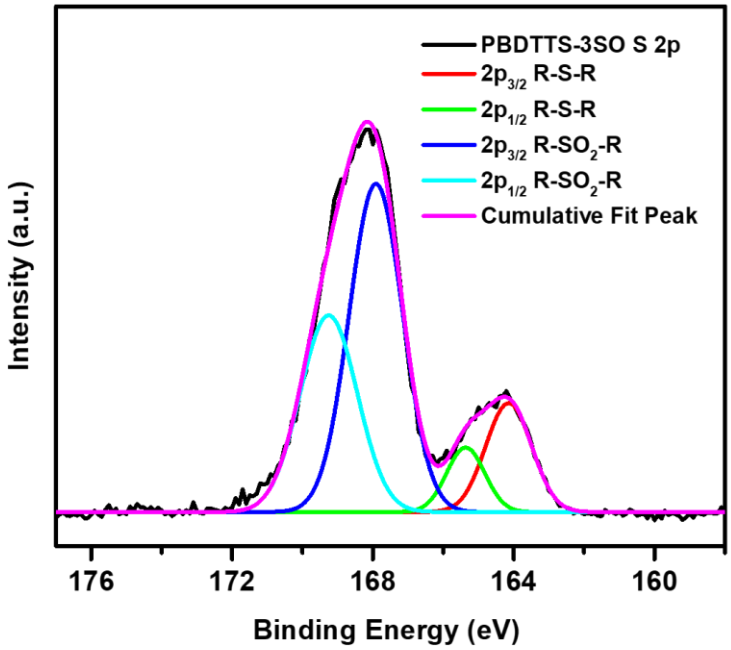


Figure S15. XPS S 2p of PBDTTS-3SO.

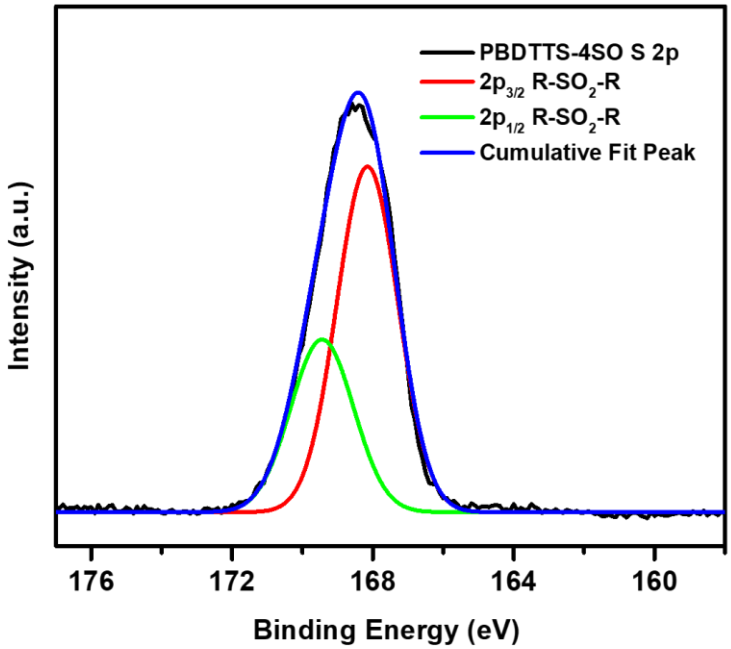


Figure S16. XPS S 2p of PBDTTS-4SO.

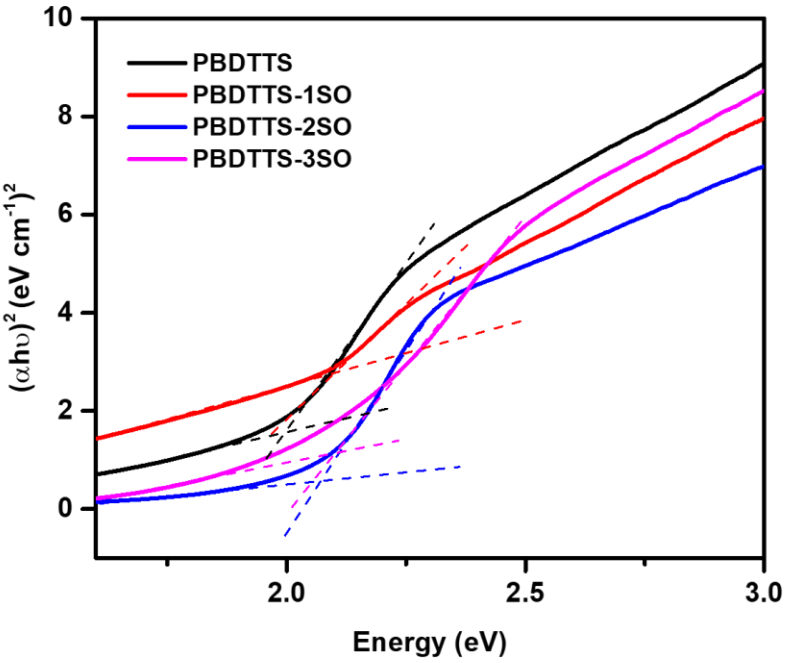


Figure S17. Tauc plot of polymers.

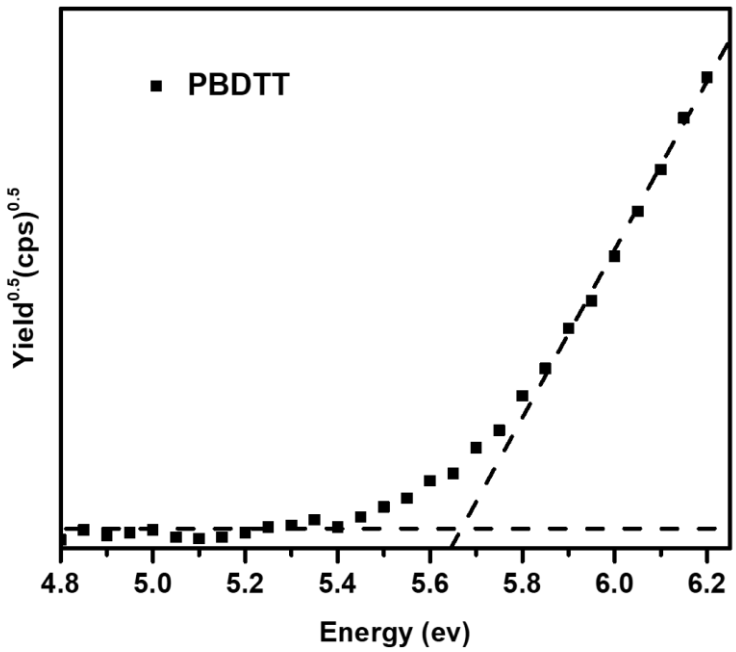


Figure S18. Photoelectron spectroscopy of PBDTT.

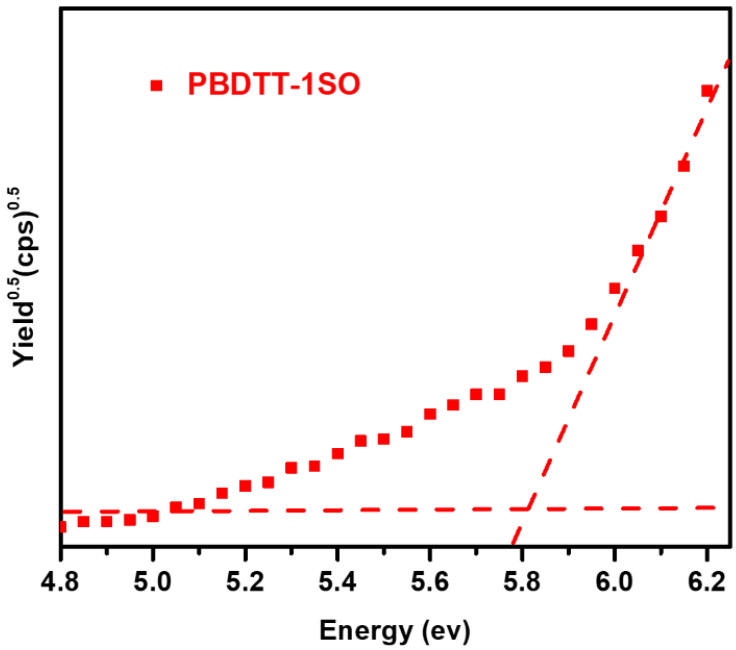


Figure S19. Photoelectron spectroscopy of PBDTT-1SO.

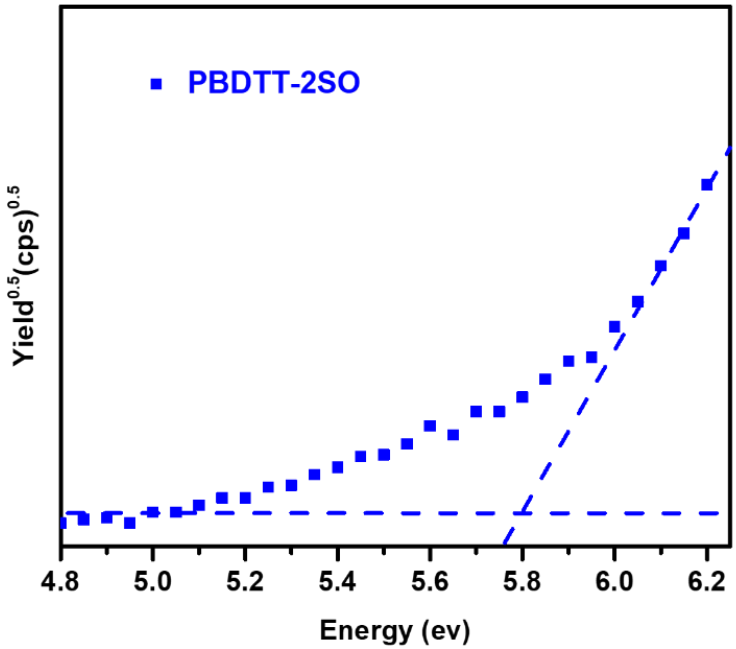


Figure S20. Photoelectron spectroscopy of PBDTT-2SO.

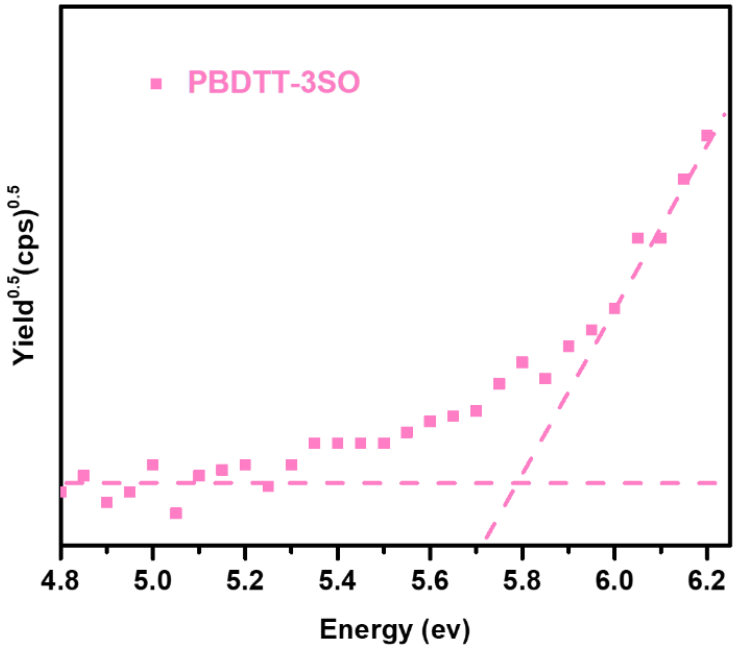


Figure S21. Photoelectron spectroscopy of PBDTT-3SO.

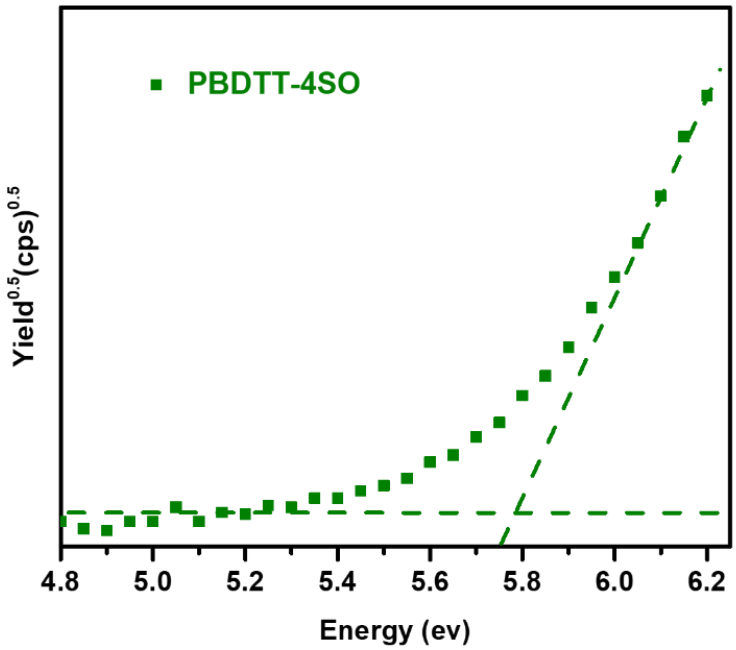


Figure S22. Photoelectron spectroscopy of PBDTT-4SO.

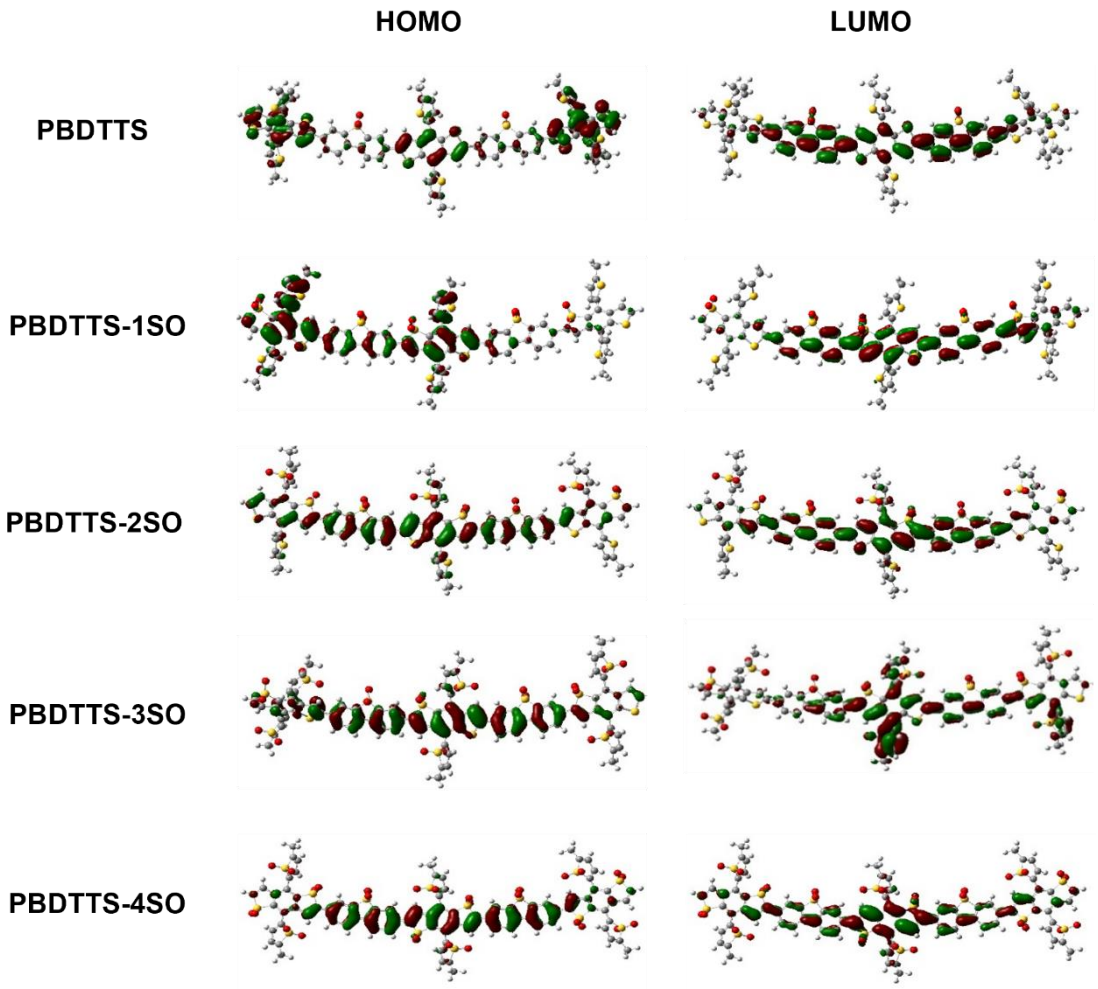


Figure S23. Calculated HOMO and LUMO levels of polymers.

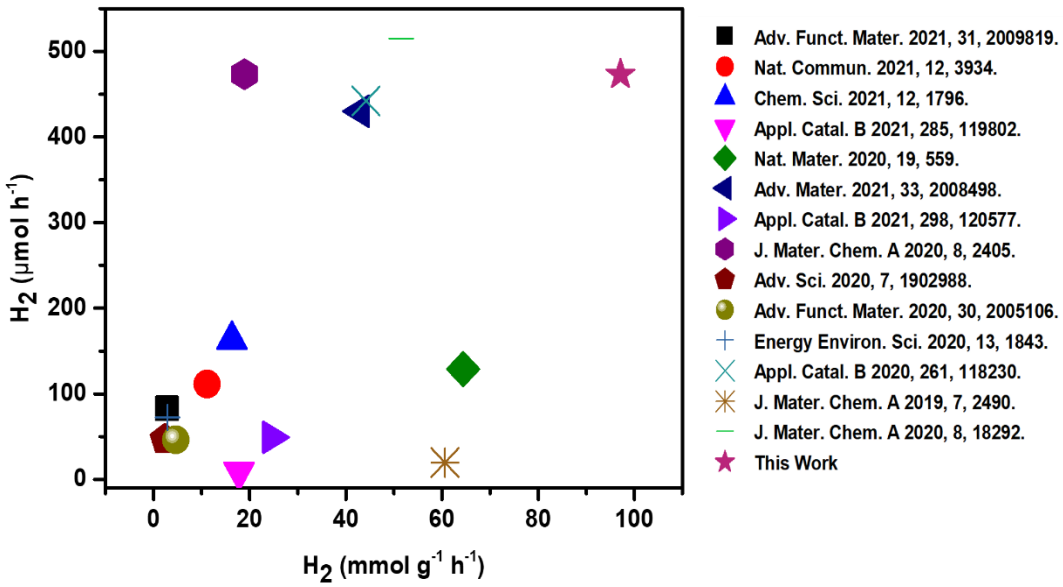


Figure S24. Comparison of HER of PBDTTS-1SO and the literature-reported polymer photocatalysts.

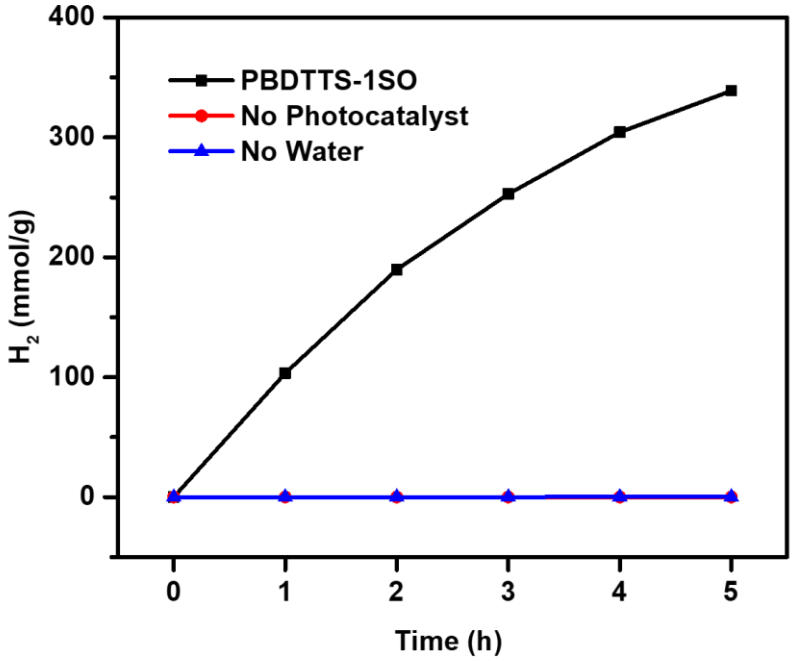


Figure S25. Control experiments of PBDTTS-1SO.

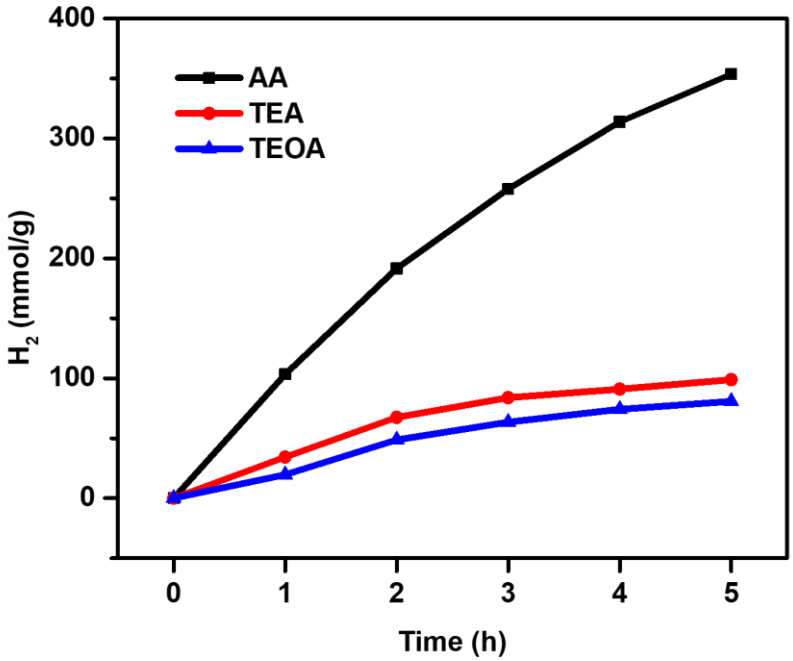


Figure S26. HER of PBDTTS-1SO with different sacrificial agents.

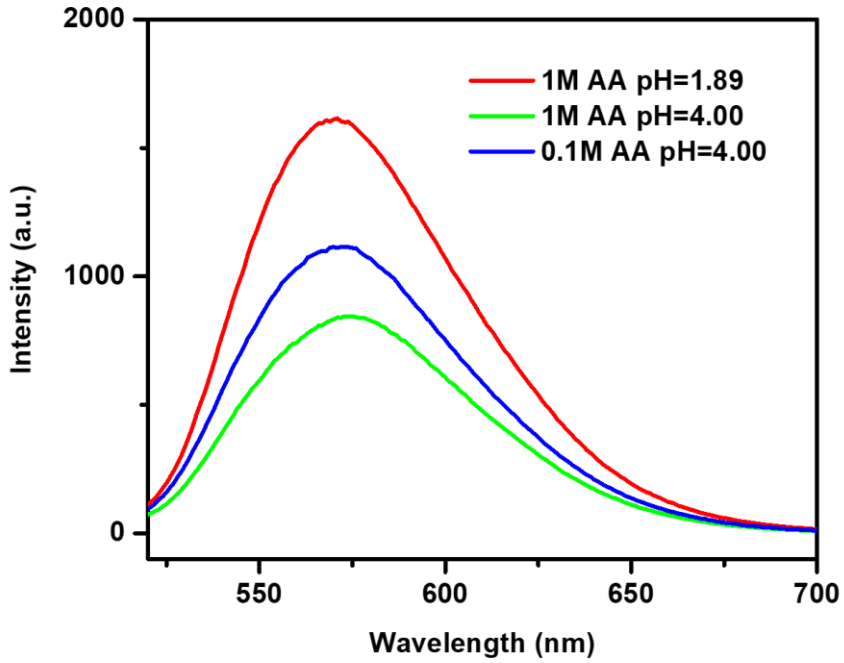


Figure S27. Fluorescence results in different conditions including 1 M AA (pH = 1.89), 0.1 M AA (pH = 4.00), and 1 M AA (pH = 4.00).

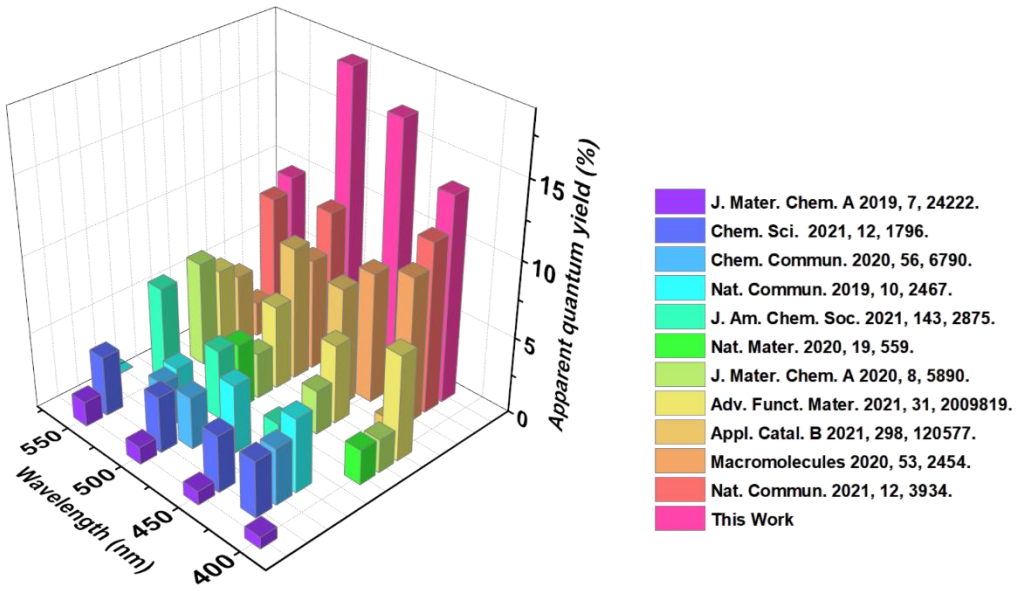


Figure S28. Comparison of AQY of PBDTTS-1SO and the literature-reported polymer photocatalysts at different wavelength.

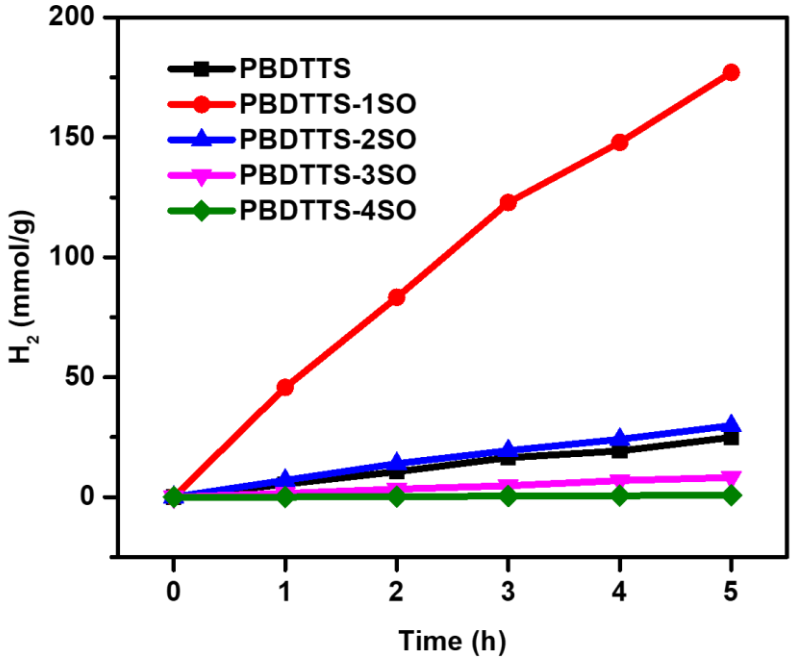


Figure S29. HER of the polymers without addition of Pt.

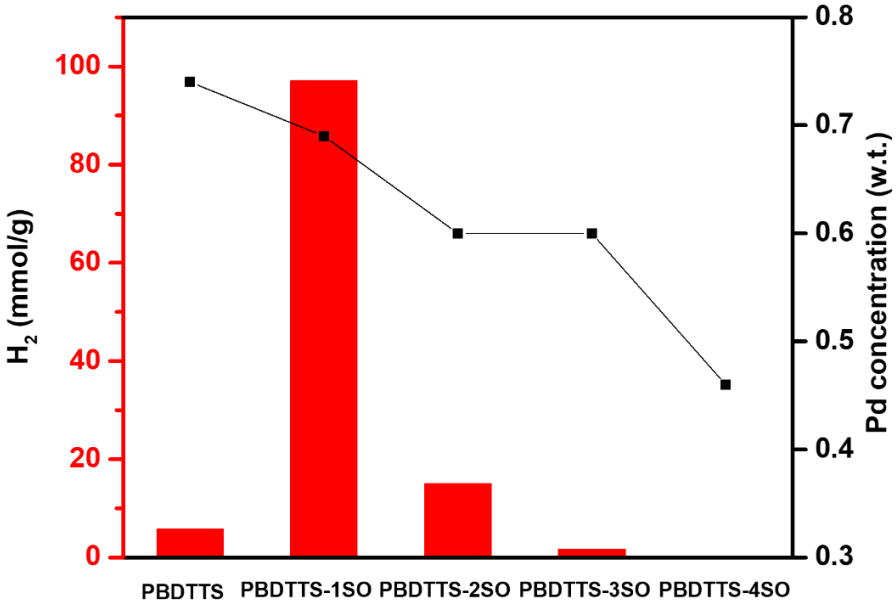


Figure S30. HER versus the content of residual Pd.

Table S2. Comparative studies of our designed polymer photocatalyst with the reported polymer photocatalysts in terms of photocatalytic hydrogen evolution.

Photocatalysts	**HER ($mmol^{-1}g^{-1}h^{-1}$)**	**HER ($\mu mol\ h^{-1}$)**	**AQY(%)** at wavelengths (nm)	**References**
PyDF	18.93	473.25 (25mg)	4.5% at 400 nm	*J. Mater. Chem. A* **2020**, 8, 2405.
DPBT	17.81	8.9 (0.5mg)	3.28/ 0.6% at 420, and 500 nm	*Appl. Catal. B* **2021**, 285, 119802.
ZnCoP-F CP	2.76	83 (30mg)	6.92/5.19/5.50/5.783.17/1.93/0.73% at 400, 450, 500, 550, 700, 760, and 850 nm	*Adv. Funct. Mater.* **2021**, 31, 2009819.
30%PEG@BT-COF	11.14	111.4 (10mg)	11.2, 9.9, 8.9, 2.9, and 1.1% at 420, 500, 550, 600, and 650 nm	*Nat. Commun.* **2021**, 12, 3934.
PyDTDO-3	16.32	163.2 (10mg)	3.70/3.73/3.68/3.93/2.14/1.05% at 420, 450, 500, 550, 600, and 650 nm	*Chem. Sci.* **2021**, 12, 1796.
D1/D2/ITIC	60.8	--	2.2/4.6/6.5/7.1/6.1/4.1% at 450, 500, 550, 600, 650, and 700 nm	*J. Am. Chem. Soc.* **2021**, 143, 2875.
PTB7-Th/EH-IDTBR	64.4	128.8 (2mg)	2.0/2.3/4.3/5.6/6.2% at 400, 500, 620, 660 and 700 nm	*Nat. Mater.* **2020**, 19, 559.
PyBS-3	43	430 (10mg)	29.3% at 420 nm	*Adv. Mater.* **2021**, 33, 2008498.
RPCN	1.4	28 (20mg)	21.1/13.0/1.74/0.84% at 420, 500, 600 and 700 nm	*Adv. Mater.* **2021**, 33, 2121455
PCPDTBSO	24.6	49.2 (2mg)	0.94/7.77/8.72/4.77/3.74% at 420, 460, 500, 550, and 600 nm	*Appl. Catal. B* **2021**, 298, 120577.
PBDTTS-1SO	**97.12**	**473 (6mg)**	**13.5/16.7/18.5/9.8% at 420, 460, 500, and 550 nm**	**This Work**

Reference

[1] a) J.-H. Kim, J. B. Park, S. C. Yoon, I. H. Jung, D.-H. Hwang, *J. Mater. Chem. C* **2016**, 4, 2170; b) G. Shu, Y. Li, Z. Wang, J.-X. Jiang, F. Wang, *Appl. Catal. B* **2020**, 261, 118230.