Supporting Information for

An efficient electron donor containing a silicon heteroatom for organic photocatalysts with high hydrogen production activity

Changzhi Han,[a] Sihui Xiang,[a] Xiaolong Feng,[a] Pengchao Zhang,[a] Yi Ren,[a] Chong Zhang[a]*, Xiaochen Wang [a]* and Jia-Xing Jiang[a,b]*

[a]Key Laboratory for Macromolecular Science of Shaanxi Province, Shaanxi Key Laboratory for Advanced Energy Devices, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China.

[b]Key Laboratory of Optoelectronic Chemical Materials and Devices (Ministry of Education), School of Optoelectronic Materials & Technology, Jianghan University, Wuhan 430056, P. R. China.

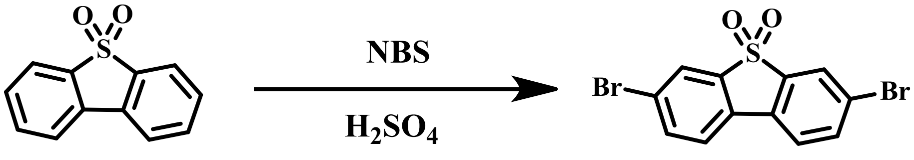
* *E-mail: chongzhangabc@snnu.edu.cn; wangxc@snnu.edu.cn; jiaxing@snnu.edu.cn*

Experimental Section

Chemicals

2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiphene (M1), 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene (M2) were obtained from Sunatech Inc. dibenzo[b,d]thiophene-S,S-dioxide, bis(pinacolato)diboron, Potassium acetate (CH_3COOK), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl_2), N-Bromosuccinimide (NBS), ascorbic acid (AA), anhydrous potassium carbonate (K_2CO_3), *N, N*-dimethylformamide (DMF) were obtained from J&K Scientific Ltd or Sigma-Aldrich. All chemicals were used as received without further purification. 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-S,S-dioxide (M3) was prepared according to the reported method.[1]

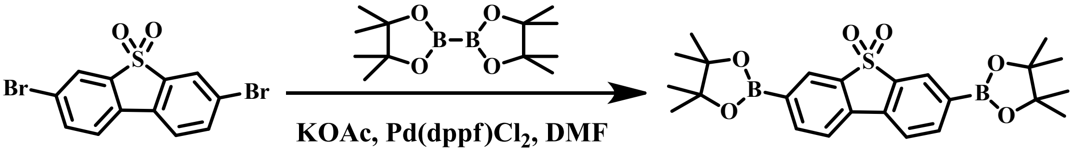
Synthesis of 3,7-dibromodibenzothiophene-S,S-dioxide



Firstly, 150 mL of concentrated sulfuric acid was added into a 250 mL single neck flask.

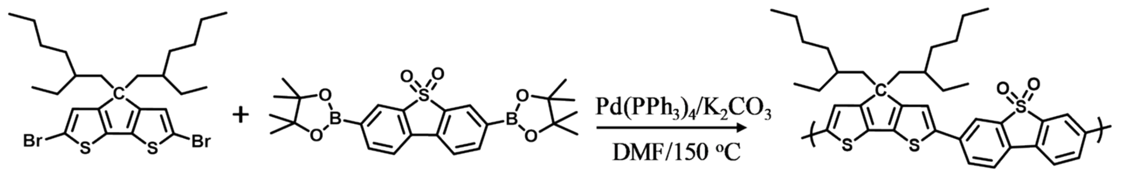
Then, dibenzothiophene-S,S-dioxide (6.05 g, 28.0 mmol) was added into the above flask under stirring. After dibenzothiophene-S,S-dioxide was completely dissolved in sulfuric acid, NBS (12.46 g, 70.0 mmol) was slowly added into dibenzothiophene-S,S-dioxide solution in several portions at 0-5 °C. Afterwards, the resulting mixture was stirred at room temperature for 24 hours. Finally, the mixture was carefully poured into ice/water mixture. The white precipitation was obtained by filtration. The un-dissolved crude product was washed successively with 20% aqueous sodium bicarbonate, water and methanol respectively. After drying in vacuum at 50 °C for 24 hours, the product was further re-crystallized from chlorobenzene to gain 4.86 g white crystal in 46% yield. ^{1}H NMR (ppm, 400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.77 (d, 2H), 7.63 (d, 2H).

Synthesis of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-S,S-dioxide



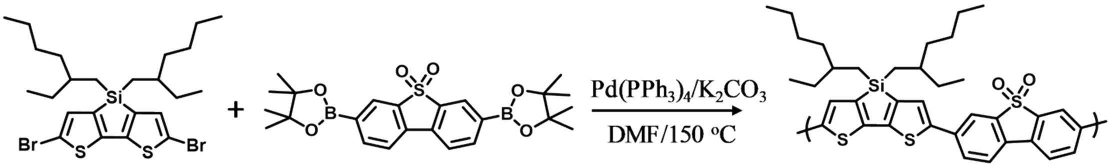
Under N_2 protection, 70 mL anhydrous DMF was added into a mixture of 3,7-dibromodibenzothiophene-S,S-dioxide (4.14 g, 11.0 mmol), bis(pinacolato)diboron (8.38 g, 33.0 mmol), Potassium acetate (6.25 g, 63.7 mmol) and Pd(dppf)Cl_2 (0.11 g, 0.13 mmol). The reaction solution was heated at 90 °C for 24 hours. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic phase was washed with water three times then the organic phase was collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum. Afterwards, the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 1:1). After drying in vacuum at 60 °C for 24 hours, the product was re-crystallized from chloroform and methanol to gain 3.4 g white crystal in 66% yield. ^{1}H NMR (ppm, 400 MHz, $CDCl_3$): δ 8.26 (s, 2H), 8.03 (d, 2H), 7.78 (d, 2H), 1.34 (s, 24).

Synthesis of PCDT-BTDO



Under nitrogen protection, M1 (0.5 mmol, 280.2 mg), M3 (0.5 mmol, 234.1 mg) and 20 mg $Pd(PPh_3)_4$ (17.3 μmol, 20 mg) were added into the mixture solution of 20 mL DMF and 4 mL K_2CO_3 aqueous solution (2 M). The reaction system was heated at 150 °C for 2 days with stirring. After cooling to 25 °C, the solid-state powder was obtained by filtration. After washed by methanol and pure water. The weight-average and number-average molecular weights are 69755 and 24500 g mol^{-1}, respectively. The PCDT-BTDO was obtained as red powder (yield: 98%).

Synthesis of PSiDT-BTDO



M2 (0.5 mmol, 288.3 mg), M3 (0.5 mmol, 234.1 mg), 20 mg $Pd(PPh_3)_4$ (17.3 μmol, 20 mg), 20 mL DMF and 4 mL K_2CO_3 aqueous were used for the polymerization reaction. The PSiDT-BTDO was obtained as red powder (yield: 73%).

Characterization

Fourier-transform infrared (FT-IR) spectra were collected on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. Solid-state ^{13}C NMR spectra were obtained on a JEOL RESONRNCE 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 molecular weight of PCDT-BTDO was measured by gel permeation chromatography (Agilent1260). The morphology 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 $BaSO_4$ as a reference sample. Thermogravimetric analysis (TGA) measurement was performed on a thermal analysis system (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 25 to 800 °C in nitrogen atmosphere with a heating rate of 20 °C min^{-1}. The residual Pd content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The particle size was measured by the confocal laser scanning microscopy (CLSM) (OLYMPUS-FV3000). For the measurement of CLSM, the photocatalytic reaction solution after the photocatalytic test was dropped on a glass slide, on which the droplet was then covered by another glass slide; afterwards the above prepared sample was directly observed by the CLSM with a 520 nm excitation light in a dark room. Dynamic light scattering (DLS) measurement was carried out on a laser particle size analyzer (90Plus). The fluorescence properties of the polymers were measured with a PerkinElmer FL 8500 fluorescence spectrophotometer by using excitation wavelength of 450 nm at room temperature. The time-resolved photoluminescence spectra were measured with a PicoQuant Fluo Time 300 spectrometer. Cyclic voltammetry (CV) measurements were carried out on CHI660E (Chenhua, Shanghai) electrochemical workstation in a three-electrode-cell system. A platinum plate and a saturated calomel electrode were employed as the counter electrode and reference electrode, respectively. The tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 1.16 g) dissolved in 30 mL acetonitrile was used as the electrolyte solution. The electrochemical workstation was taken with a scan rate of 100 mV s^{-1}. Before the electrochemical test, polymer (10 mg) was dispersed in isopropanol containing 5 wt% Nafion (mass ratio of 1:30) and then pipet part of the mixed solution onto the working electrode. The photocurrent was 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 prepared electrode from the polymer catalyst and 5 wt% Nafion (mass ratio of 1:30) was immersed in photocatalytic solution.

Photocatalytic hydrogen generation experiment

The photocatalytic hydrogen production experiment of the resulting polymer photocatalysts was performed on an all-glass automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight Technology Co., Ltd.) linking with an on-line gas chromatograph. First of all, 10 mg as-synthesized polymer was ultrasonically dispersed in 10 mL DMF (dispersant) for 10 minutes. Then, 90 mL ascorbic acid (AA) aqueous solution was added to form 100 mL mixture solution (the concentration of AA in the mixed solution is 1M), and the result mixture solution was poured into photo-reactor with magneton. After the dissolved air in photocatalytic system was degassed to remove, the photo-reactor was irradiated by a 300 W Xe lamp under vacuum. The photocatalytic reaction temperature was kept at 10 ^{o}C by circulating cooling water. A 420 nm filter was used to obtain the simulated visible light irradiation ($\lambda > 420$ nm) by filtering out ultraviolet light. The produced hydrogen was measured online by gas chromatograph. When TEOA or TEA was adopted as the sacrificial agent, 10 mg polymer photocatalyst was dispersed in a mixed solution containing 40 mL deionized water, 30 mL TEOA or TEA, and 30 mL methanol as dispersant.

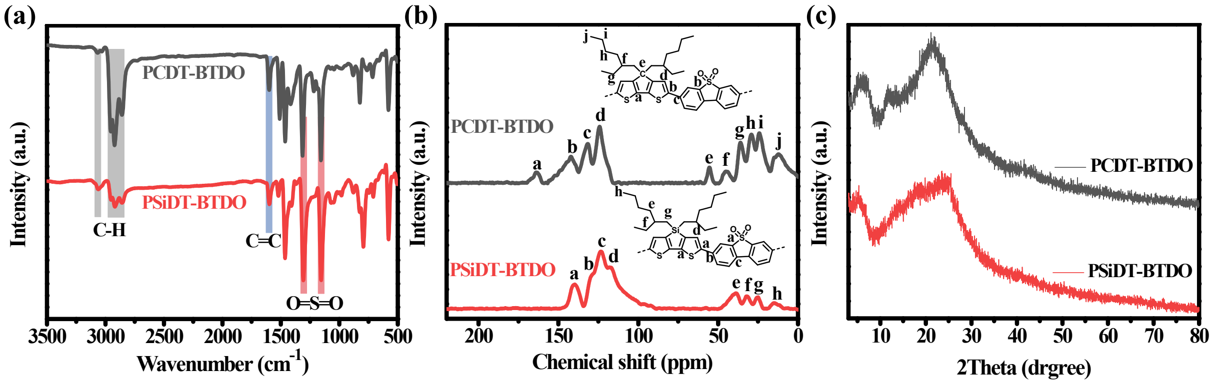


Fig. S1 The (a) FT-IR spectra, (b) solid-state ^{13}C NMR spectra and (c) XRD patterns of the polymers.

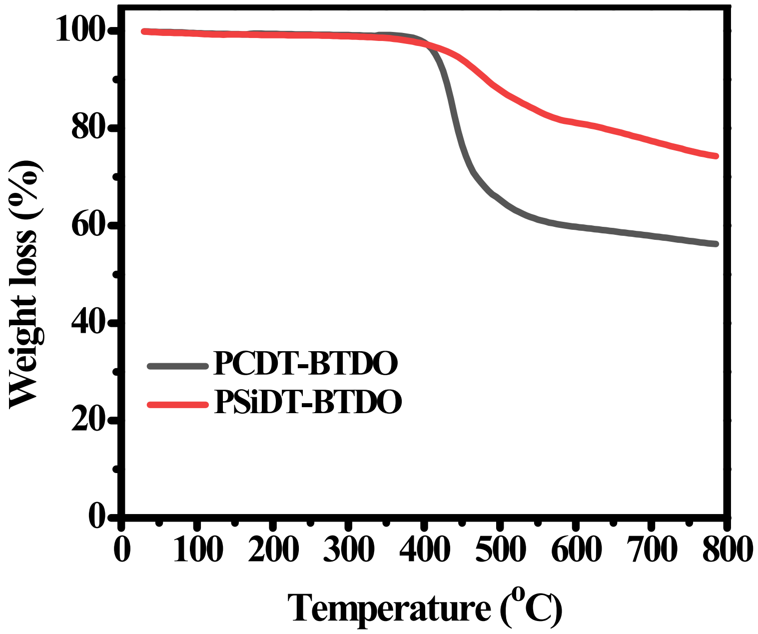
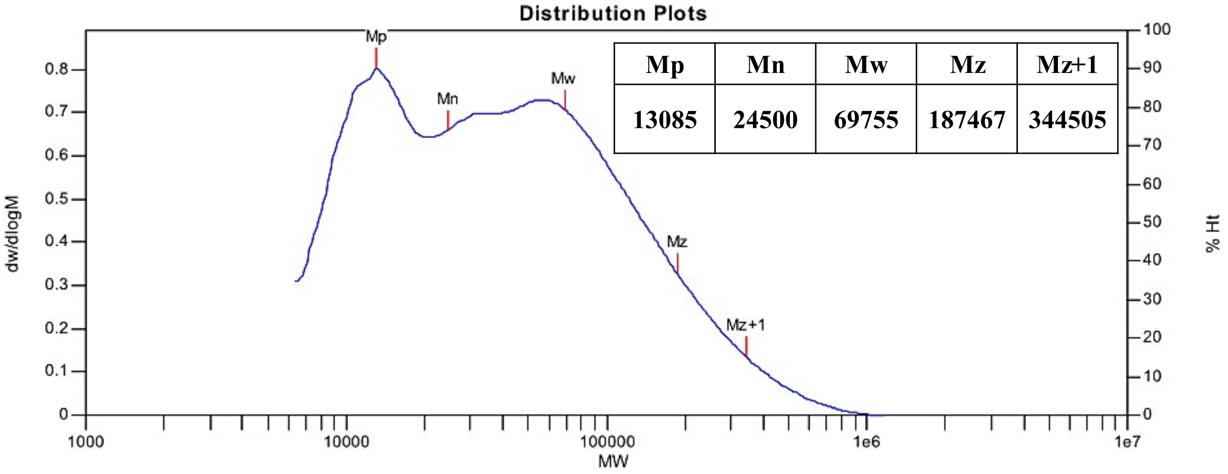


Fig. S2 Thermogravimetric analysis traces.



Mp	Mn	Mw	Mz	Mz+1
13085	24500	69755	187467	344505

Fig. S3 The gel permeation chromatogram spectrum of PCDT-BTDO for molecular weight.

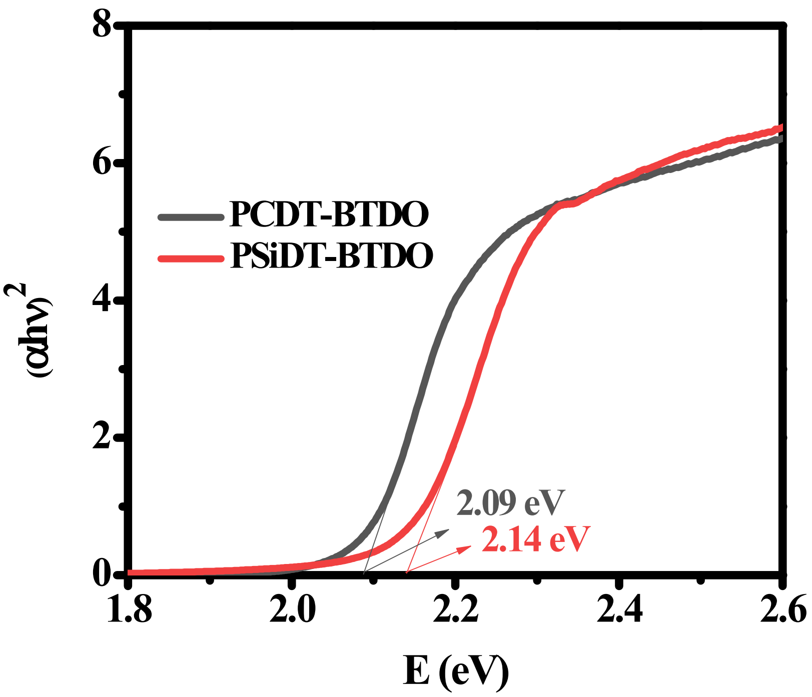


Fig. S4 Tauc plots of the Kubelka-Munk function vs. energy.

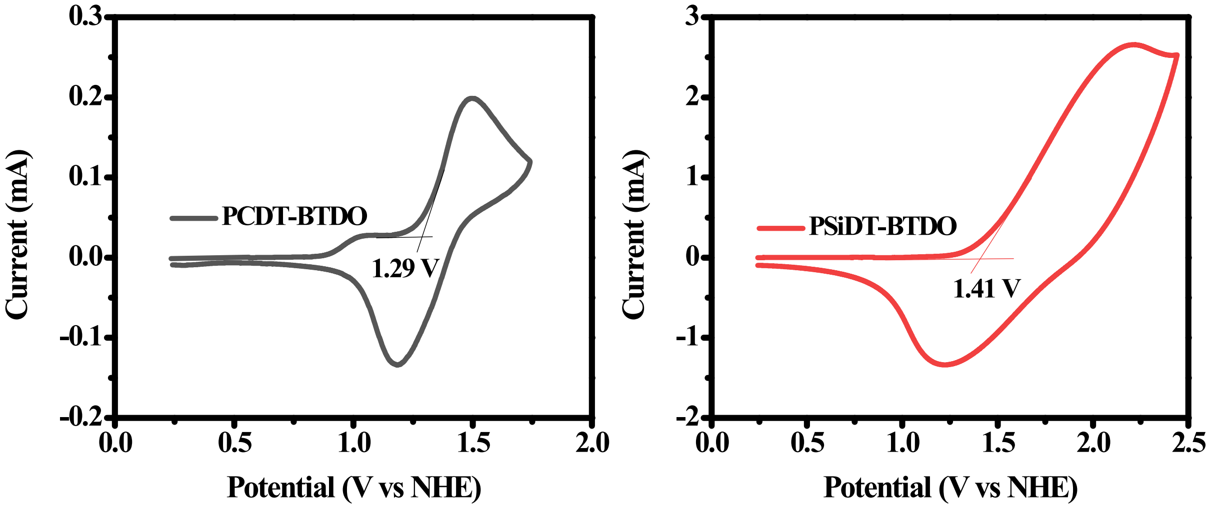


Fig. S5 Cyclic voltammetry curves of the polymers.

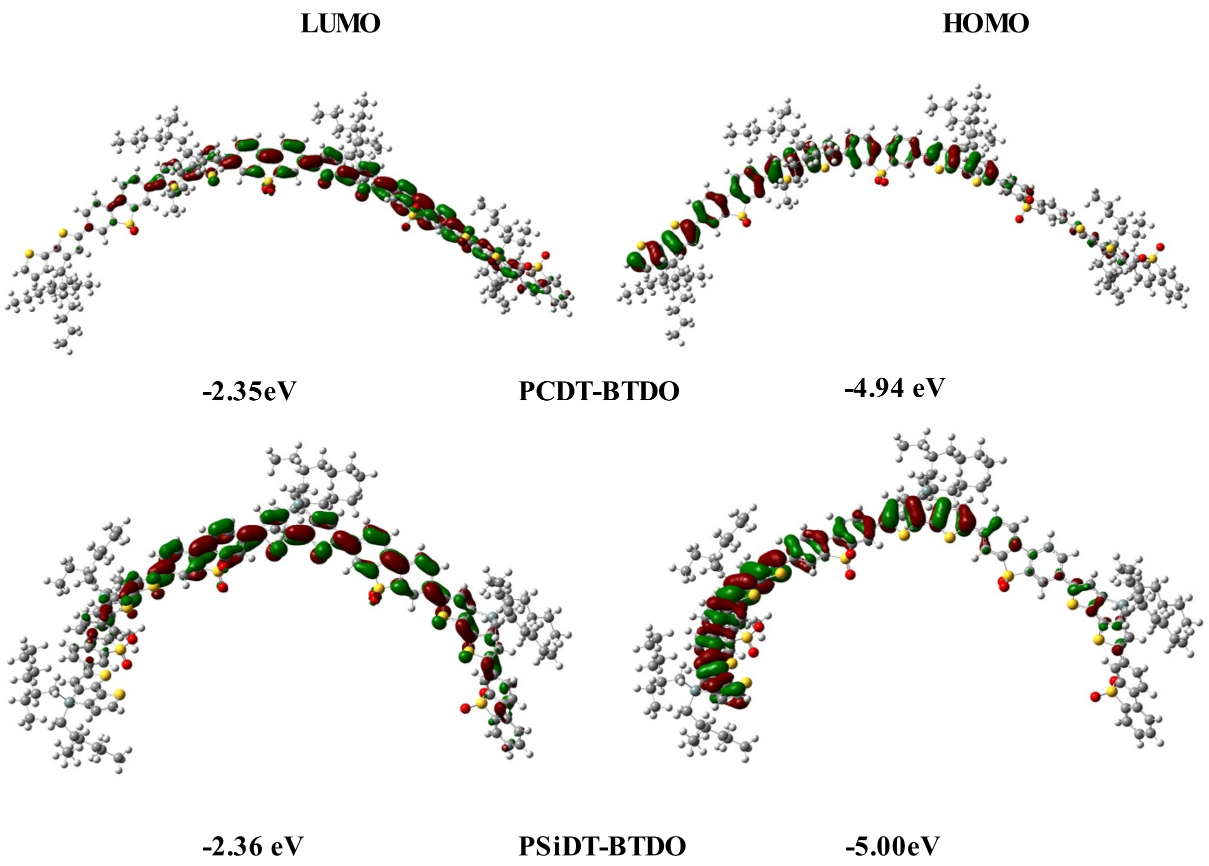


Fig. S6 HOMO and LUMO orbitals distribution of the polymers from DFT calculation.

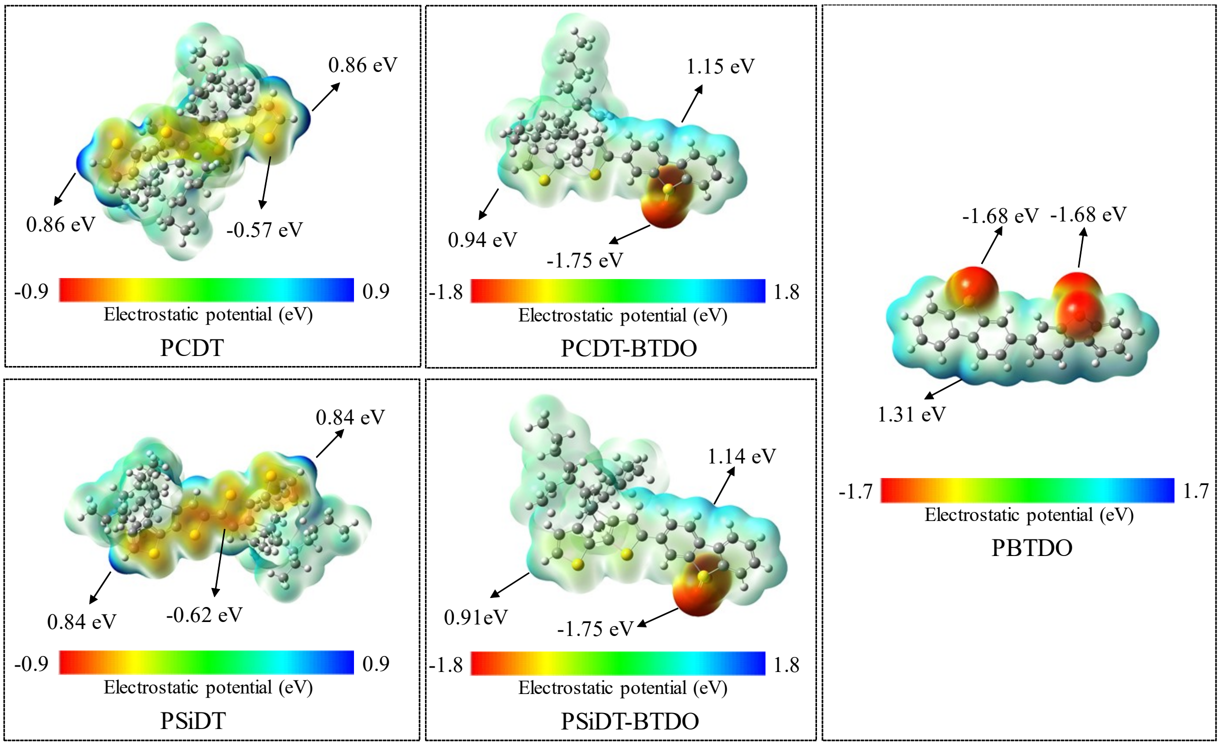


Fig. S7 Molecular electrostatic potential of the polymers. The positive region colored in blue is the donor site, while the negative region colored in red is the acceptor site. It revealed that the ESP value on the sulfone group of BTDO unit decreased from -1.68 eV of PBTDO to -1.75 eV of PSiDT-BTDO, while the positive ESP value on BTDO unit decreased from 1.31 eV for PBTDO to 1.14 eV for PSiDT-BTDO. Meanwhile, the positive ESP value on SiDT unit increased from 0.84 eV for PSiDT to 0.91 eV for PSiDT-BTDO, suggesting the electron transfer from SiDT to BTDO unit in PSiDT-BTDO, which is the feature of D-A behavior. A similar variation trend for the ESP values was also observed among PCDT, PCDT-BTDO and PBTDO, indicating the D-A character of PCDT-BTDO.

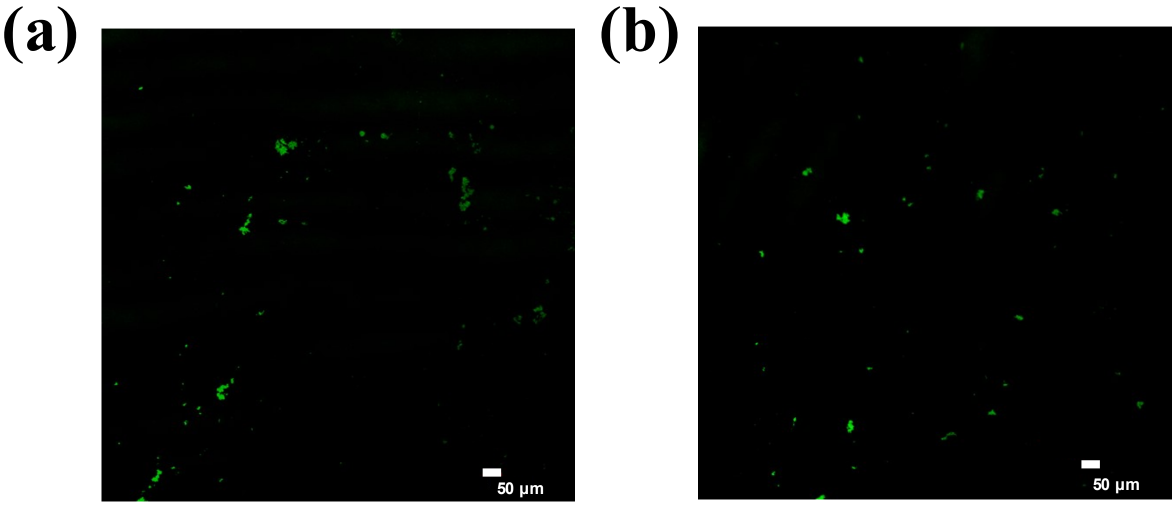


Fig. S8 The confocal laser scanning microscopy images of (a) PCDT-BTDO and (b) PSiDT-BTDO.

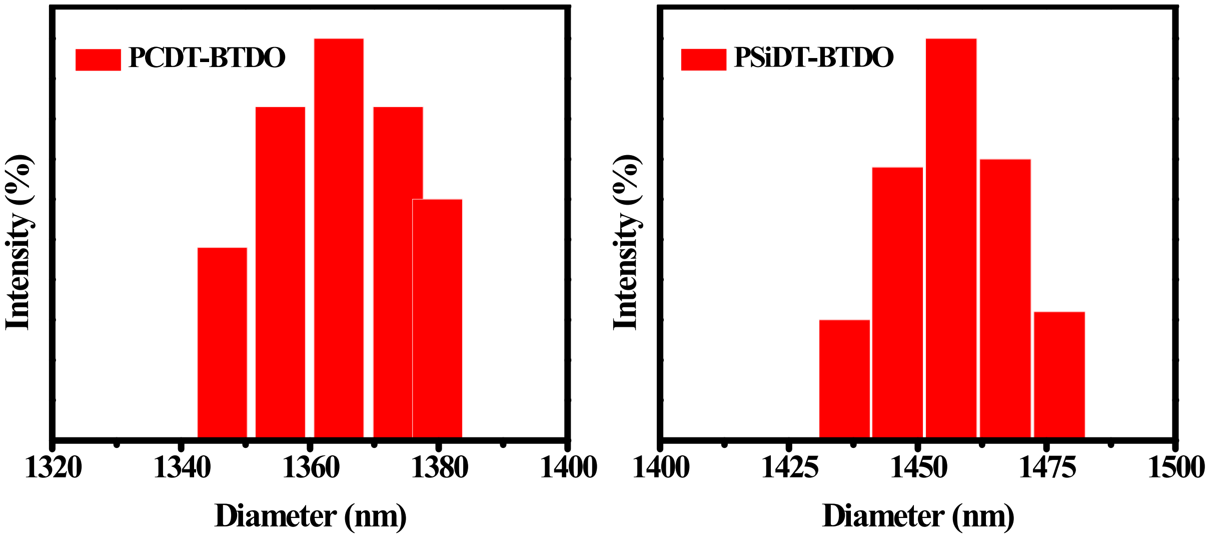


Fig. S9 Particle size measurement of the polymers.

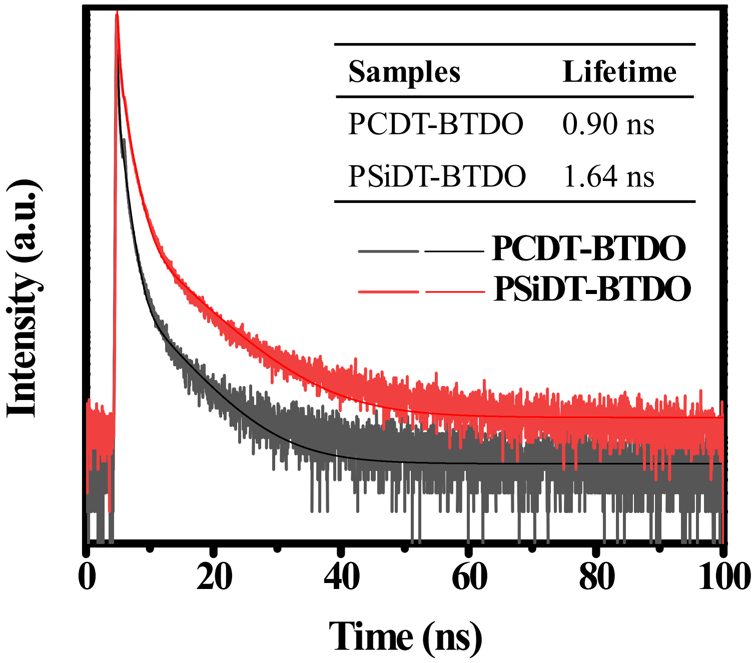


Fig. S10 Time-resolved fluorescence decay spectra of the polymer dispersion in photocatalytic solution.

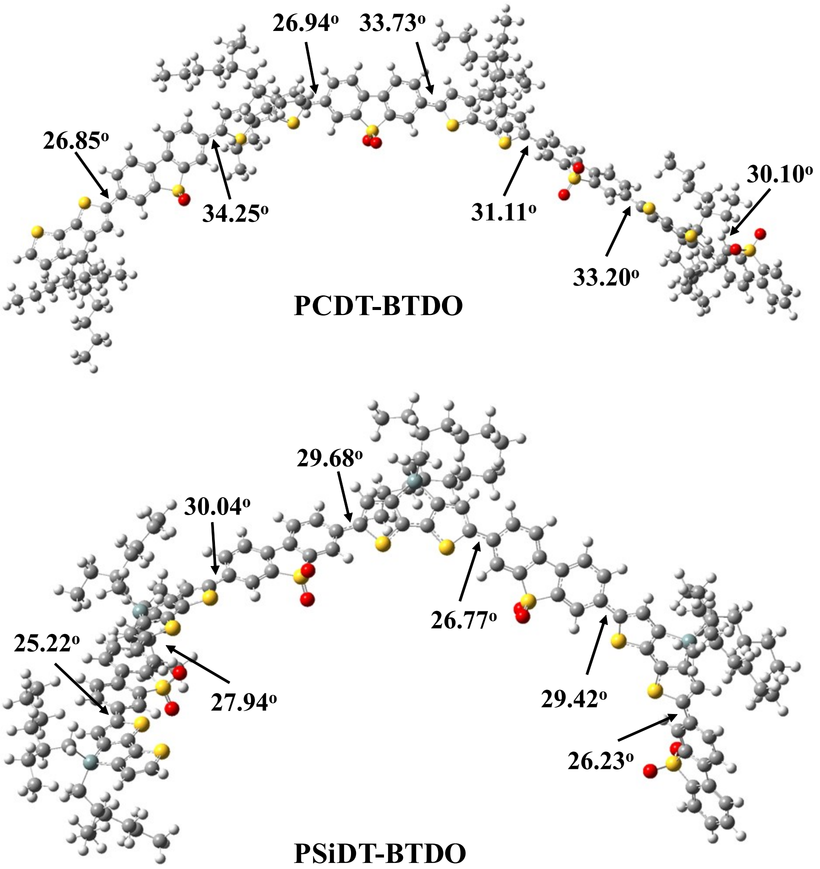


Fig. S11 The DFT geometry optimizations and the dihedral angles of the polymers.

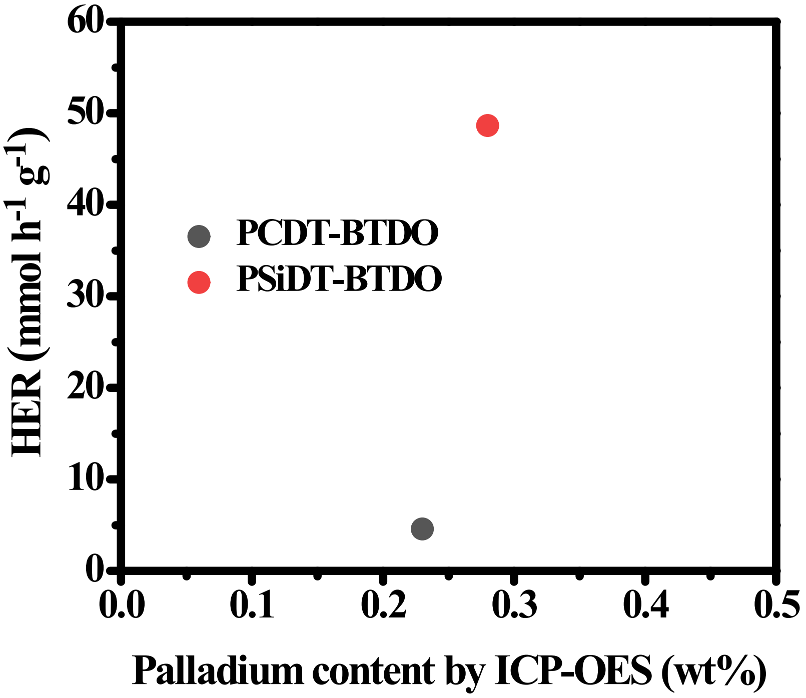


Fig. S12 The relationship between HER values of bare PCDT-BTDO and PSiDT-BTDO under UV-Vis light and their Pd contents.

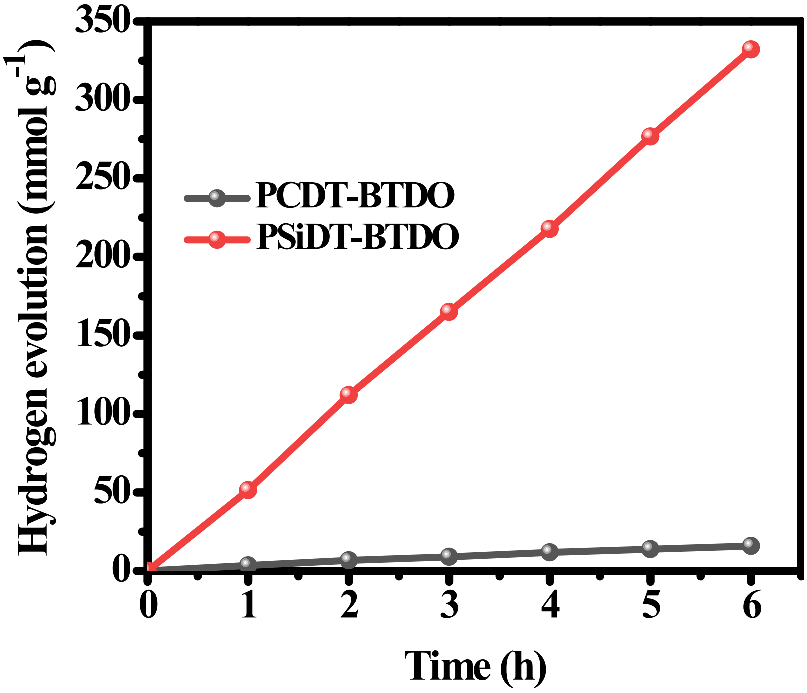


Fig. S13 Time course of hydrogen evolution for the polymers under visible light with 3wt% Pt.

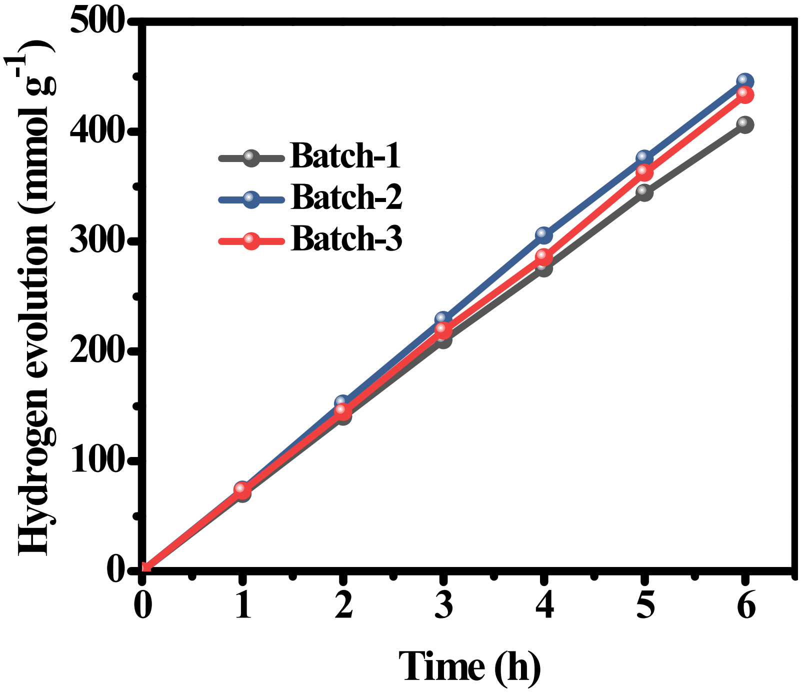


Fig. S14 Time course of hydrogen evolution for PSiDT-BTDO (10 mg) produced from different batches under UV-Vis light (λ > 300 nm).

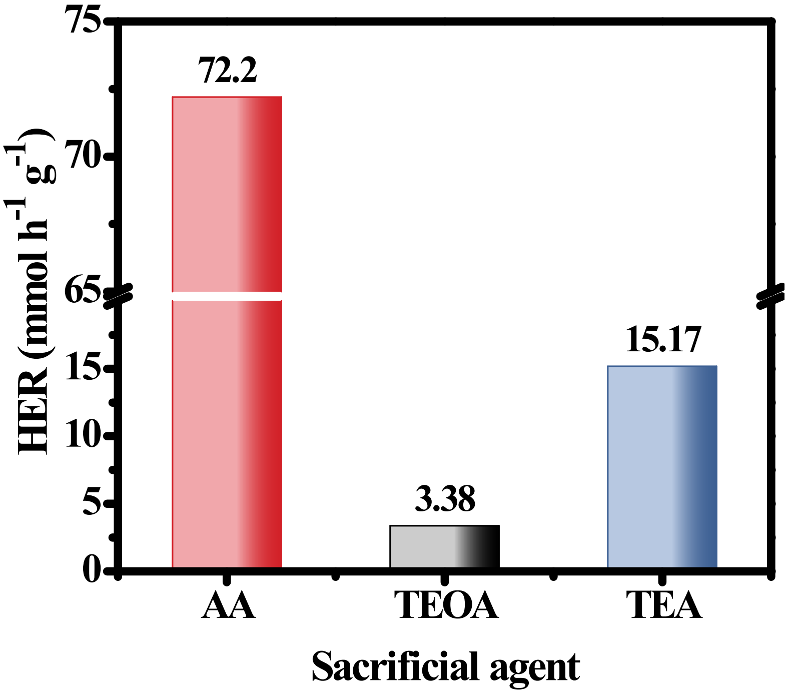


Fig. S15 The HER values of PSiDT-BTDO with different sacrificial agents under UV-Vis light irradiation (λ > 300 nm) with 3 wt% Pt.

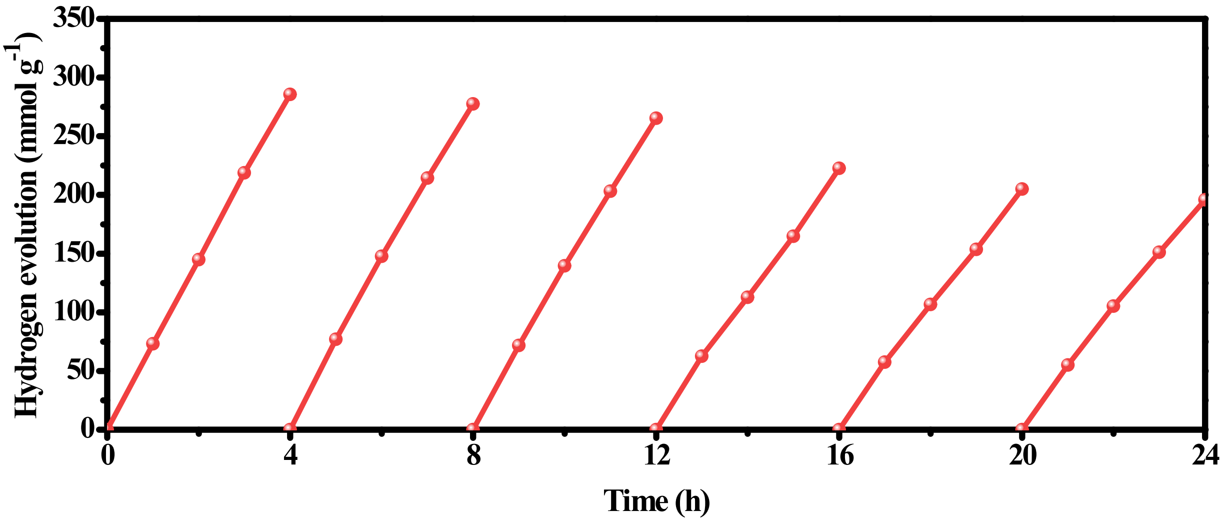


Fig. S16 Stability test of PSiDT-BTDO with 3 wt% Pt under UV-Vis light.

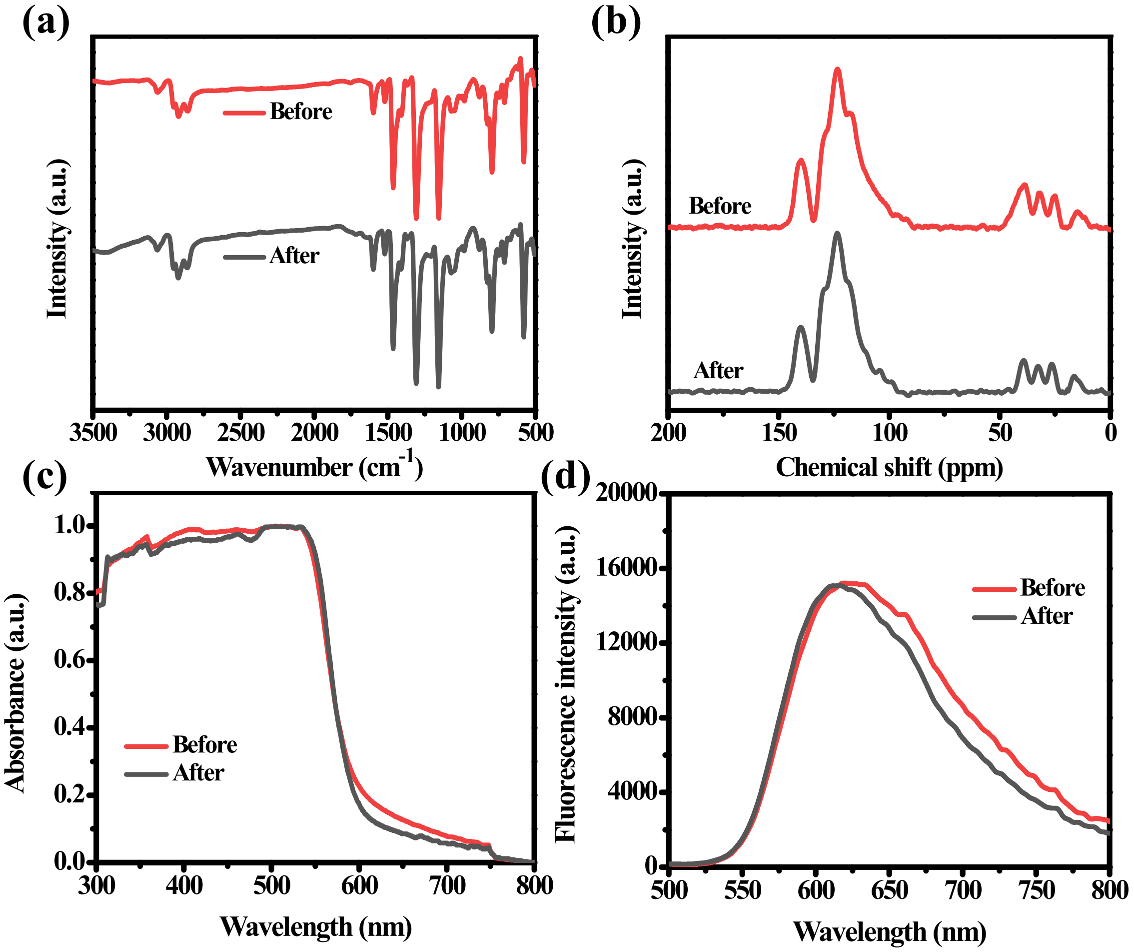


Fig. S17 The structure characterization of (a) FT-IR spectra, (b) solid-state ^{13}C NMR spectra, (c) UV-Vis absorption spectra and (d) fluorescence emission spectra of PSiDT-BTDO before and after photocatalytic reaction.

Table S1. The fitting parameters of the time-resolved photoluminescence decay curves for the polymer dispersion in photocatalytic solution.

Polymer	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	Rel_1 (%)	Rel_2 (%)	Rel_3 (%)	Adj. R-Square	$\tau_{average}$ (ns)
PCDT-BTDO	0.13	0.90	6.24	45.60	47.72	6.68	0.996	0.90
PSiDT-BTDO	0.26	1.18	7.48	28.97	59.40	11.63	0.998	1.64

Tri-exponential function fitting was employed to analyze the time-resolved photoluminescence decay curves, $\tau_{average}$ was the average recombination lifetime calculated by the following equation:

$$\tau_{average} = \tau_1 * Rel_1\% + \tau_2 * Rel_2\% + \tau_3 * Rel_3\%$$

Table S2. The summary of the photocatalytic performances of polymeric photocatalysts for hydrogen evolution from water splitting (λ > 300 nm).

Photocatalysts	**cocatalyst**	**sacrificial agent**	**HER (mmol h^{-1} g^{-1})**	**Optical gap (eV)**	**Ref.**
PSiDT-BTDO	3 wt% Pt	AA	72.20	2.14	This work
Py-T-BTDO-3	1 wt% Pt	AA	127.9	2.07	2
DBTD-CMP1	3 wt% Pt	TEOA	9.20	2.53	3
PyBS-3	3 wt% Pt	AA	105	2.54	4
P2	3 wt% Pt	TEA	20.3	2.22	5
TP-BTDO-2	1 wt% Pt	AA	161.28	2.01	6
CP1	0.5 wt% Pt	AA	30.81	1.98	7
PyDTDO-3	No	AA	24.97	1.81	8
BTT-CPP	No	AA	37.87	2.40	9
PyDOBT-1	3 wt% Pt	TEOA	12.99	2.37	10
PyTP-2	0.2 wt% Pt	AA	62.52	1.93	11
PF6A-SF	No	TEA	36.43	2.74	12
PDBTSO-T	3 wt% Pt	AA	147	2.22	13
PySEO-1	3 wt% Pt	TEOA	9.48	1.90	14
P16PySO	No	TEOA	15.50	2.31	15

P-TS	No	TEA	10.28	2.56	16
PyDF	3 wt% Pt	TEOA	18.93	2.24	17
cLaP1	1 wt% Pt	TEA	2.30	2.41	18
PCP10	No	TEA	8.63	--	19
PySO	No	TEA	11.2	2.58	20
S-CMP3	No	TEA	6.08	2.56	21
$F_{0.5}$CMP	No	Na_2S/Na_2SO_4	1.76	2.3	22
P1	3 wt% Pt	TEOA	0.30	2.3	23
Triazine-Ph-CPP	No	TEOA	16.29	2.83	24
P28	No	TEA	1.34	2.45	25
SP-CMP	No	TEA	1.15	2.84	26
PAE-D	3 wt% Pt	TEOA	4.16	2.70	27
T-COF@CdS-3	1 wt% Pt	AA	12.25	--	28
BDF-TAPT-COF	8 wt% Pt	AA	1.39	2.57	29
TFA-COF	3 wt% Pt	TEOA	0.08	2.40	30

References

1 K. C. Moss, K. N. Bourdakos, V. Bhalla, K. T. Kamtekar, M. R. Bryce, M. A. Fox, H. L. Vaughan, F. B. Dias and A. P. Monkman, *J. Org. Chem.*, 2010, **75**, 6771-6781.

2 C. Han, S. Xiang, P. Xie, P. Dong, C. Shu, C. Zhang and J.-X. Jiang, *Adv. Func. Mater.*, 2022, **32**, 2109423.

3 Z. Wang, X. Yang, T. Yang, Y. Zhao, F. Wang, Y. Chen, J. H. Zeng, C. Yan, F. Huang and J.-X. Jiang, *ACS Catal.*, 2018, **8**, 8590-8596.

4 C. Shu, C. Han, X. Yang, C. Zhang, Y. Chen, S. Ren, F. Wang, F. Huang and J.-X. Jiang, *Adv. Mater.*, 2021, **33**, 2008498.

5 W.-R. Wang, J. Li, Q. Li, Z.-W. Xu, L.-N. Liu, X.-Q. Chen, W.-J. Xiao, J. Yao, F. Zhang and W.-S. Li, *J. Mater. Chem. A*, 2021, **9**, 8782-8791.

6 C. Han, S. Xiang, S. Jin, L.-W. Luo, C. Zhang, C. Yan and J.-X. Jiang, *J. Mater. Chem. A*, 2022, **10**, 5255-5261.

7 W.-Y. Huang, Z.-Q. Shen, J.-Z. Cheng, L.-L. Liu, K. Yang, X. Chen, H.-R. Wen and S.-Y.

Liu, *J. Mater. Chem. A*, 2019, **7**, 24222-24230.

8 C. Han, P. Dong, H. Tang, P. Zheng, C. Zhang, F. Wang, F. Huang and J.-X. Jiang, *Chem. Sci.*, 2021, **12**, 1796-1802.

9 J.-l. Wang, G. Ouyang, D. Wang, J. Li, J. Yao, W.-S. Li and H. Li, *Macromolecules*, 2021, **54**, 2661-2666.

10 Y. Zhao, W. Ma, Y. Xu, C. Zhang, Q. Wang, T. Yang, X. Gao, F. Wang, C. Yan and J.-X. Jiang, *Macromolecules*, 2018, **51**, 9502-9508.

11 S. Xiang, C. Han, C. Shu, C. Zhang and J.-X. Jiang, *Sci. China Mater.*, 2022, **65**, 422-430.

12 R. Li, C. Zhang, C.-X. Cui, Y. Hou, H. Niu, C.-H. Tan, X. Yang, F. Huang, J.-X. Jiang and Y. Zhang, *Polymer*, 2022, **240**, 124509.

13 Y. Liu, J. Wu and F. Wang, *Appl. Catal. B*, 2022, **307**, 121144.

14 C. Shu, Y. Zhao, C. Zhang, X. Gao, W. Ma, S.-B. Ren, F. Wang, Y. Chen, J. H. Zeng and J.-X. Jiang, *ChemSusChem*, 2020, **13**, 369-375.

15 C. Cheng, X. Wang and F. Wang, *Appl. Surf. Sci.*, 2019, **495**, 143537.

16 Y. Bai, D. J. Woods, L. Wilbraham, C. M. Aitchison, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *J. Mater. Chem. A*, 2020, **8**, 8700-8705.

17 X. Gao, C. Shu, C. Zhang, W. Ma, S.-B. Ren, F. Wang, Y. Chen, J. H. Zeng and J.-X. Jiang, *J. Mater. Chem. A*, 2020, **8**, 2404-2411.

18 A. Vogel, M. Forster, L. Wilbraham, Charlotte L. Smith, A. J. Cowan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Faraday Discuss.*, 2019, **215**, 84-97.

19 L. Li, W.-y. Lo, Z. Cai, N. Zhang and L. Yu, *Macromolecules*, 2016, **49**, 6903-6909.

20 C. Dai, S. Xu, W. Liu, X. Gong, M. Panahandeh-Fard, Z. Liu, D. Zhang, C. Xue, K. P. Loh and B. Liu, *Small*, 2018, **14**, 1801839.

21 R. S. Sprick, Y. Bai, A. A. Y. Guilbert, M. Zbiri, C. M. Aitchison, L. Wilbraham, Y. Yan, D. J. Woods, M. A. Zwijnenburg and A. I. Cooper, *Chem. Mater.*, 2019, **31**, 305-313.

22 V. S. Mothika, P. Sutar, P. Verma, S. Das, S. K. Pati and T. K. Maji, *Chem. Eur. J.*, 2019, **25**, 3867-3874.

23 J. Yu, X. Sun, X. Xu, C. Zhang and X. He, *Appl. Catal. B*, 2019, **257**, 117935.

24 J. Wang, G. Ouyang, Y. Wang, X. Qiao, W.-S. Li and H. Li, *Chem. Commun.*, 2020, **56**, 1601-1604.

25 R. S. Sprick, L. Wilbraham, Y. Bai, P. Guiglion, A. Monti, R. Clowes, A. I. Cooper and M. A. Zwijnenburg, *Chem. Mater.*, 2018, **30**, 5733-5742.

26 R. S. Sprick, B. Bonillo, M. Sachs, R. Clowes, J. R. Durrant, D. J. Adams and A. I. Cooper, *Chem. Commun.*, 2016, **52**, 10008-10011.

27 Z.-A. Lan, M. Wu, Z. Fang, X. Chi, X. Chen, Y. Zhang and X. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 16355-16359.

28 Y. Wang, Z. Hu, W. Wang, H. He, L. Deng, Y. Zhang, J. Huang, N. Zhao, G. Yu and Y.-N. Liu, *Chem. Sci.*, 2021, **12**, 16065-16073.

29 G.-B. Wang, F.-C. Zhu, Q.-Q. Lin, J.-L. Kan, K.-H. Xie, S. Li, Y. Geng and Y.-B. Dong, *Chem. Commun.*, 2021, **57**, 4464-4467.

30 C. Liu, Y. Xiao, Q. Yang, Y. Wang, R. Lu, Y. Chen, C. Wang and H. Yan, *Appl. Surf. Sci.*, 2021, **537**, 148082.