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Electronic supplementary information (ESI)

Bandgap engineering of a novel peryleno[1,12-bcd] thiophene sulfone based conjugated co-polymers for significantly enhanced hydrogen evolution without co-catalyst

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1. Synthetic route of monomers and polymers

The synthetic route of 3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide is shown in **Scheme S1**. And the intermediate peryleno[1,12-bcd]thiophene was synthesized according to the previous work.¹



Scheme S1. The synthetic route of 3,10-dibromoperyleno [1,12-bcd]thiophene 1,1-dioxide

Synthesis of 3,10-dibromoperyleno [1,12-bcd]thiophene. The peryleno[1,12-bcd]thiophene (284 mg, 1 mmol) was dissolved in 50 mL dichloromethane (DCM) solution in a three-necked flask and the *N*-bromosuccinimide (355 mg, 2 mmol) was slowly dropped into the mixture solution. Then the reaction solution was evenly stirred for 12 h at room temperature (25 °C). The reaction was then quenched with water and the mixture solution was further extracted with DCM. The crude product was purified by column chromatography (eluent: pure petroleum ether, solid phase:silica gel) to give yellow-green powder, 3,10-dibromoperyleno [1,12-bcd]thiophene (385 mg, 88 %).¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 7.5 Hz, 2H), 8.40 (t, *J* = 6.9 Hz, 4H), 7.94 (t, *J* = 8.1 Hz, 2H). HRMS (EI-MS) m/z calcd. For C₂₀H₈Br₂S: 437.8713. [M⁺]. Found: 437.8718.

Synthesis of 3,10-dibromoperyleno [1,12-bcd]thiophene 1,1-dioxide. The 3,10-dibromoperyleno [1,12-bcd]thiophene (437 mg, 1 mmol) was dissolved in acetic acid (50 mL) solution in a three-necked flask and the H₂O₂ (5 mL, 33%) aqueous solution

was slowly dropped into the mixture solution. Then the reaction solution was evenly stirred for 1-3 h at 90 °C. The reaction was then quenched with water and the mixture solution was further extracted with DCM. The crude product was purified by column chromatography (eluent: petroleum ether: dichloromethane = 1:2 (v/v), solid phase: silica gel) to give orange-red powder, 3,10-dibromoperyleno [1,12-bcd]thiophene 1,1-dioxide (200 mg, 42 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.92 (s, 2H), 7.69 (dd, *J* = 8.5, 7.6 Hz, 2H). HRMS (EI-MS) m/z calcd. For C₂₀H₈Br₂O₂S: 469.8612. [M⁺]. Found: 469.8612.

Synthesis of PS-1: Light yellow powder 230 mg, yield 78.8 %. Diboronic ester arenes (1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**A**) (330 mg, 1 mmol) and dibromo arene (3,7-dibromodibenzo[b,d]thiophene 5,5-dioxide) (**C**) (371 mg, 1 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.23 wt % from ICP-AES.

Synthesis of PS-2: Orange-red powder 210 mg, yield 53.8 %. Diboronic ester arenes (1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**A**) (330 mg, 1 mmol) and dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (**D**) (469 mg, 1 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 2.1 wt % from ICP-AES.

Synthesis of PS-3: Yellow-green powder 280 mg, yield 65.1 %. Diboronic ester arenes (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide) (B) (468 mg, 1 mmol) and dibromo arene (dibromo arene (3,7-dibromodibenzo[b,d]thiophene 5,5-dioxide) (C) (371 mg, 1 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.32 wt % from ICP-AES.

Synthesis of PS-4: Yellow powder 265 mg, yield 58.9 %. Diboronic ester arenes (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide) (B) (468 mg, 1 mmol) and dibromo arene (dibromo arene (dibromo arene (3,7-

dibromodibenzo[b,d]thiophene 5,5-dioxide) (**C**) (362 mg, 0.975 mmol), dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (**D**) (12 mg, 0.025 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.89 wt % from ICP-AES.

Synthesis of PS-5: Yellow-brown powder 270 mg, yield 55.6 %. Diboronic ester arenes (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide) (B) (468 mg, 1 mmol) and dibromo arene (dibromo arene (dibromo arene (3,7-dibromodibenzo[b,d]thiophene 5,5-dioxide) (C) (352 mg, 0.95 mmol), dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (D) (24 mg, 0.05 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.30 wt % from ICP-AES.

Synthesis of PS-6: Brown powder 275 mg, yield 56.7 %. Diboronic ester arenes (3,7bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide) (B) (468 mg, 1 mmol) and dibromo arene (dibromo arene (dibromo arene (3,7dibromodibenzo[b,d]thiophene 5,5-dioxide) (C) (333 mg, 0.9 mmol), dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (D) (47 mg, 0.1 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.80 wt % from ICP-AES.

Synthesis of PS-7: Brown-red powder 275 mg, yield 59.4 %. Diboronic ester arenes (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide) (B) (468 mg, 1 mmol) and dibromo arene (dibromo arene (dibromo arene (3,7-dibromodibenzo[b,d]thiophene 5,5-dioxide) (C) (296 mg, 0.8 mmol), dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (D) (94 mg, 0.2 mmol) was used in Suzuki–Miyaura polymerization. Pd residual 0.56 wt % from ICP-AES.

Synthesis of PS-8: Black powder 230 mg, yield 54.9 %. Diboronic ester arenes (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene 5,5-dioxide)
(B) (468 mg, 1 mmol) and dibromo arene (3,10-dibromoperyleno[1,12-bcd]thiophene 1,1-dioxide) (D) (469 mg, 1 mmol) was used in Suzuki–Miyaura polymerization. Pd

residual 1.50 wt % from ICP-AES.

2. Characterization of the Samples.

¹H spectra were characterized on the Bruker AM-400 MHz and ¹³C solid spectra were characterized on the Super Conducting Fourier NMR Spectrometer-500MHZ/AVANCEIII. High-resolution mass spectra (HRMS) characterizations were measured on the Waters GCT Premier spectrometer. The FTIR spectra were measured on NIswew COLET 380 spectrometer with a standard KBr pellet technique. Powder XRD patterns was carried out on a RigakuD/MAX 2550 diffract meter, and the test conditions are under 100 mA and 40 kV (Cu K radiation, $\lambda = 1.5406$ Å). The Scanning Electron Microscope (SEM) spectra was recorded on S-3400N to obtain the sample morphologies. DRS UV-vis characterizations were obtained on a Varian Cary 500 spectrophotometer. ICP-AES characterizations were obtained on Inductively Coupled Plasma Atomic Emission Spectrometer (167 nm-785 nm/725). Photoluminescence (PL) spectrum was carried out on Hitachi F-4500 fluorescence spectrophotometer at room temperature and the excitation wavelength of the PL emission spectra was 385 nm. The time-resolved PL decay spectra were carried out at 427 nm for PS-1, 548 nm for PS-2, 410 nm for PS-3, PS-4 and PS-5 and 422 nm for PS-6 and PS-7. The value of the goodness-of-fit parameter (χ^2) is between 1 and 1.5, and indicates good credibility of the calculated data in Decay Kinetics Calculation. Specifically, the PS-8 sample is black and the PL emission spectra and time-resolved PL decay spectra were not detected for **PS-8**. The water contact angle experiment was carried out on JC2000C1. The dynamic light scattering (DLS) measurement was carried out on to determine the particle size of polymers in the reaction mixture (water/TEOA = 5:1). These polymers were under ultrasound in mixture solution for half an hour at 25 °C. The Surface area mean diameter (D^[3,2]) was determined by calculation formula:

$$\mathsf{D}^{[3,2]} = \frac{\sum_{1}^{n} D_{iv_{i}}^{3}}{\sum_{1}^{n} D_{iv_{i}}^{2}}$$

3. Electrochemical analysis

Cyclic voltammetry (CV) curves were recorded on CHI650E electrochemical

workstation with the traditional three-electrode system (glassy carbon electrode, Pt wire and saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode respectively) to confirm the energy band location of PS-1~PS-8. And they were measured in the electrolyte of 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) in DCM, the scan rate was 100 mV s⁻¹, and the ferrocene/ferrocenium (Fc/Fc⁺) was employed as an external potential reference. The calculation formula of HOMO (eV) is E_{HOMO} = -4.8 eV - (E_{ox_onset} (vs SCE)- E^{ox}_{Fc/Fc+} (vs SCE)). The transient electrochemical impedance spectra (EIS) and photocurrent responses (It) of samples were also obtained on a CHI650E electrochemical workstation with a classic three-electrode system (Pt wire as counter electrode, and Ag/AgCl as reference electrode). The working electrode preparation process is as follows: Mix 20 mg of samples (PS-1~PS-8) and 10 µL of a Nafion (5 %) aqueous solution with ethanol as solvent and grind into slurry. The slurry was uniformly coated on ITO glasses and the ITO glassed were fired at 120 K for 1 hour to obtain the desired working electrode. The I-t measurements were performed with the light on and off (300 W Xe-lamp, λ > 420 nm) in a 0.5 M Na₂SO₄ aqueous solution, and the bias was 0 V versus Ag/AgCl. For EIS, the frequency range was $10^2 - 10^6$ Hz and the amplitude was 10 mV at the open circuit voltage.



for 30 minutes

Scheme S2. Photocatalytic process of polymer PS-5.

4. SEM image of the PS-1~PS-8 polymers



Fig. S1 SEM image of the PS-1~PS-8 polymers. Scale bar: 2.00 μm.

5. The absorption and emission spectra for PS-1~PS-8 in THF solution and cyclic voltammograms curves of ferrocene/ferrocenium (Fc/Fc⁺) redox couple



Fig. S2 Cyclic voltammetry measurements of ferrocene/ferrocenium (Fc/Fc⁺) in THF solution.



Fig. S3 DRS and PL spectra (λ exc = 385 nm) of as-prepared samples in THF solution.



Fig. S4 DRS and PL spectra (λ exc = 385 nm) of as-prepared samples in THF solution.

6. The contrast FT-IR spectra and UV-Vis diffuse reflection spectra of

before and after irradiation



Fig. S5 The FT-IR of PS-1, PS-2, PS-3 and PS-4 after photocatalysis experiment.



Fig. S6 The FT-IR of PS-5, PS-6, PS-7 and PS-8 after photocatalysis experiment.



Fig. S7 DRS of PS-1, PS-2, PS-3 and PS-4 after photocatalysis experiment.



Fig. S8 DRS of PS-5, PS-6, PS-7 and PS-8 after photocatalysis experiment.





Fig. S9 Wavelength-dependent AQY and DRS spectrum of PS-1, PS-3, PS-4, PS-6 and PS-7 (λ = 420, 435, 475, 500, 520, 550, 630 nm. Reaction conditions: 50 mL water, 10 mL TEOA, 12.5 mg photocatalyst under visible-light.

8. Optimized structures of the dimers of the designed model



Fig. S10 Optimized structures of the dimers of the designed model Model 1 (a), 2 (b), 3 (c) and 4 (d) from DFT calculations.

9. The fitted fluorescence lifetimes and corresponding amplitudes of

photoinduced charge carriers in sample

Table S1. The fitted fluorescence lifetimes and corresponding amplitudesof photoinduced charge carriers in **PS-1** to **PS-8**.

Sample	τ1 [ns] (Rel.%)	τ2 [ns] (Rel.%)	τ [ns]	χ²
PS-1	0.91 (93.98)	2.02 (6.02)	0.97	1.024
PS-2	0.87 (85.45)	1.63 (14.55)	0.98	0.996
PS-3	0.86 (79.94)	1.58 (20.06)	1.00	1.031
PS-4	0.87 (79.16)	1.58 (20.84)	1.01	1.007
PS-5	0.86 (75.27)	1.55 (24.73)	1.03	0.996
PS-6	1.00 (97.31)	2.22 (2.69)	1.03	0.650
PS-7	0.89 (83.8)	1.78 (16.2)	1.04	1.030

10. The reported work previously

Materials	light source	H ₂ Production (mmol g ⁻¹ h ⁻¹)	AQY	Ref
P7	λ > 420 nm	1.49	7.2 % (420 nm)	2
P10	λ > 420 nm	3.26	11.6 % (420 nm)	3
FSO-FS	λ > 420 nm	3.4	6.8 % (420 nm)	4
Flu-SO	λ > 420 nm	5.04	2.13 % (420 nm)	5
Р7-Е	λ > 420 nm	5.99	4.2 % (420 nm)	6
PS-5	λ > 420 nm	7.5	15.3 % (420 nm); 1.93 % (550 nm)	This work

Table S2. Recent representative photocatalytic H₂ evolution activities of sulfone-based liner polymers

11. The ¹H NMR, HRMS of monomer



Fig. S11 ¹H NMR spectrum of 3,7-dibromodibenzo[b,d] thiophene 5,5-dioxide in CDCl₃.



Fig. S12 ¹H NMR spectrum of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)dibenzo[b,d] thiophene 5,5-dioxide in CDCl₃.



Fig. S13 1 H NMR spectrum of compound 1-nitroperylene in CDCl₃.



Fig. S14 ¹H NMR spectrum of peryleno[1,12-bcd]thiophene in DMSO-d6.



Fig. S15 HRMS of peryleno[1,12-bcd]thiophene.



Fig. S16 ¹H NMR spectrum of 3,10-dibromoperyleno [1,12-bcd]thiophene in CDCl₃.



Fig. S17 HRMS of 3,10-dibromoperyleno [1,12-bcd]thiophene.



Fig. S18 ¹H NMR spectrum of 3,10-dibromoperyleno [1,12-bcd]thiophene 1,1-dioxide in CDCl_{3.}



Fig. S19 HRMS of 3,10-dibromoperyleno [1,12-bcd]thiophene 1,1-dioxide.

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