

**Boosting Exciton Dissociation and Charge Separation in Pyrene-Based Linear  
Conjugated Polymers for Efficient Photocatalytic Hydrogen Production**

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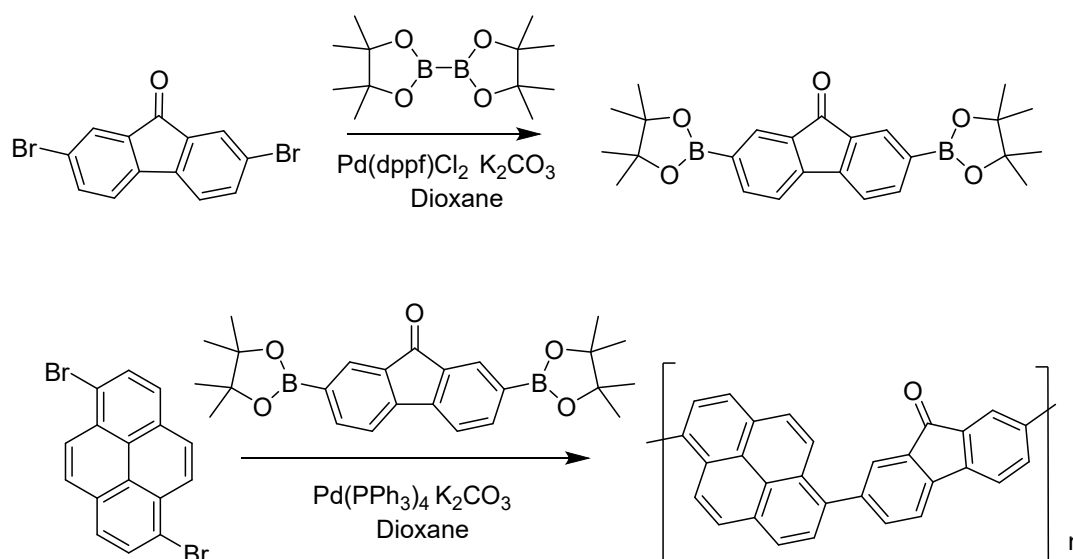
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## Experimental Section

### Synthesis of PyFO

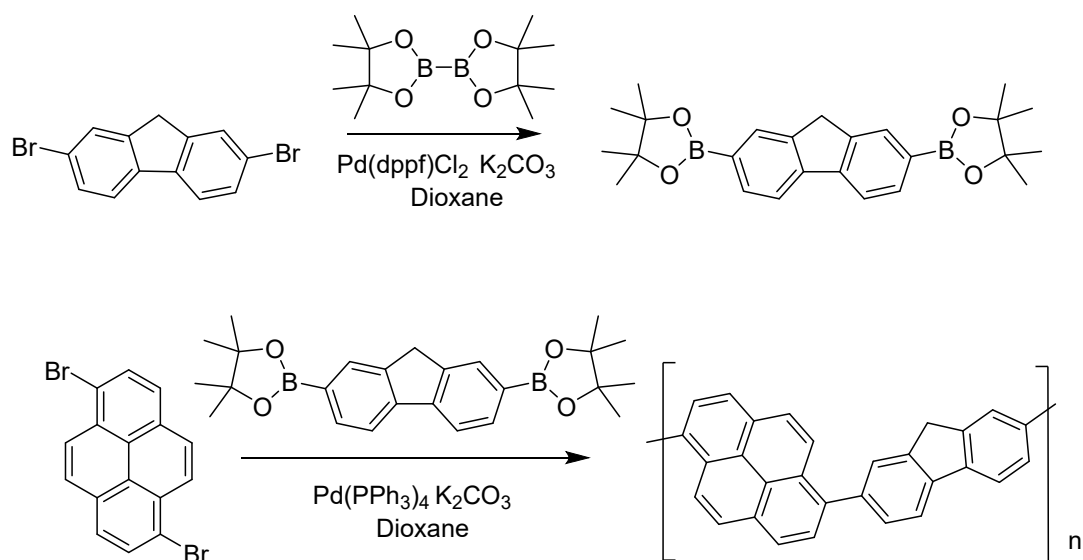


To a mixture of 2,7-dibromo-9H-fluoren-9-one (338 mg, 1.0 mmol), bis(pinacolato)diboron (762 mg, 3.0 mmol), potassium carbonate (414.6 mg, 5.0 mmol) and Pd(dppf)Cl<sub>2</sub> (73.2 mg, 0.1 mmol) was added 1,4-dioxane (50 mL), and then thoroughly degassed by three cycles of freeze-pump-thaw under nitrogen atmosphere. Then the reaction mixture was heated up to reflux for overnight. The reaction mixture was cooled to room temperature, added with water, and extracted with ethyl acetate, the combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness, the residue was purified by column chromatography using hexane/EtOAc (4/1) as an eluent. The first fraction was collected, evaporated and dried under vacuum, to afford a light yellow solid (276.5 mg, 64% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.12 (s, 2H), 7.95-7.93 (d, 2H), 7.56-

7.54 (d, 2H), 1.34 (s, 24H).

To a 50 mL Schlenk flask, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (216 mg, 0.50 mmol) and 1,6-dibromopyrene (180 mg, 0.50 mmol) were dissolved in 1,4-dioxane (25 mL) and 2M  $K_2CO_3$  (5 mL) were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine) palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at 110°C for 3 d. The precipitated dark solid was filtered off and re-dissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum (82 % yield).

### Synthesis of PyCZ

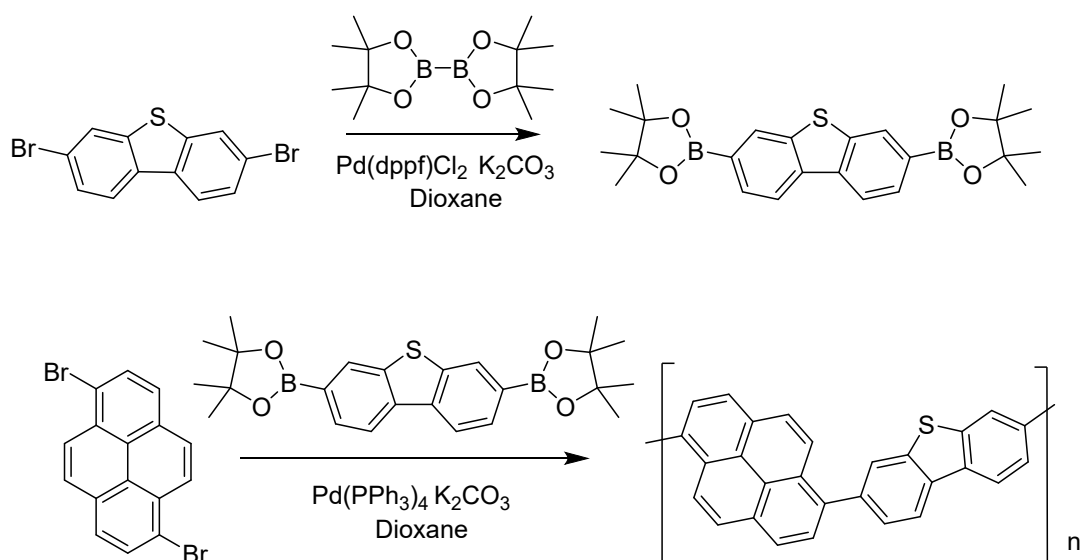


To a mixture of 2,7-dibromo-9H-fluorene (324 mg, 1.0 mmol), bis(pinacolato)diboron (762 mg, 3.0 mmol), potassium carbonate (414.6 mg, 5.0 mmol) and Pd(dppf)Cl<sub>2</sub> (73.2 mg, 0.1 mmol) was added 1,4-dioxane (50 mL), and then thoroughly degassed by three cycles of freeze–pump–thaw under nitrogen atmosphere. Then the reaction mixture was heated up to reflux for overnight. The reaction mixture was cooled to room temperature, added with water, and extracted with ethyl acetate, the combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness, the residue was purified by column chromatography using hexane/EtOAc (4/1) as an eluent. The first fraction was collected, evaporated and dried under vacuum, to afford a light yellow solid (204.9 mg, 49% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01 (s, 2H), 7.86 - 7.81 (m, 4H), 3.89 (s, 2H), 1.37 (s, 24H).

To a 50 mL Schlenk flask, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene (209 mg, 0.50 mmol) and 1,6-dibromopyrene (180 mg, 0.50 mmol) were dissolved in 1,4-dioxane (25 mL) and 2M K<sub>2</sub>CO<sub>3</sub> (5 mL) were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine) palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at 110°C for 3 d. The precipitated dark solid was filtered off and re-dissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and

dried under vacuum (76 % yield).

### Synthesis of PyDBP

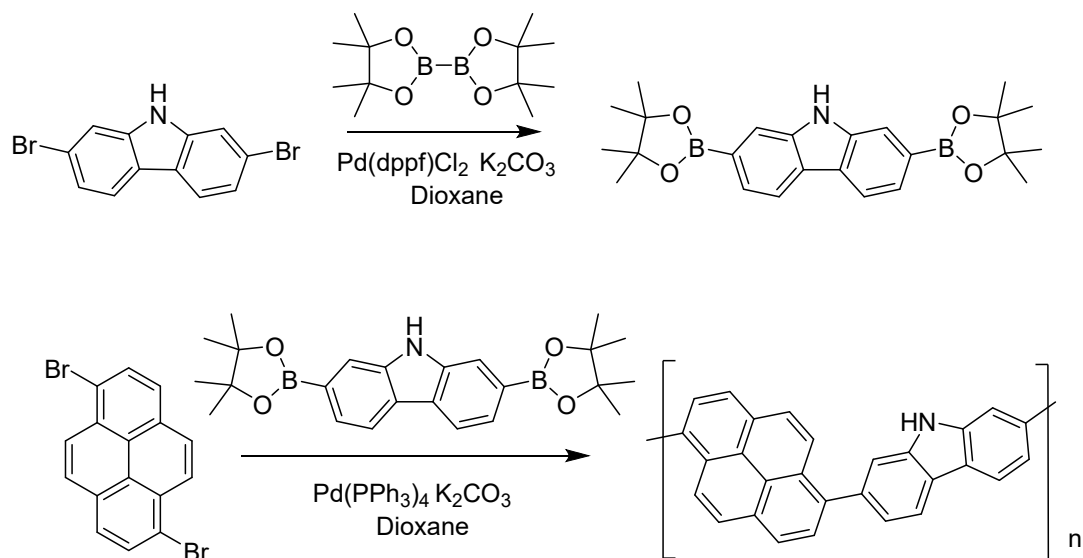


To a mixture of 3,7-dibromodibenzo[b,d]thiophene (342 mg, 1.0 mmol), bis(pinacolato)diboron (762 mg, 3.0 mmol), potassium carbonate (414.6 mg, 5.0 mmol) and Pd(dppf)Cl<sub>2</sub> (73.2 mg, 0.1 mmol) was added 1,4-dioxane (50 mL), and then thoroughly degassed by three cycles of freeze-pump-thaw under nitrogen atmosphere. Then the reaction mixture was heated up to reflux for overnight. The reaction mixture was cooled to room temperature, added with water, and extracted with ethyl acetate, the combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness, the residue was purified by column chromatography using hexane/EtOAc (4/1) as an eluent. The first fraction was collected, evaporated and dried under vacuum, to afford a light yellow solid (226.8

mg, 52% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.33 (s, 2H), 8.18 (d, 2H), 7.87 (d, 2H), 1.38 (s, 24H).

To a 50 mL Schlenk flask, 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]thiophene (218 mg, 0.50 mmol) and 1,6-dibromopyrene (180 mg, 0.50 mmol) were dissolved in 1,4-dioxane (25 mL) and 2M  $\text{K}_2\text{CO}_3$  (5 mL) were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine) palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at  $110^\circ\text{C}$  for 3 d. The precipitated dark solid was filtered off and re-dissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum (69 % yield).

### Synthesis of PyFE



To a mixture of 2,7-dibromo-9H-carbazole (325 mg, 1.0 mmol), bis(pinacolato)diboron (762 mg, 3.0 mmol), potassium carbonate (414.6 mg, 5.0 mmol) and Pd(dppf)Cl<sub>2</sub> (73.2 mg, 0.1 mmol) was added 1,4-dioxane (50 mL), and then thoroughly degassed by three cycles of freeze–pump–thaw under nitrogen atmosphere. Then the reaction mixture was heated up to reflux for overnight. The reaction mixture was cooled to room temperature, added with water, and extracted with ethyl acetate, the combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated to dryness, the residue was purified by column chromatography using hexane/EtOAc (4/1) as an eluent. The first fraction was collected, evaporated and dried under vacuum, to afford a light yellow solid (222.14 mg, 53% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.10 (d, J = 8.0 Hz, 2H), 8.04 (br, 1H), 7.93 (s, 2H), 7.68 (dd, J = 8.0 Hz, J = 0.7 Hz, 2H), 1.39 (s, 24H).

To a 50 mL Schlenk flask, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (210 mg, 0.50 mmol) and 1,6-dibromopyrene (180 mg, 0.50 mmol) were dissolved in 1,4-dioxane (25 mL) and 2M K<sub>2</sub>CO<sub>3</sub> (5 mL) were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine) palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at 110°C for 3 d. The precipitated dark solid was filtered off and re-dissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and

dried under vacuum (55 % yield).

## **Materials**

All chemicals and reagents were of analytical grade materials and used as received without further purification. The 1,6-Dibromopyrene, Bis(pinacolato)diboron, Potassium carbonate, [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II),  $\text{Pd}(\text{PPH}_3)_4$ , 1,4-Dioxane were purchased from Macklin Chemicals. 2,7-Dibromo-9-fluorenone 96%, 2,7-Dibromofluorene, 3,7-Dibromodibenzothiophene, 2,7-Dibromocarbazole were all supplied by Energy Chemical.

## **Characterization**

Fourier transformed infrared (FTIR) spectra were tested on a Nicolet Avatar 6700 FT-IR spectrometer (Thermo Fisher, America).  $^{13}\text{C}$  Solid state NMR (cross polarization magic-angle spinning (CP/MAS)) spectra were carried out on a Bruker Avance 400 MHz spectrometer operating at 100.6 MHz. The UV-vis diffuse reflection spectra (UV-vis DRS) of the as pristine PyFO, PyDBP, PyFE and PyCZ powders were carried out on a Shimadzu UV-2550 UV-vis-NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) data was carried out by a VG ESCALAB250 surface measurement system. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 electron microscope. ESR measurements in X-band (microwave frequency  $\approx 9.87$  GHz) were performed at 293 K by a Bruker EMX CW micro spectrometer equipped with an ER 4119HS-WI high-sensitivity optical



resonator with a grid in the front side. The samples were illuminated by a 300 W Xe lamp with 420 nm cut-off filter (LOT Oriel). All the samples were measured under the same conditions (microwave power: 6.74 mW, receiver gain:  $2 \times 10^4$ , modulation frequency: 100 kHz, modulation amplitude: 3 G, Sweep time: 45 s).  $g$  values have been calculated from the resonance field  $B_0$  and the resonance frequency  $\nu$  using the resonance condition  $h\nu = g\beta B_0$ . The calibration of the  $g$  values was performed using DPPH (2, 2-diphenyl-1-picrylhydrazyl) ( $g = 2.0036 \pm 0.00004$ ). Thermogravimetric analysis was performed on an EXSTAR6000 by heating samples at  $10 \text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$  in open aluminium pans to  $800 \text{ }^\circ\text{C}$ . fs-TAS measurements were collected with a femtosecond Ti/Sapphire regenerative amplifier laser system (Spitfire-Pro, Spectra-Physics Company), and an automated data acquisition transient absorption spectrometer (Ultrafast, Helios) was used to record transient absorption spectra of the photocatalysts. The amplifier produced a 150 fs pulse at 800 nm (repetition rate at 1 kHz, average output energy was 2.5 W). In our experiments, the pump laser (340 nm) was obtained from the second harmonic generated from the 800 nm output from the Spitfire amplifier ( $\approx 95.0\%$  of the amplified output). The probe pulse (continuum white-light spectrum, 420 to 780 nm) was generated using the remaining 5.0% of the amplified 800 nm output, Supporting Information. Additionally, ns-TAS spectra were collected from a LP-920 laser system (Edinburgh Instruments). The Xenon lamp was the probe light source (450 W, model Xe900), which traversed the sample cell and the signal was recorded by an array detector (absorption mode) and a single detector (kinetic mode), all of the as-prepared catalysts were dispersed in glycol. None Pt

nanoparticles were added in transient absorption spectroscopy experiments.

The working electrodes was fabricated as follows: 5 mg photocatalyst powder was added into 4 mL ethanol solution containing 20  $\mu\text{L}$  0.25% of Nafion under ultrasound for 1 h to obtain a slurry. Then, 0.5 mL of the slurry homogeneously dropped on a FTO glass (2 cm  $\times$  3.5 cm). After being calcined for 1 h in a tube furnace at 150  $^{\circ}\text{C}$  ( $\text{N}_2$  carrier gas), an electrode was obtained. Electrochemical impedance spectra (EIS) and transient photocurrent experiments were conducted on a IM6e electrochemical workstation (Zahner Elektrik, Germany) with a standard three-electrode system, which employed as-fabricated electrodes as the working electrode, a platinum plate as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. A Xe arc lamp (350 W) with a cut-off filter ( $\lambda > 420$  nm) was used as the light source. 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as the electrolyte.

### **Photocatalytic hydrogen evolution method and parameters**

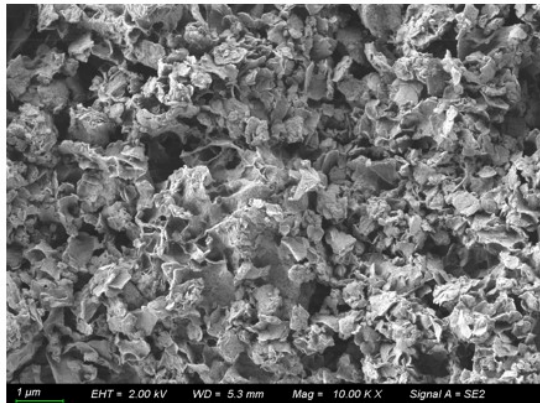
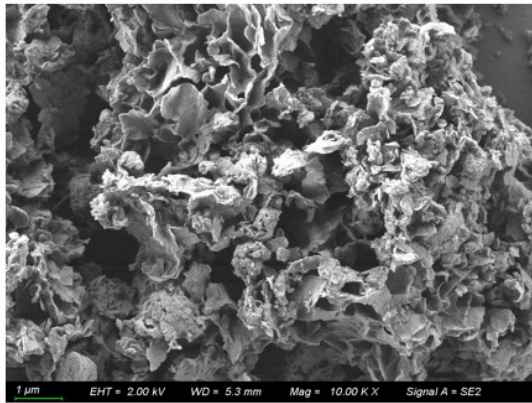
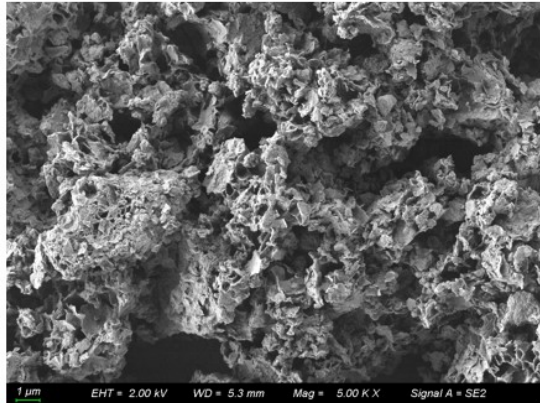
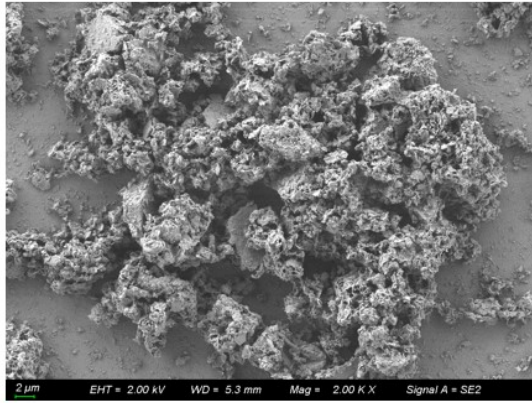
The photocatalytic water splitting reaction under visible-light irradiation was performed in a 250 mL Pyrex top-irradiation reaction vessel with a stationary temperature at 5  $^{\circ}\text{C}$ , which was connected to a glass closed gas system (Labsolar-6A, Perfect Light). In a typical process, 1 mg of photocatalyst was dispersed in a Pyrex reaction cell with 100 mL 0.1 M ascorbic acid aqueous solution. The reaction cell was sealed, and then irradiated with a 350 W Xe lamp (PLS-SXE300, Beijing Perfect Light Technology Co., Ltd,  $\lambda > 420$  nm). During the photocatalytic reaction, the suspension was continuously stirred. The generated hydrogen was detected by GC-

9500 online chromatograph. The apparent quantum efficiency (AQE) was measured under the same condition, the following equation was used to calculate the quantum efficiency

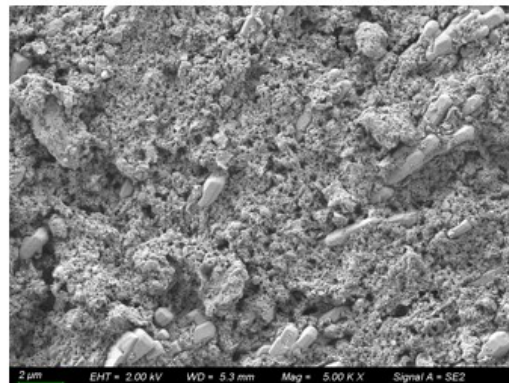
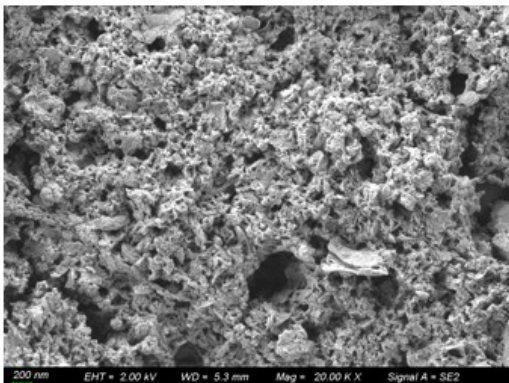
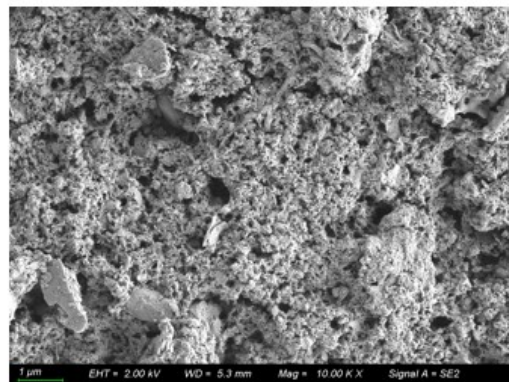
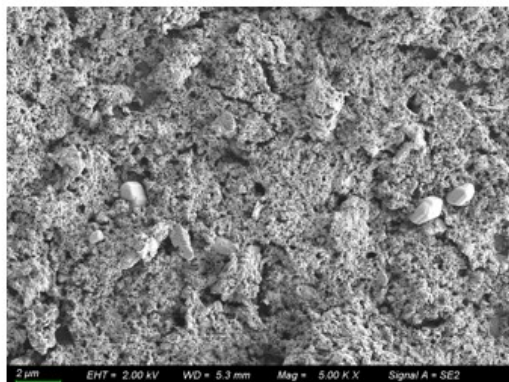
$$\eta = \frac{2 \times M \times h \times c \times N_A}{S \times P \times t \times \lambda} \times 100\%$$

### **Calculations Details and Discussions:**

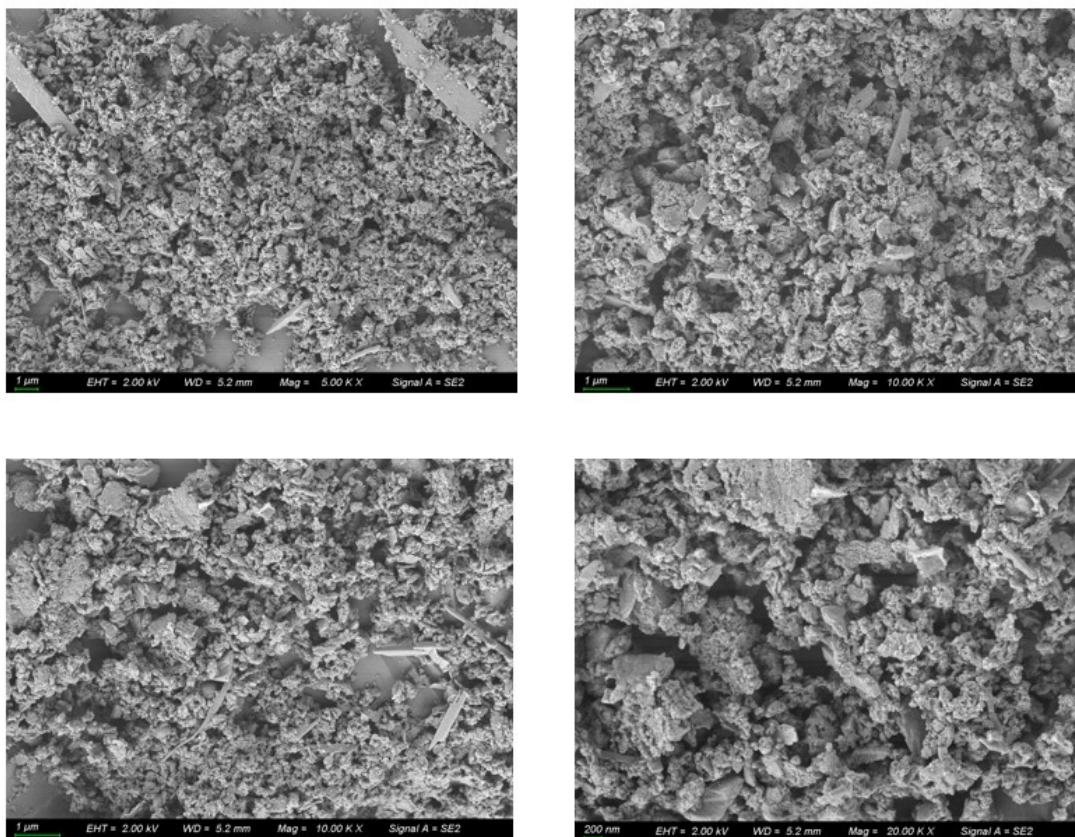
All calculations were performed using Gaussian 09 software package. According to density functional theory (DFT), the geometric optimization of the PyFO, PyDBP, PyFE, PyCZ cross sections were performed at the B3LYP/6-311g (d, p) level. The calculation results of the molecular electrostatic potential (ESP) are obtained by Gaussian 09 software.<sup>1</sup>



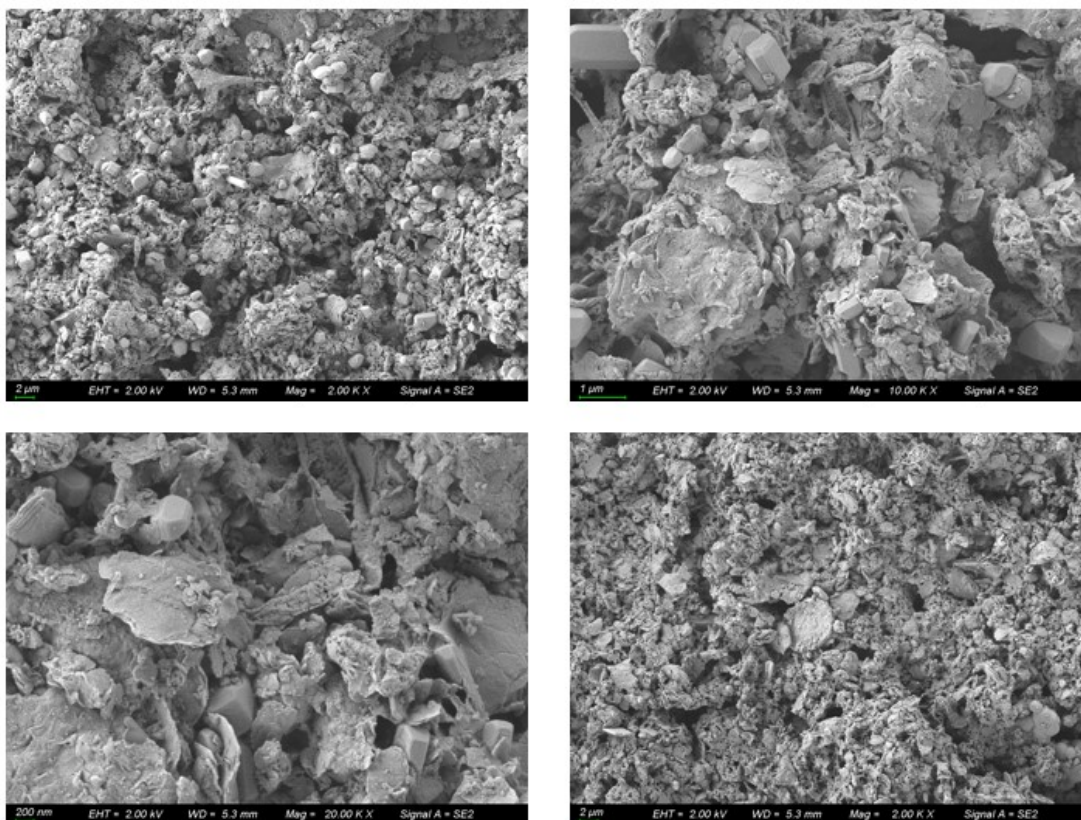
**Figure S1.** SEM image of PyFO.



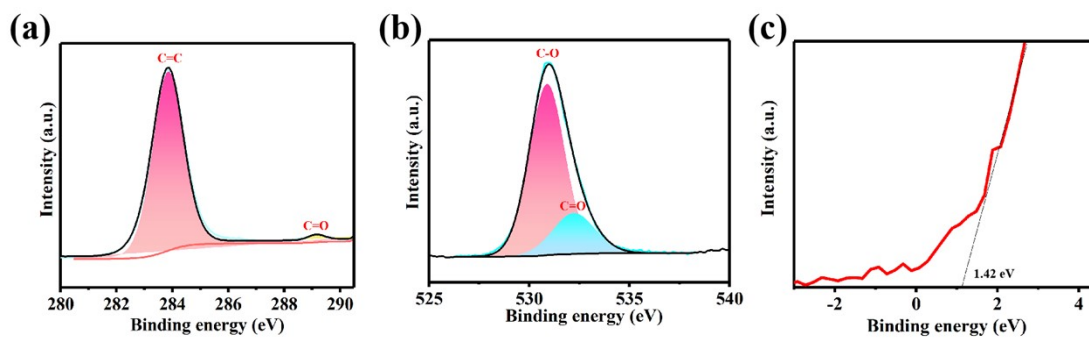
**Figure S2.** SEM image of PyFE.



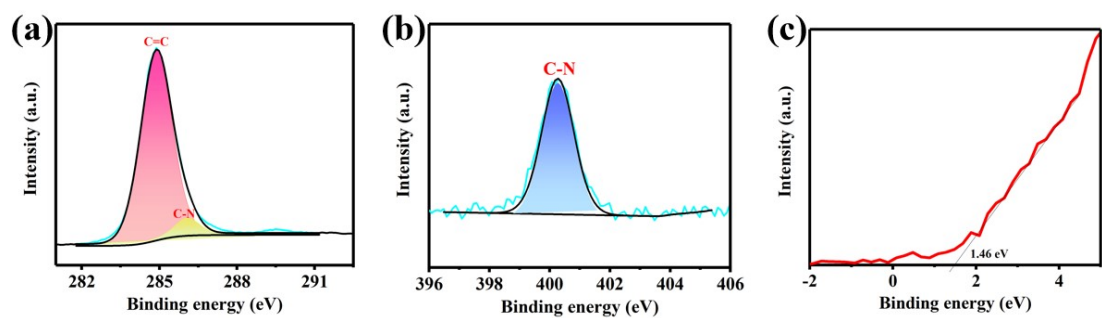
**Figure S3.** SEM image of PyDBP.



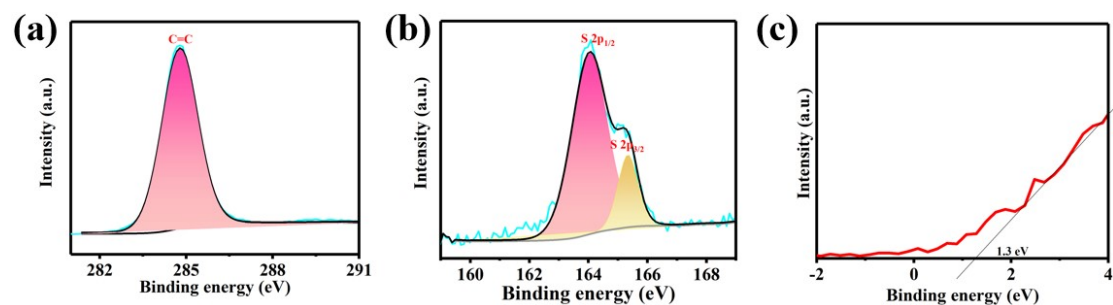
**Figure S4.** SEM image of PyCZ.



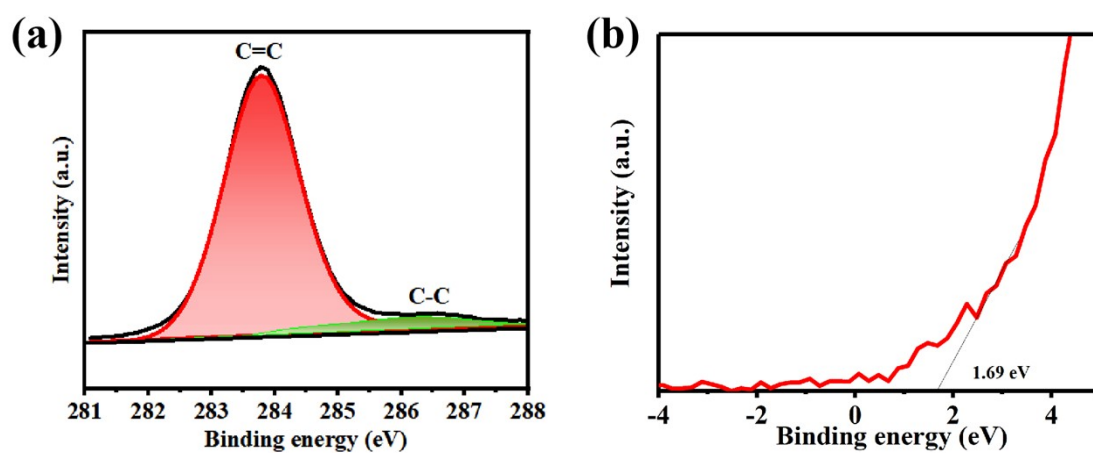
**Figure S5.** (a) XPS C1s spectra of PyFO. (b) XPS O1s spectra of PyFO. (c) XPS valence band spectra of PyFO.



**Figure S6.** (a) XPS C1s spectra of PyCZ. (b) XPS N1s spectra of PyCZ. (c) XPS valence band spectra of PyCZ.



**Figure S7.** (a) XPS C1s spectra of PyDBP. (b) XPS S1s spectra of PyDBP. (c) XPS valence band spectra of PyDBP.



**Figure S8.** (a) XPS C1s spectra of PyFE. (c) XPS valence band spectra of PyFE.

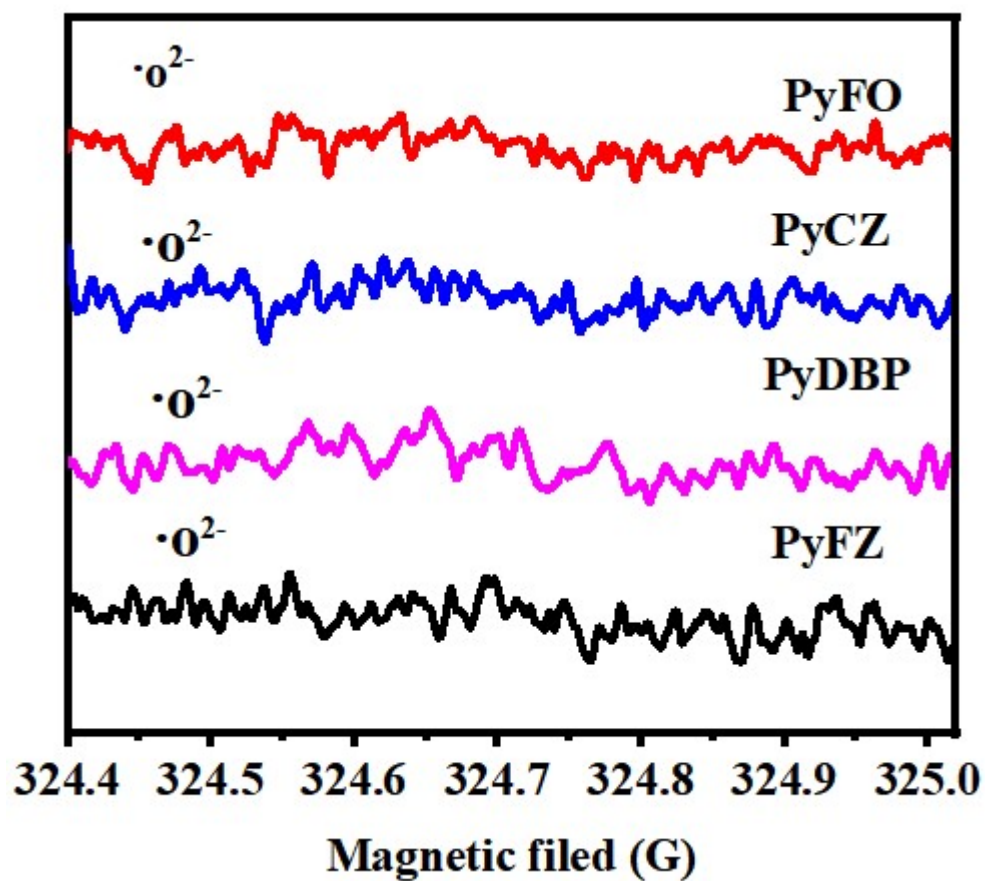


Figure S9. ESR spectrum of four copolymers in the darkness ( $\cdot\text{O}_2^-$ ).



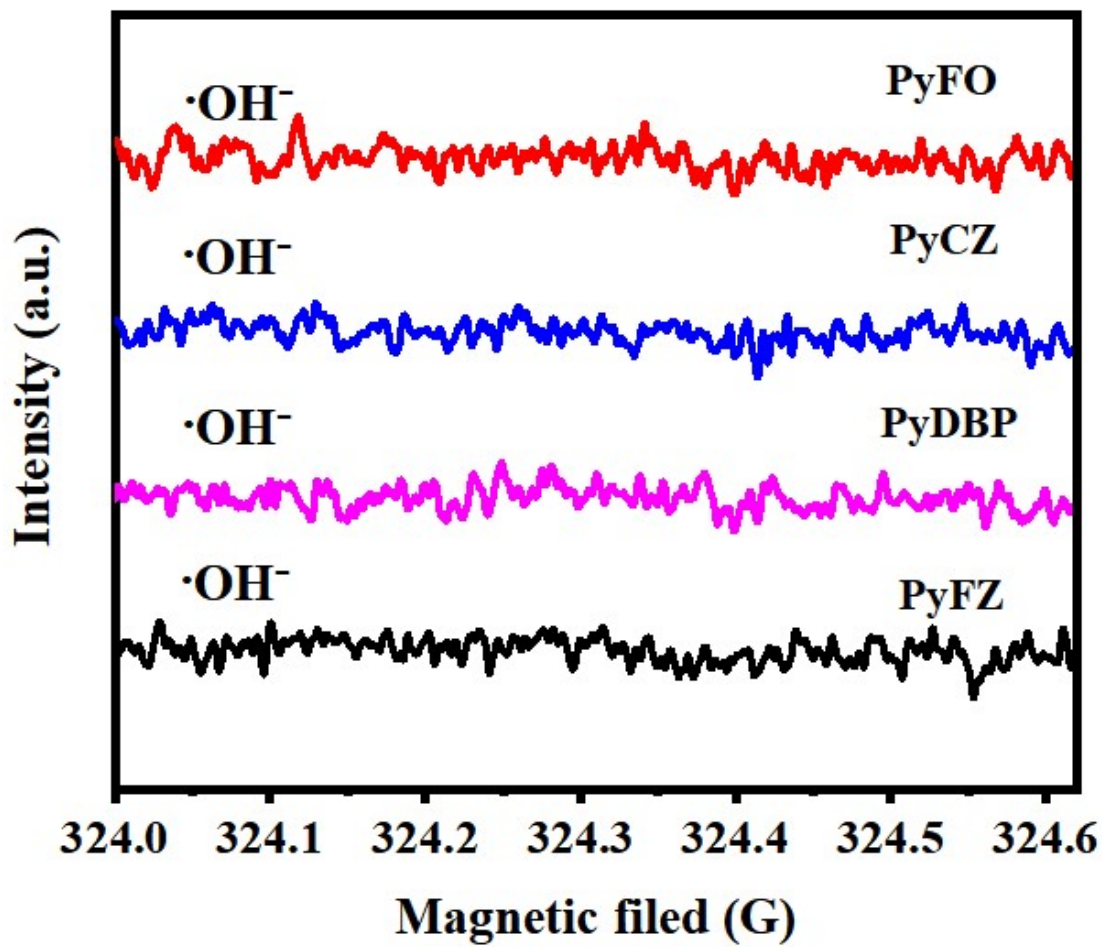


Figure S10. ESR spectrum of four copolymers in the darkness ( $\cdot\text{OH}^-$ ).

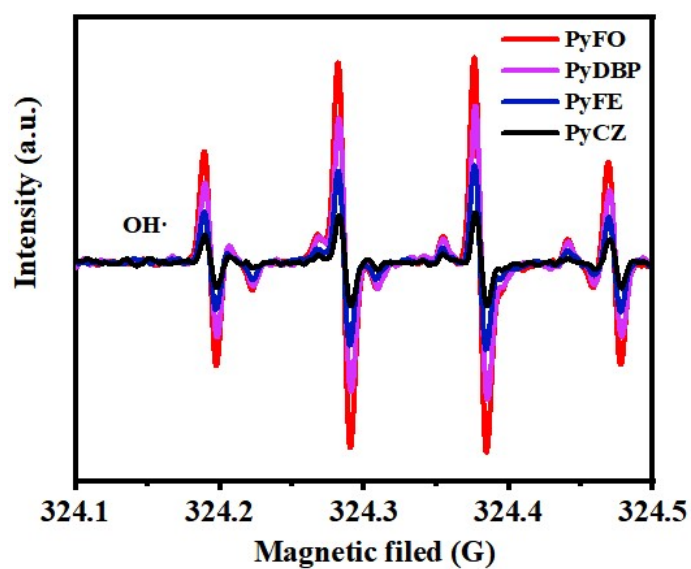
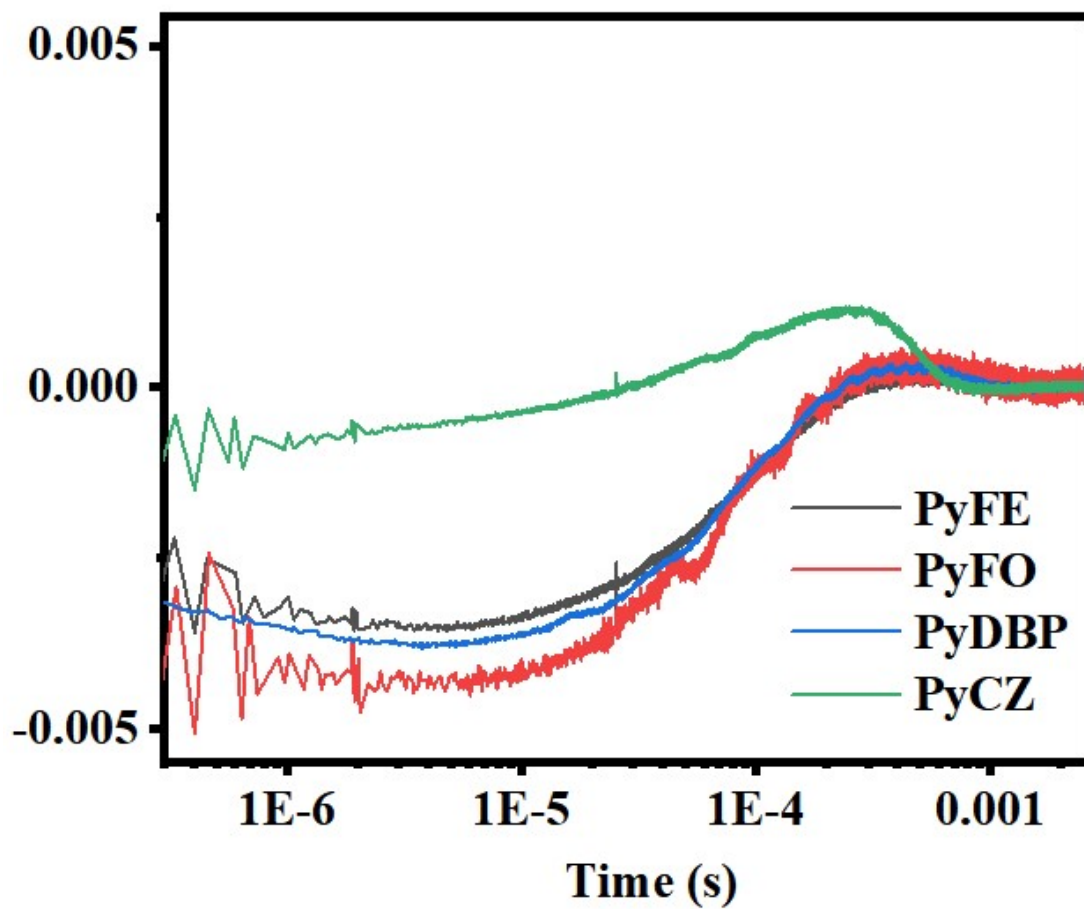


Figure S11. ESR spectrum of four copolymers under lights ( $\text{OH}\cdot$ ).



**Figure S12.** Transient photovoltage (TPV) responses of four COPs.

**Table S1.** Comparison of photocatalytic HER performance of pyrene-based linear copolymers.

Catalyst	Sacrificial agent	Amount Photocatalyst (mg)	Activity ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Light source	AQE %	Ref.
PrPy	TEOA	100	79	>300 nm	-	S1
CP-CMP10	DEA	100	167	>420 nm	-	S2
Py-B	AA	6	1600	>420 nm	-	
Py-T	AA	6	38100	>420 nm		S3
Py-Tt	AA	6	45800	>420 nm	-	
Py-Ttt	AA	6	38900	>420 nm		
PySEO-1	TEOA	50	9477	> 420nm	4.1 % at 400 nm	S4
PySEO-2	C	50	20314	> 420nm		
PyP2/CN	TEOA	50	600	> 420nm	20.5 %	S5
CP1	AA	6	30810	> 420nm	1.62 % at 550 nm	S6
BBT-SC2NH2	TEOA	30	8200	> 420nm	3.3 % at 420 nm	S7
PyTA-BC-COF	AA	1	1183	> 420nm	1.46 % at 420 nm	S8

P-FSO	TEOA	50	8000	> 420nm	8.5 % at 420 nm	S9
B-BT-1,4-E	TEOA	30	11820	> 420nm	3.7 % at 420 nm	S10
PyFO	AA	2	108400	> 420nm	35.2 % at 420 nm	this work

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