

Supporting Information

Enhanced Fe(III)/Fe(II) cycle in heterogeneous photocatalysis–self–Fenton system for organic pollutants degradation

Rong Ji^{a,b}, Jingran Yi^a, Xinyu Sun^a, Yuming Dong^{a*}, Chengsi Pan^a, Hui Zhao^a, Yongfa Zhu^c

Table of contents

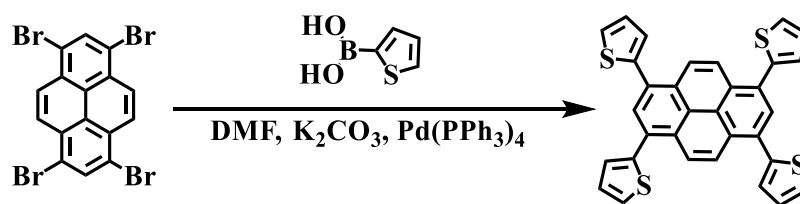
1. Experimental section.....	3
Synthesis of 1,3,6,8-tetrakis(2-thienyl)pyrene ^[1]	3
Synthesis of 1,3,6,8-tetrakis(5-bromo-2-thienyl)pyrene ^[2]	3
Synthesis of 3,7-dibromodibenzothiophene <i>S,S</i> -dioxide ^[3]	4
Synthesis of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide[4]	5
Synthesis of Fe-Py-Tp-BDTO	6
Photoelectrochemical Measurements.....	7
Rotating ring-disk electrode (RRDE) measurement	8
Photocatalytic in situ production of H ₂ O ₂	8
Photocatalytic evolution of [•] O ₂ ⁻	9
DFT Calculations	9
2. Results and Discussion	11
Table S1. The weight of Fe in the Fe-Py-Tp-BDTO detected by ICP-MS	11
Table S2. The calculated energy for O ₂ adsorption at active sites of Py-Tp-BDTO and Fe-Py-Tp-BDTO	12
TableS3 Selected results obtained for pollutant removal by photocatalysis-self-Fenton methods	13
Fig. S5. (a) Solid-state ¹³ C NMR spectra and the assignment of carbon atoms in the polymers of Py-Tp-BDTO; (b) The powder X-ray diffraction patterns of Fe-Py-Tp-BDTO and Py-Tp-BDTO.	14
Fig. S6. Nitrogen adsorption/desorption isotherms of Fe-Py-Tp-BDTO and Py-Tp-BDTO.....	15
Fig. S7. The SEM images of (a) Py-Tp-BDTO, (b) Fe-Py-Tp-BDTO; The TEM images of (c) Py-Tp-BDTO, (d) Fe-Py-Tp-BDTO; (e-h) EDS mapping images of Fe-Py-Tp-BDTO; Atomic force microscope (AFM) image and corresponding height of (i) Py-Tp-BDTO, (j) Fe-Py-Tp-BDTO.....	16
Fig. S8. XPS spectra of C 1s over Py-Tp-BDTO and Fe-Py-Tp-BDTO.....	17
Fig. S9. The HOMO and LUMO orbital distribution of the two samples based on DFT simulation (gray: C, yellow: S, red: O, white: H, purple: Fe).	18
Fig. S10. Time profiles of H ₂ O ₂ production for Py-Tp-BDTO and Fe-Py-Tp-BDTO in water (solution: 30 mL H ₂ O or 10 mg L ⁻¹ 4-chlorophenol, O ₂ bubbling; light source: Xe lamp with an AM1.5G filter).....	19
Fig. S11. H ₂ O ₂ production on Py-Tp-BDTO with different catalyst concentrations plotted as a function of irradiation time.	20
Fig. S12. H ₂ O ₂ production on Py-Tp-BDTO at different temperatures plotted as a function of irradiation time.	21
Fig. S13. (a) H ₂ O ₂ yield curve under incommensurate atmosphere of Py-Tp-BDTO; (b) Photocatalytic yield of [•] O ₂ ⁻ detected by NBT method of Py-Tp-BDTO.....	22
Fig. S14. Adjustment of Fe concentration (Condition: catalyst = 0.6 g L ⁻¹ , 4-CP = 10 mg L ⁻¹ , 300 W Xe lamp, AM1.5).	23
Fig. S15. Linear-sweep RDE voltammograms of (a) Py-Tp-BDTO and (b) Fe-Py-Tp-BDTO measured at different rotating speeds; (c) Koutecky-Levich plots of Py-Tp-	

BDTO and Fe-Py-Tp-BDTO (at -0.8V vs. Ag/AgCl).	24
Fig. S16. The fs-TA spectra (a) and (b); (c) Transient-state PL spectra of Py-Tp-BDTO and Fe-Py-Tp-BDTO; Pseudocolor plots of Cyclic voltammograms of Fe-Py-Tp-BDTO in (d) H ₂ O and (e) 4-chlorophenol; (f) Electrochemical impedance spectra of Py-Tp-BDTO and Fe-Py-Tp-BDTO.	25
Fig. S17. (a) UV-Vis absorption spectra of Py-Tp-BDTO and Fe-Py-Tp-BDTO (inset: Plots of transformed Kubelka-Munk function versus photon energy of Py-Tp-BDTO and Fe-Py-Tp-BDTO); (b-c) Mott-Schottky plots of Py-Tp-BDTO and Fe-Py-Tp-BDTO; (d) Estimated band structure of all samples.	26
Fig. S18. Electron-hole distribution in excited states.	28
Fig. S19. The Zeta potential of Py-Tp-BDTO and Fe-Py-Tp-BDTO.	29
Fig. S20. Ultra-high-performance LC-MS of degradation solution (a) degradation in 5 min and (b) degradation in 30 min.	30
Fig. S21. (a) Possible pathway of 4-chlorophenol degradation; (b) Mechanism of Fe-Py-Tp-BDTO based photocatalysis-self-Fenton degradation of 4-chlorophenol.	31
3. References.	32

1. Experimental section

Synthesis of 1,3,6,8-tetrakis(2-thienyl)pyrene^[1]

1.04 g of 1,3,6,8-tetrabromopyrene (2.0 mmol), 1.52 g of 2-thienylboronic acid (12.0 mmol), and 0.2 g of Pd(PPh₃)₄ (0.17 mmol) were added to a 100 mL flask. Then 40 mL of anhydrous DMF and 8 mL of K₂CO₃ aqueous (2.0 M) were added to the reaction flask. After that, the mixture was stirred and protected with N₂, and heated to 110 °C for 72 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂, the organic phase was collected and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then the residue was purified by column chromatography (petroleum ether/CH₂Cl₂ = 1:1), and after drying under vacuum at 50 °C for 24 h, a yellow powdery final product named 1,3,6,8-tetrakis(2-thienyl)pyrene in 65% yield. ¹H NMR (δ, 400 MHz, DMSO-d₆): δ 8.56 (s, 4H), 8.20 (s, 2H), 7.85 (dd, J = 5.2, 1.2, 4H), 7.57 (dd, J = 3.5, 1.2, 4H), 7.34 (m, 4H). MALDI-MS: 530.34.



Scheme. S1. The synthetic route of 1,3,6,8-tetra(thiophen-2-yl)pyrene.

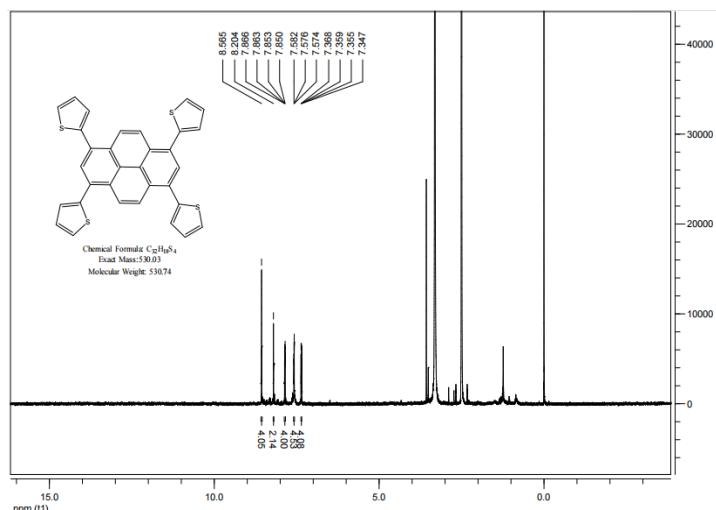
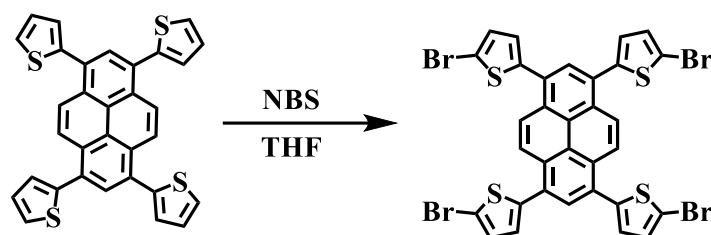


Fig. S1 The ¹H NMR spectrum of 1,3,6,8-tetra(thiophen-2-yl)pyrene.

Synthesis of 1,3,6,8-tetrakis(5-bromo-2-thienyl)pyrene^[2]

530.8 mg of 1,3,6,8-tetrakis(2-thienyl)pyrene (1 mmol) was dissolved in 25 mL of anhydrous tetrahydrofuran (THF) with constant stirring. Then, 1.07 g of *N*-bromosuccinimide (NBS) (6.0 mmol) was added slowly to the above solution in several

portions at room temperature. After that, the resulting mixture was stirred at room temperature for 24 h. Finally, the yellow precipitate was obtained by filtration as the crude product, and the crude product was washed several times successively with water and acetone, respectively. After vacuum drying at 50 °C for 24 h, the final product named 1,3,6,8-tetrakis(5-bromo-2-thienyl)pyrene (M2) was obtained in the form of a yellow powder with a yield of 82%.MALDI-MS: 846.03.



Scheme. S2. The synthetic route of 1,3,6,8-tetrakis (5-bromothio-phen-2-yl) pyrene (M2).

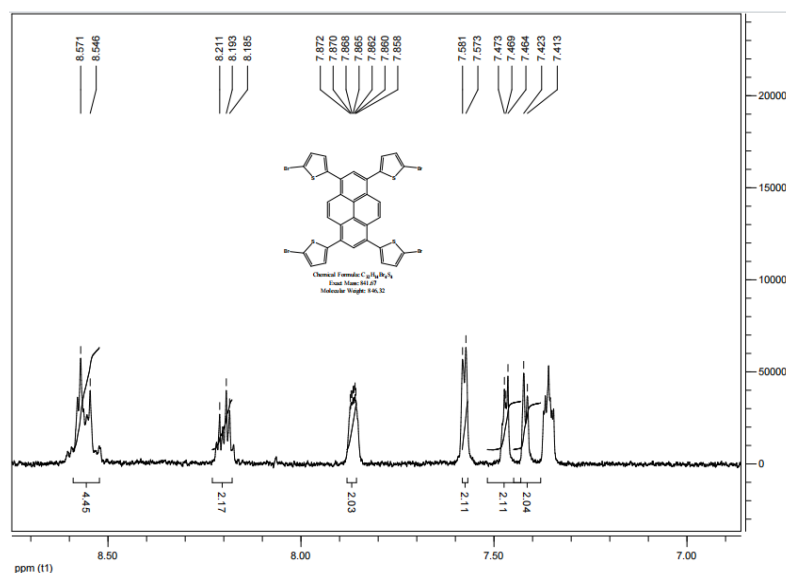
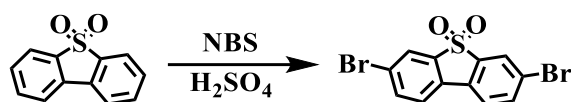


Fig. S2. The ^1H NMR spectrum of 1,3,6,8-tetrakis (5-bromothio-phen-2-yl) pyrene (M2).

Synthesis of 3,7-dibromodibenzothiophene *S,S*-dioxide^[3]

6.05 g of dibenzo[*b,d*]thiophene-*S,S*-dioxide (28.0 mmol) was dissolved in 150 mL of concentrated H_2SO_4 with vigorous stirring. Next, 12.46 g of NBS (70.0 mmol) was slowly added to the above solution in several portions at 0–5 °C. After that, the resulting mixture was stirred for 24 h at room temperature. The mixture was carefully poured into ice water and a white precipitate of the crude product was obtained by filtration. Finally, the crude product was washed sequentially with aqueous sodium bicarbonate (20%), water and methanol, respectively, and the product was further recrystallized from chlorobenzene after drying under vacuum at 50 °C for 24 h. White crystals named 3,7-dibromodibenzothiophene *S,S*-dioxide (M3) were obtained in

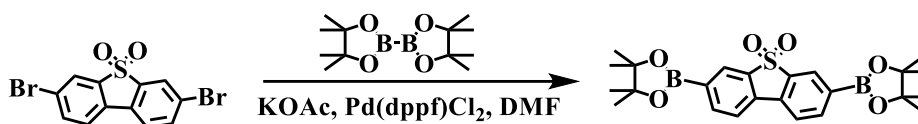
about 39% yield.



Scheme. S3. The synthetic route of 3,7-dibromodibenzo[*b,d*]thiophene-*S,S*-dioxide (M3).

Synthesis of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene 5,5-dioxide[4]

Under N₂ protection, 4.14 g of 3,7-dibromodibenzo[*b,d*]thiophene *S,S*-dioxide (11.0 mmol) was dispersed in 70 mL of anhydrous DMF, and 8.38 g of bis(pinacolato)diboron (33.0 mmol), 6.25 g of potassium acetate (CH₃COOK, 63.7 mmol), and 0.11 g of dichloropalladium (Pd(dppf))Cl₂, 0.13 mmol) were added sequentially to form a mixed solution. Then the above reaction solution was heated at 90 °C for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂, the organic phase was collected and dried with anhydrous Na₂SO₄. The solvent was removed under vacuum, and then purified by column chromatography (petroleum ether/CH₂Cl₂ = 1:1). Finally, after drying in vacuum at 50 °C for 24 h, the product was recrystallized with chloroform and methanol to afford white crystals named 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (M4) in about 50% yield. ¹H NMR (δ, 400 MHz, CDCl₃): δ 8.02 (s, 2H), 7.95 (dd, *J* = 7.8, 0.9, 2H), 7.94 (d, *J* = 7.8, 2H), 0.85 (s, 24).MALDI-MS: 468.18.



Scheme. S4. The synthetic route of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene-*S,S*-dioxide (M4).

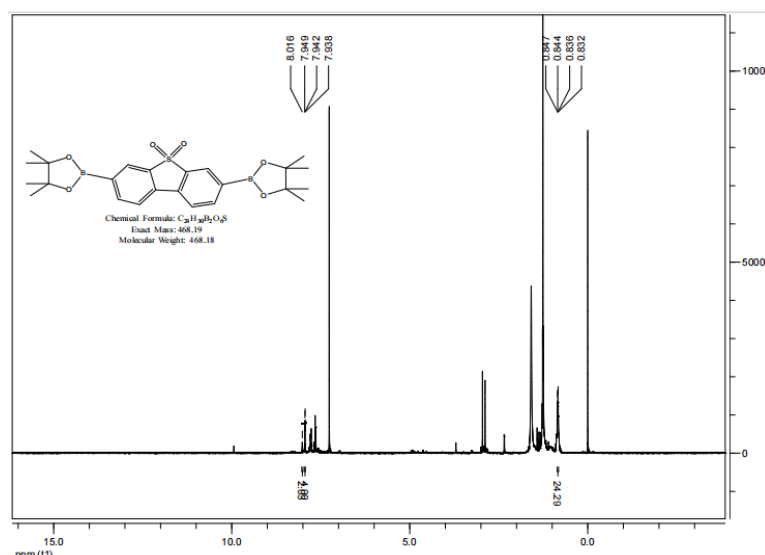
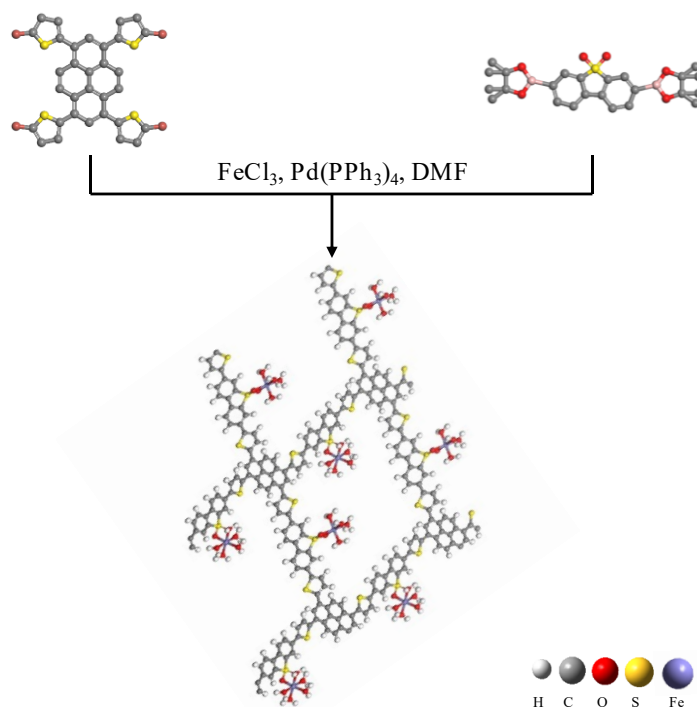


Fig. S3. The ^1H NMR spectrum of 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene-*S,S*-dioxide (M3).

Synthesis of Fe-Py-Tp-BDTO

First, 423.2 mg M2 (0.5 mmol), 468.2 mg M3 (1.0 mmol) and 20.0 mg $\text{Pd}(\text{PPh}_3)_4$ (17.3 μmol) were added to a 100 mL two-necked flask filled with N_2 , and then 20 mL of anhydrous DMF and 4 mL of K_2CO_3 aqueous (2.0 M) were added to the flask. Then 60 mg, 120 mg and 240 mg of FeCl_3 were dissolved in 5 mL of water and added to the flask. And the above mixed solutions were stirred at 150 $^\circ\text{C}$ for 48 h. After cooling, the precipitates were obtained by filtration, washed with dichloromethane, methanol, and deionized water for several times, and dried under vacuum at 120 $^\circ\text{C}$ for 48 h (Scheme S5). The insoluble orange-red powdery iron-based conjugated polymers were obtained and named as Fe(60)-Py-Tp-BDTO, Fe(120)-Py-Tp-BDTO and Fe(240)-Py-Tp-BDTO, wherein the optimal sample was named Fe-Py-Tp-BDTO for the convenience of observation and comparison. In addition, the synthesis of the iron-free organic conjugated polymer Py-Tp-BDTO was carried out in a manner consistent with that described above, except for the absence of FeCl_3 .



Scheme. S5. The synthetic route of Fe–Py–Tp–BDTO (gray: C, yellow: S, red: O, white: H, brick red: Br, pink: B, purple: Fe).

Photoelectrochemical Measurements

The electrochemical and photoelectrochemical analyses were conducted by the CHI660E electrochemical workstation in a three-electrode setup. Shortly, 0.05 g photocatalyst and 25 μL resin are dissolved in 225 μL ethanol. Then 30 μL of this mixture is dipped onto fluorine-doped tin oxide (FTO) glass ($1 \times 2 \text{ cm}^2$) and regarded as corresponding working electrodes. A Pt plate and a saturated Ag/AgCl electrode are as the counter electrode and the reference electrode respectively. In addition, the transient photocurrent, electrochemical impedance spectra (EIS) and Mott–Schottky used a 0.5 M Na_2SO_4 aqueous solution as the electrolyte.

A glassy carbon rotating disk electrode (ALS, RRDE–3A Ver.3.0, Japan) served as the substrate for working electrode. The working electrode was prepared as followed: prepared samples (5 mg) was dispersed in EtOH (2 mL) containing Nafion (50 μL) by ultrasonication. The slurry (20 μL) was put onto the disk electrode and dried at room temperature. The linear sweep voltammograms (LSV) were obtained in an O_2 -saturated 0.1 M phosphate buffer solution ($\text{pH} = 7$) at room temperature with a scan rate 10 mV s^{-1} and different rotation speeds after O_2 bubbling for 1 hour. Simultaneously, the rotating speed of the working electrode was 600 rpm, 800 rpm, 1000 rpm, 1200 rpm and 1600 rpm, respectively. The average number of electrons (n) was calculated by

Koutecky–Levich equation^[5]:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0D_0^{2/3}V^{-1/6}$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is transferred electron number, F is Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 ($1.26 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in 0.1 M phosphate buffer solution ($2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is kinetic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), respectively.

Rotating ring–disk electrode (RRDE) measurement

A ring–disk electrode (ALS, RRDE–3A Ver.3.0, Japan) served as the substrate for working electrode. The working electrode was prepared as RDE measurements. The WOR activity was obtained in a 0.1 M phosphate buffer solution ($\text{pH} = 7$) under Ar atmosphere at a scan rate 10 mV s^{-1} and a rotation speed of 1000 rpm. The Pt ring electrode was fixed potential of +1.2 V (vs. Ag/AgCl) for detecting the produced H_2O_2 from the disk electrode. The phosphate buffer solution electrolyte was purged with Ar for 1 h prior to the measurements.

Photocatalytic in situ production of H_2O_2

The H_2O_2 concentration in the heterogeneous solution was determined by a potassium titanium oxalate method as reported and we used before. After given time intervals, 1.5 mL of suspension was filtrated with a $0.22 \mu\text{m}$ filter to further remove the photocatalysts, followed by the addition of 1 mL of potassium titanium oxalate solution (0.5 M). The concentration of the H_2O_2 was calculated based on the absorbance at 400 nm by a UV–vis spectrophotometer. The solution then changed from transparent to yellow due to the formation of a complex between potassium titanium oxalate and H_2O_2 . The absorbance at 400 nm was used to determine the concentration of H_2O_2 and monitored by a UV–vis spectrometer (UV–752, Shanghai Jinghua Technology Co.)^[6].

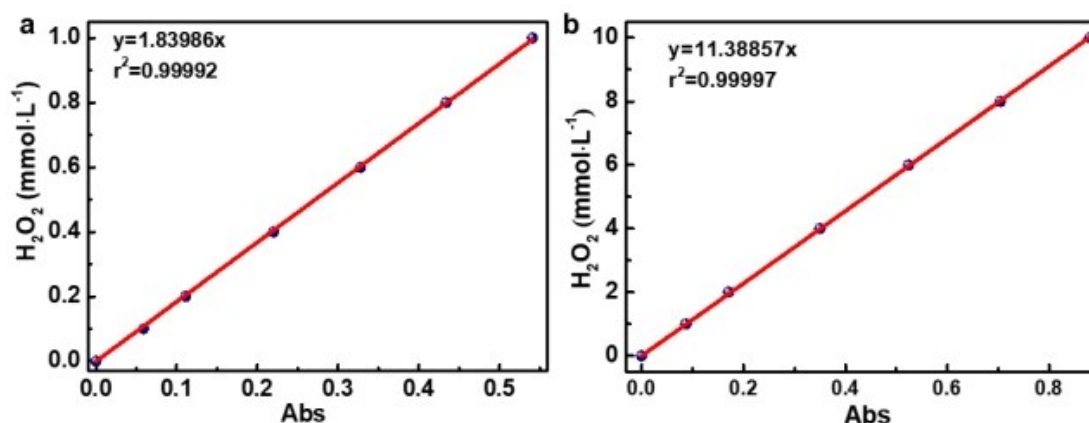
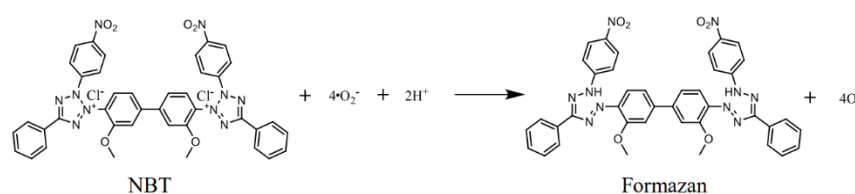


Fig. S4. The calibration curves of photocatalytic H₂O₂ production (a) low concentration, (b) high concentration.

Photocatalytic evolution of $\cdot\text{O}_2^-$

The concentration of $\cdot\text{O}_2^-$ was measured by detected the decay of NBT (nitro blue tetrazolium) using UV-vis spectroscopy. 3 mL of liquid was filtrated with a 0.22 μm filter to remove the photocatalysts. The photocatalytic generation of $\cdot\text{O}_2^-$ was determined by the degradation of NBT, which was detected by the absorbance change at the wavelength of 259 nm. The mole ratio of generated $\cdot\text{O}_2^-$ and reacted NBT was 4:1 according to the following equation^[7]:



DFT Calculations

Theoretical calculations were carried out through Density Functional Theory (DFT) with Gaussian 09 software^[8]. B3LYP/6-311G(d) method was used for molecular optimization^[9-12]. Frequency calculations were performed to ensure that the stability configuration has no imaginary frequency. The solvent effect of H₂O was taken into account using self-consistent reaction field (SCRF) based on the solvation model density (SMD) implicit solvent model^[13]. The hole-electron analysis was calculated with Multiwfn 3.8(dev)^[14, 15]. The adsorption energy (E_{ads}) of O₂ was calculated as follows^[16]:

$$E_{\text{ads}}(\text{O}_2) = E(\cdot\text{O}_2) - E(\cdot) - E(\text{O}_2)$$

where $E(\cdot\text{O}_2)$, $E(\cdot)$ and $E(\text{O}_2)$ are the total energy of samples with O₂ adsorbates on the surface, the energy of pristine samples surface and O₂, respectively. At room

temperature, the Gibbs free energy for each model was calculated by the following equation:

$$G(T) = E_{\text{ele}} + G_{\text{corr}}(T) = E_{\text{ele}} + \text{ZPE} + \Delta G_{0 \rightarrow T}$$

where E_{ele} , $G_{\text{corr}}(T)$, ZPE and $\Delta G_{0 \rightarrow T}$ were electronic energy, thermal corrections to Gibbs free energy, zero-point energy and contribution by heating the system from 0 K to 298.15 K.

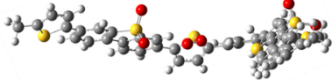
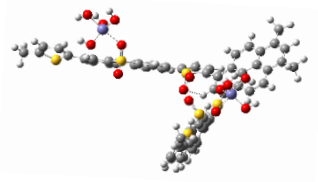
2. Results and Discussion

Table S1. The weight of Fe in the Fe–Py–Tp–BDTO before and after reaction detected by ICP–MS

Sample	Elements	Weight%
before	Fe	0.58%
after	Fe	0.49%

The weight of Fe in the Fe–Py–Tp–BDTO before and after reaction has no obvious change.

Table S2. The calculated energy for O₂ adsorption at active sites of Py–Tp–BDTO and Fe–Py–Tp–BDTO

Computational model		
	Py–Tp–BDTO	Fe –Py–Tp–BDTO
E _{ads}	–1.95 eV	–1.57 eV

TableS3 Selected results obtained for pollutant removal by photocatalysis–self–Fenton methods

Photocatalysts	Conditions	TOC results	Ref.
Cv–PCNNS–550	50 mL of 10 mg L ^{−1} MTZ solution, $\lambda > 420$ nm	62%, 100 min	Chem. Eng. J. 2024, 12, 113568.
CPBA–CN	20 mL of 20 mg L ^{−1} 4–chlorophenol solution, AM 1.5	74.5%, 60 min	Environ. Res. 2023, 222, 115361.
Coral–B–CN	50 mL of 20 mg L ^{−1} 4–chlorophenol solution, AM 1.5	70.3%, 50 min	J. Hazard. Mater. 2023, 449, 131017.
HCN–Co	50 mL of 10 mg L ^{−1} CIP solution, 380 nm $< \lambda < 760$ nm	16%, 50 min	Sep. Purif. Technol. 2025, 354, 129456.
rGO/SA–TCPP	50 mL of 10 mg L ^{−1} SDM or SDZ solution, LED lights	67.9%, 8 h	Chem. Eng. J. 2024, 484, 149552.
C ₃ N ₄ –SA–Fe1Ca5	33 mg/L ATZ solution, LED lights	38.15%, 6 h	Sci. Total. Environ. 2024, 934, 173112.
KCN–0.5	50 mL of 10 mg L ^{−1} BPA solution, $\lambda > 420$ nm	63.8%, 60 min	Appl. Catal. B–Environ. 2023, 331, 122716
Fe–Py–Tp–BDTO	30 mL of 10 mg L ^{−1} 4–chlorophenol solution, AM 1.5	79.1%, 30 min	This work

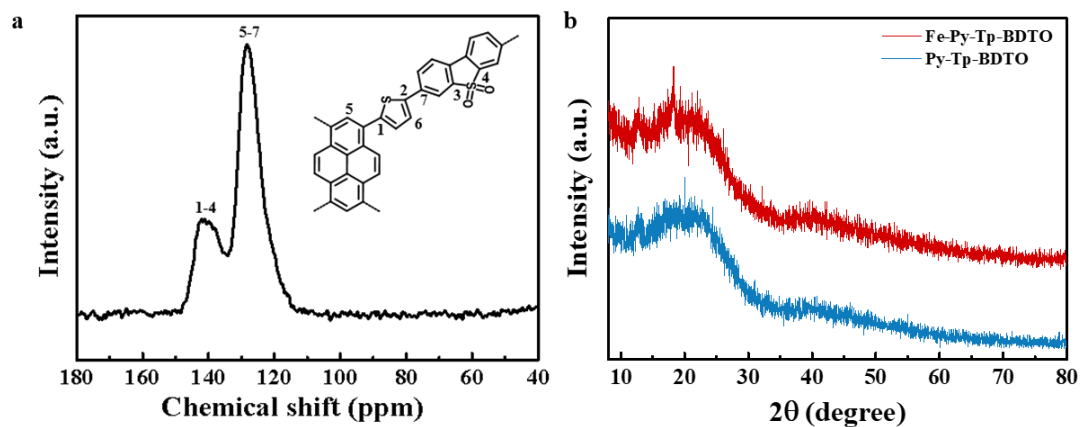


Fig. S5. (a) Solid-state ^{13}C NMR spectra and the assignment of carbon atoms in the polymers of Py-Tp-BDTP; (b) The powder X-ray diffraction patterns of Fe-Py-Tp-BDTP and Py-Tp-BDTP.

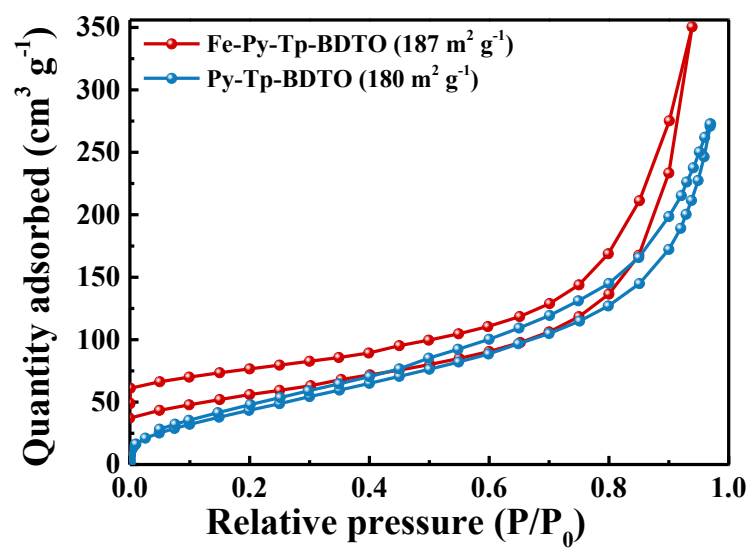


Fig. S6. Nitrogen adsorption/desorption isotherms of Fe-Py-Tp-BDTO and Py-Tp-BDTO.

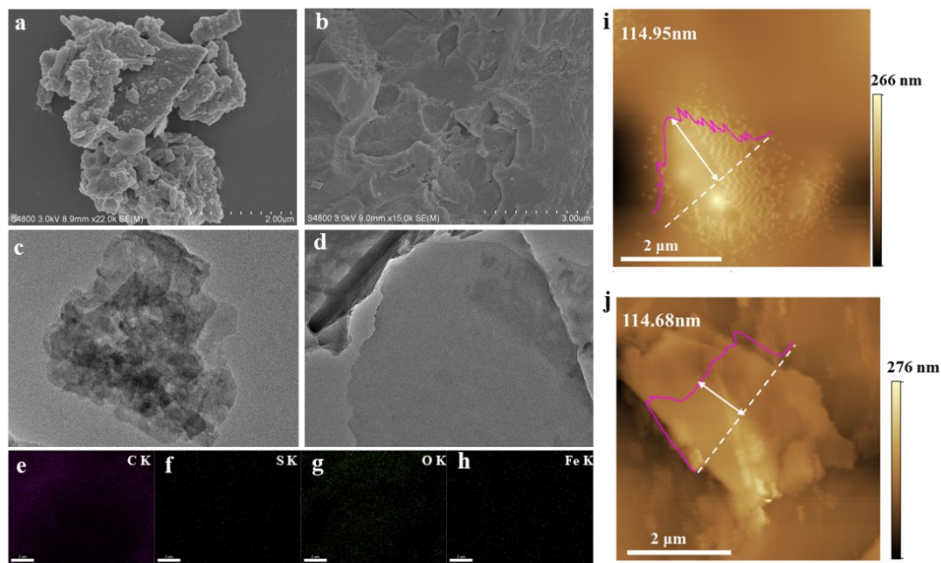


Fig. S7. The SEM images of (a) Py-Tp-BDTO, (b) Fe-Py-Tp-BDTO; The TEM images of (c) Py-Tp-BDTO, (d) Fe-Py-Tp-BDTO; (e-h) EDS mapping images of Fe-Py-Tp-BDTO; Atomic force microscope (AFM) image and corresponding height of (i) Py-Tp-BDTO, (j) Fe-Py-Tp-BDTO.

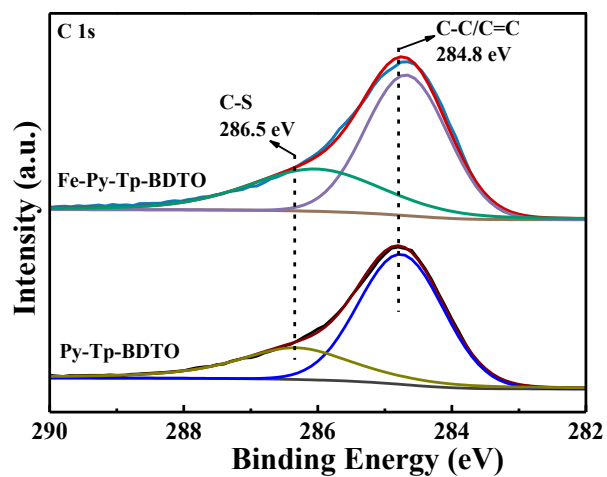


Fig. S8. XPS spectra of C 1s over Py-Tp-BDTO and Fe-Py-Tp-BDTO.

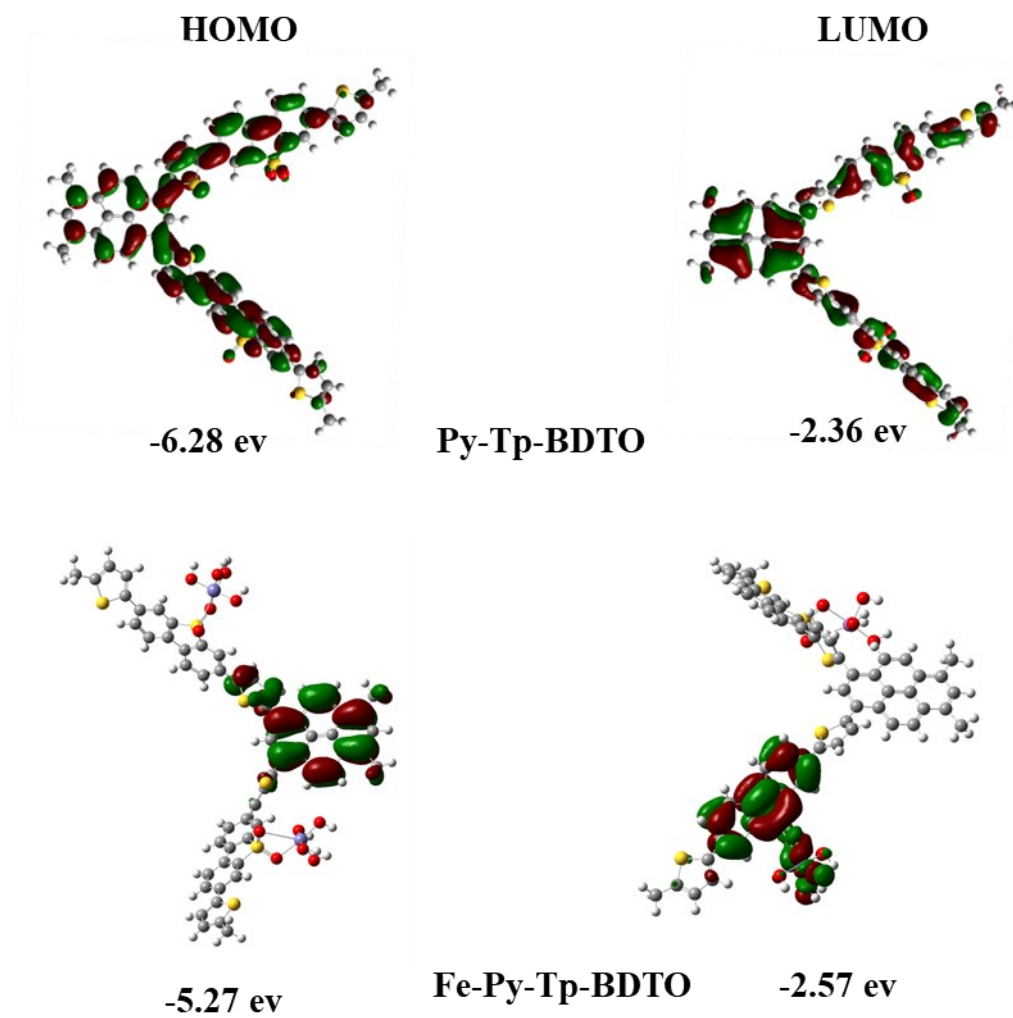


Fig. S9. The HOMO and LUMO orbital distribution of the two samples based on DFT simulation (gray: C, yellow: S, red: O, white: H, purple: Fe).

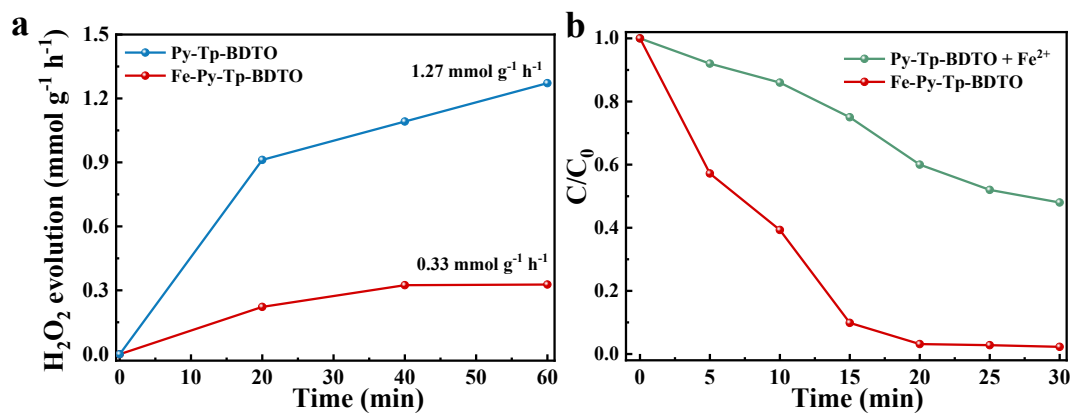


Fig. S10. (a) Time profiles of H_2O_2 production for Py-Tp-BDTO and Fe-Py-Tp-BDTO in water; (b) Degradation ability for 4-chlorophenol over different system (solution: 30 mL H_2O or 10 mg L⁻¹ 4-chlorophenol, O_2 bubbling; light source: Xe lamp with an AM1.5G filter).

Compared with the degradation activity of heterogeneous photocatalysis-self-Fenton system, the photocatalytic degradation efficiency with the addition of Fe^{2+} was only 52% (Fig. S10b).

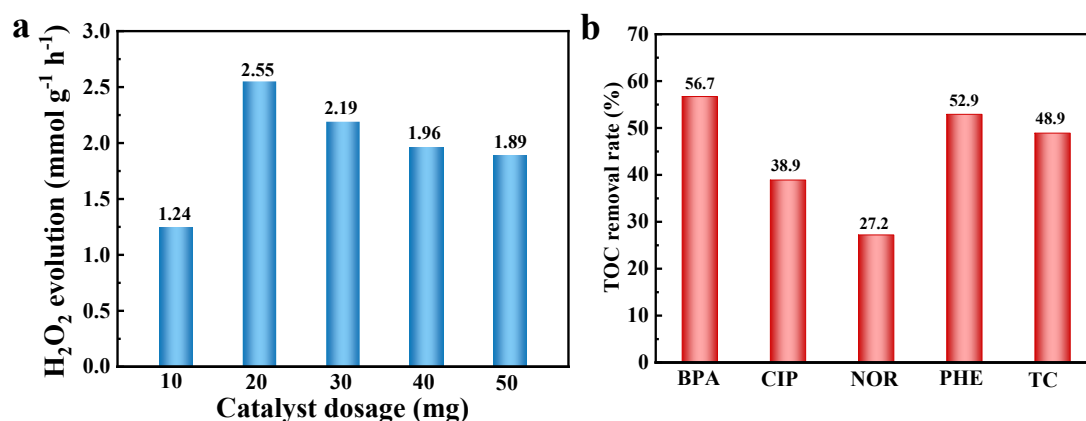


Fig. S11. (a) H₂O₂ production on Py–Tp–BDTO with different catalyst concentrations plotted as a function of irradiation time; (b) TOC removal rate for different organic pollutants (solution: 30 mL 10 mg L⁻¹ 4-chlorophenol, O₂ bubbling; light source: Xe lamp with an AM1.5G filter. BPA: bisphenol A, CIP: ciprofloxacin; NOR: norfloxacin; PHE: phenol; TC: tetracycline).

As shown in Fig. S11a, the rate of 1.24 mmol g⁻¹ h⁻¹ when the concentration of Py–Tp–BDTO was lower (10 mg). And when the dosage of Py–Tp–BDTO was increased from 10 mg to 20 mg, its H₂O₂ preparation rate was increased by 2.1-fold to 2.55 mmol g⁻¹ h⁻¹. Further increasing the Py–Tp–BDTO dosage to 50 mg, the activity decreased dramatically to 1.89 mmol g⁻¹ h⁻¹, which demonstrated that the decrease in activity of Py–Tp–BDTO at 50 mg was due to incident light was shielded. Fe–Py–Tp–BDTO possesses a steady and wide degradation ability for many organic pollutants (Fig. S11b)

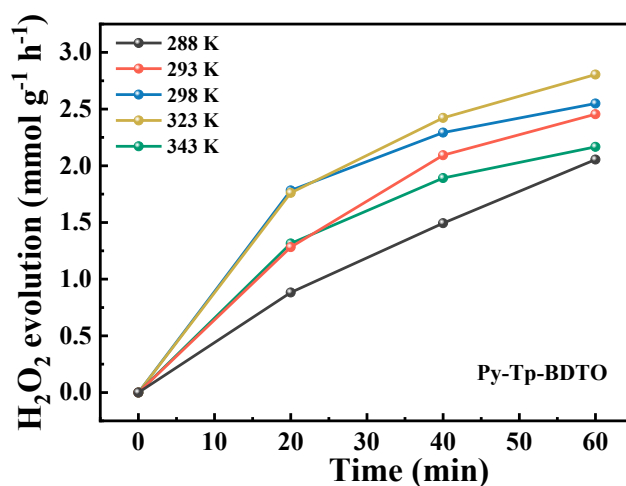


Fig. S12. H₂O₂ production on Py-Tp-BDTO at different temperatures plotted as a function of irradiation time (solution: 30 mL 10 mg L⁻¹ 4-chlorophenol, O₂ bubbling; light source: Xe lamp with an AM1.5G filter).

The reaction temperature was increased from 288 K to 343 K to observe the variation of H₂O₂ preparation rate with time. Average preparation rate of H₂O₂ from Py-Tp-BDTO was 2.41 mmol g⁻¹ h⁻¹, therefore, the effect of temperature increase on the H₂O₂ preparation rate of D- π -A organic conjugated polymer was not significant.

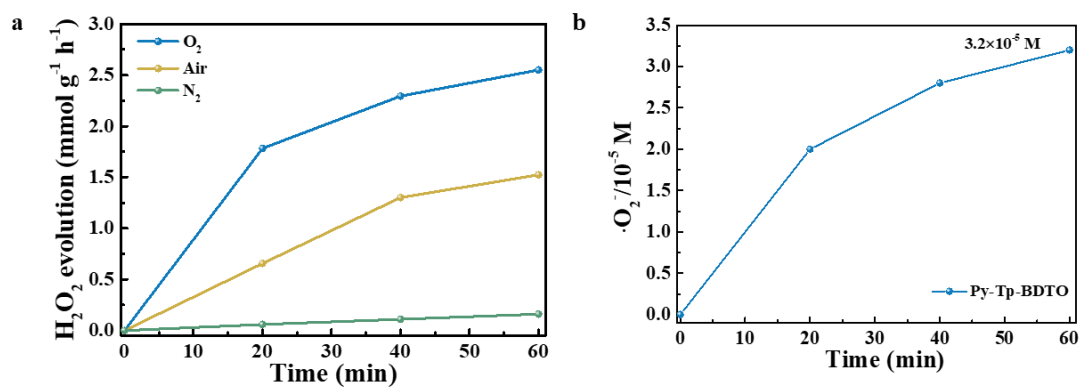


Fig. S13. (a) H_2O_2 yield curve under different atmosphere of Py-Tp-BDTO; (b) Photocatalytic yield of $\cdot\text{O}_2^-$ detected by NBT method of Py-Tp-BDTO (solution: 30 mL 10 mg L⁻¹ 4-chlorophenol, O_2 bubbling; light source: Xe lamp with an AM1.5G filter).

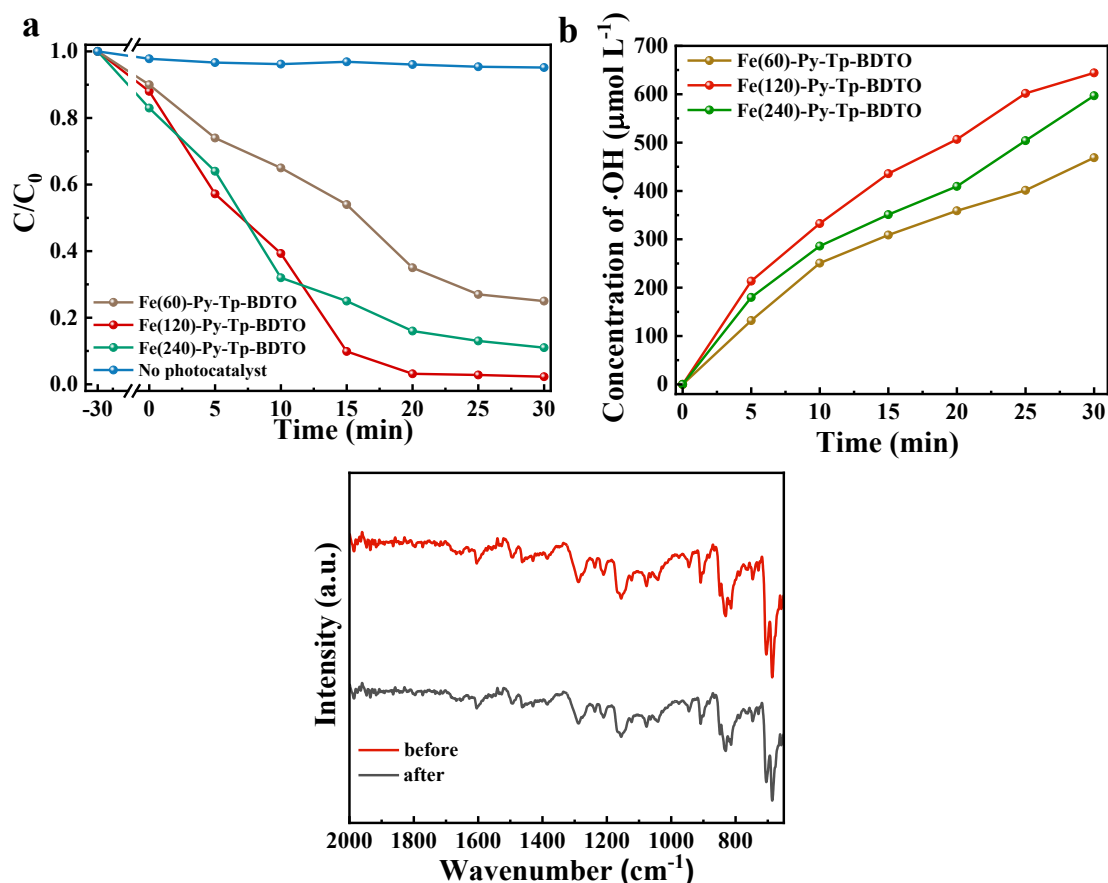


Fig. S14. (a) Adjustment of Fe concentration (Condition: catalyst = 0.6 g L^{-1} , 4-CP = 10 mg L^{-1} , 300 W Xe lamp, AM1.5); (b) $\cdot\text{OH}$ yield profile of all samples; (c) FT-IR of the Fe-Py-Tp-BDTO before reaction and after 20 cycles reaction.

When the photocatalyst is not exposed to light within the first 30 minutes, and there is no photocatalyst in the system, the pollutants cannot be degraded (Fig. S14a). In addition, the generation of $\cdot\text{OH}$ radical was explored in depth, firstly, the coumarin fluorescence method was used to capture the $\cdot\text{OH}$ radicals, and $\cdot\text{OH}$ quantification experiments were carried out in different samples (Fig. S14b). The structure and functional groups of Fe-Py-Tp-BDTO exhibit negligible changes before and after 20 cycle stability test (Fig. S14c).

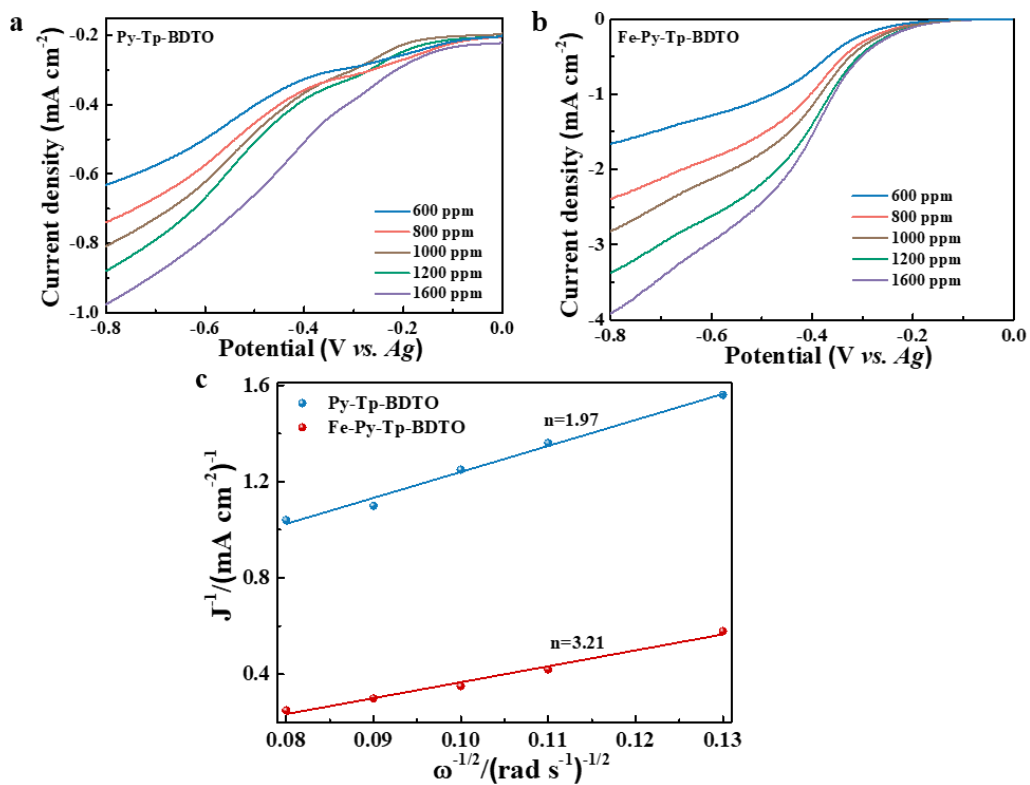


Fig. S15. Linear-sweep RDE voltammograms of (a) Py-Tp-BDTO and (b) Fe-Py-Tp-BDTO measured at different rotating speeds; (c) Koutecky-Levich plots of Py-Tp-BDTO and Fe-Py-Tp-BDTO (at -0.8V vs. Ag/AgCl).

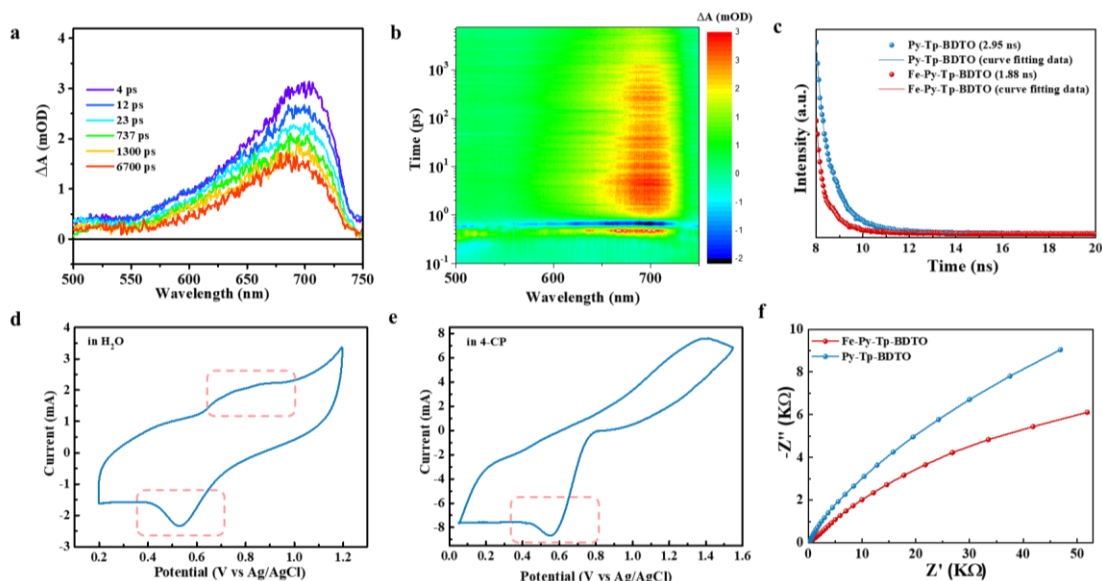


Fig. S16. The fs-TA spectra (a) and (b); (c) Transient-state PL spectra of Py-Tp-BDTO and Fe-Py-Tp-BDTO; Pseudocolor plots of Cyclic voltammograms of Fe-Py-Tp-BDTO in (d) H₂O and (e) 4-chlorophenol; (f) Electrochemical impedance spectra of Py-Tp-BDTO and Fe-Py-Tp-BDTO.

Fig. S16a–b indicates that a slow photo-exciton consumption in Py-Tp-BDTO. The shorter fluorescence lifetime of Fe-Py-Tp-BDTO (1.88 ns) compared to Py-Tp-BDTO (2.95 ns) further demonstrates that the D- π -A structure can accelerate the rate of the photogenerated carriers migration significantly (Fig. S16c). A pair of redox peaks locates at 0.58 V/0.82 V (vs. Ag/AgCl) is clearly observed, showing the reversible conversion between Fe(III) and Fe(II) (Fig. S16d). The main reason why no oxidation peak is found in the 4-chlorophenol solution is that the Fe(II) is oxidized by in-situ H₂O₂ to achieve Fe(III)/Fe(II) cycle during photocatalytic process (Fig. S16e). Besides, more efficient transfer and separation of charge carriers for Fe-Py-Tp-BDTO are also reflected by smaller arc radius (Fig. S16f).

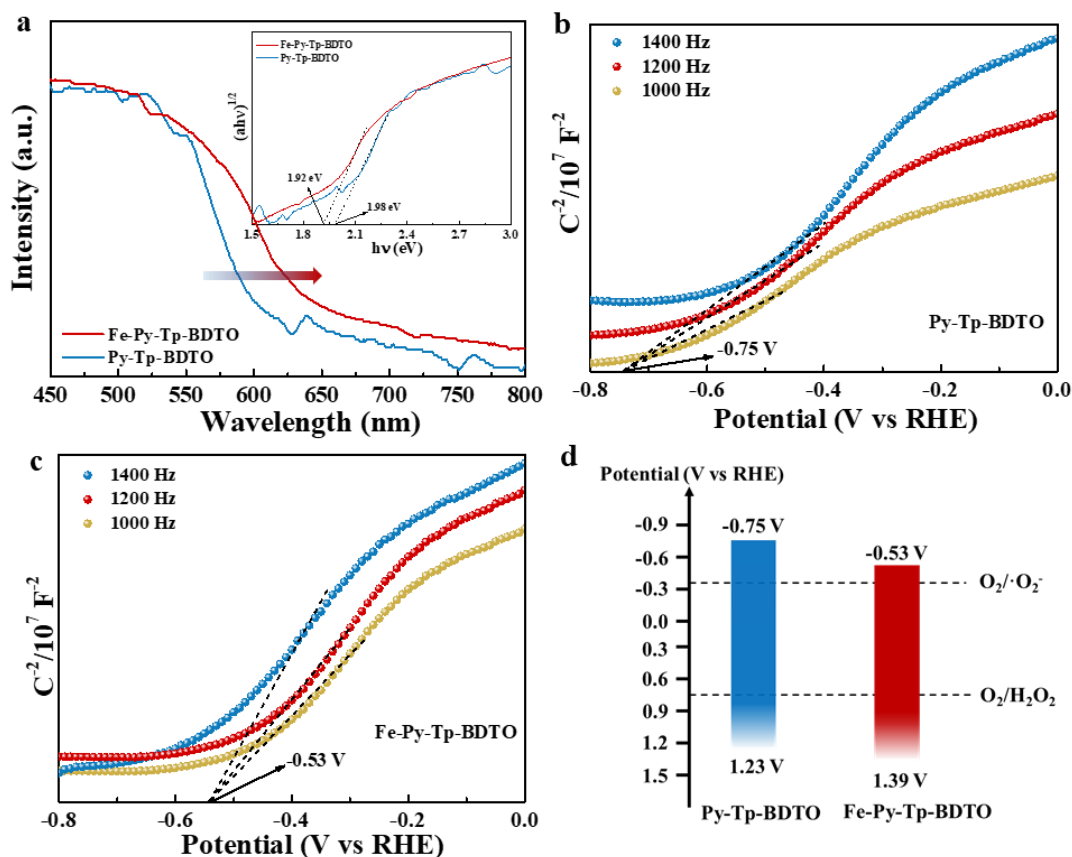


Fig. S17. (a) UV–Vis absorption spectra of Py–Tp–BDTO and Fe–Py–Tp–BDTO (inset: Plots of transformed Kubelka–Munk function versus photon energy of Py–Tp–BDTO and Fe–Py–Tp–BDTO); (b–c) Mott–Schottky plots of Py–Tp–BDTO and Fe–Py–Tp–BDTO; (d) Estimated band structure of all samples.

The solid–state optical properties and energy band structures of Fe–Py–Tp–BDTO and Py–Tp–BDTO were investigated using UV–Vis spectrum and Mott–Schottky curves. Fe–Py–Tp–BDTO shows a red–shifted compared to Py–Tp–BDTO of the light absorption edge, indicating that Fe–Py–Tp–BDTO can absorb more visible light during photocatalysis. The calculated optical bandgap of Py–Tp–BDTO is 1.98 eV, and that of Fe–Py–Tp–BDTO is 1.92 eV (inset of Fig. S17a). In addition, according to the results of the Mott–Schottky spectra (Fig. S17b–c), both Fe–Py–Tp–BDTO and Py–Tp–BDTO are n–type semiconductors, and the conduction band (CB) positions of the two are derived from the conversion of the flat band potentials. The CBs of Fe–Py–Tp–BDTO and Py–Tp–BDTO are -0.53 V and -0.75 V , respectively, and such conduction band positions are fully satisfied for the preparation of H_2O_2 by O_2 reduction. Meanwhile, combined with the results of band gap analysis, the valence band (VB) positions of both Fe–Py–Tp–BDTO and Py–Tp–BDTO were obtained. The above results also demonstrate once again that the Fe–based conjugated polymers can fully meet the

requirements for the in-situ preparation of H_2O_2 and decompose H_2O_2 to prepare abundant $\cdot\text{OH}$. And the $\cdot\text{OH}$ co-mineralize pollutants in concert with the holes (h^+) on the valence band of Fe-Py-Tp-BDTO.

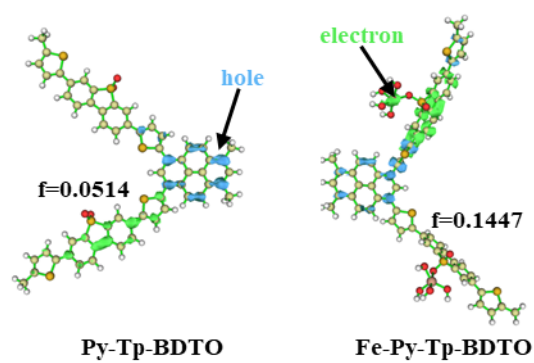


Fig. S18. Electron-hole distribution in excited states.

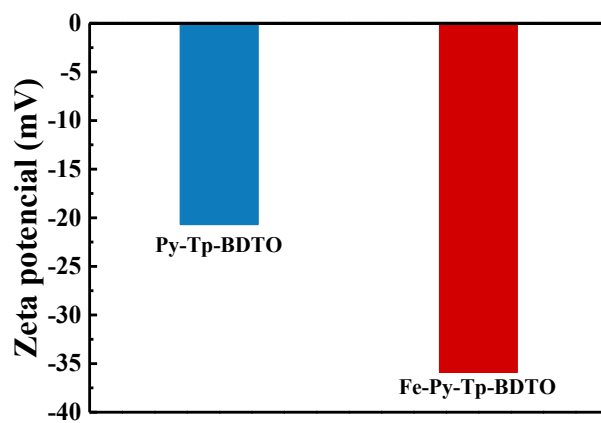


Fig. S19. The Zeta potential of Py-Tp-BDTO and Fe-Py-Tp-BDTO.

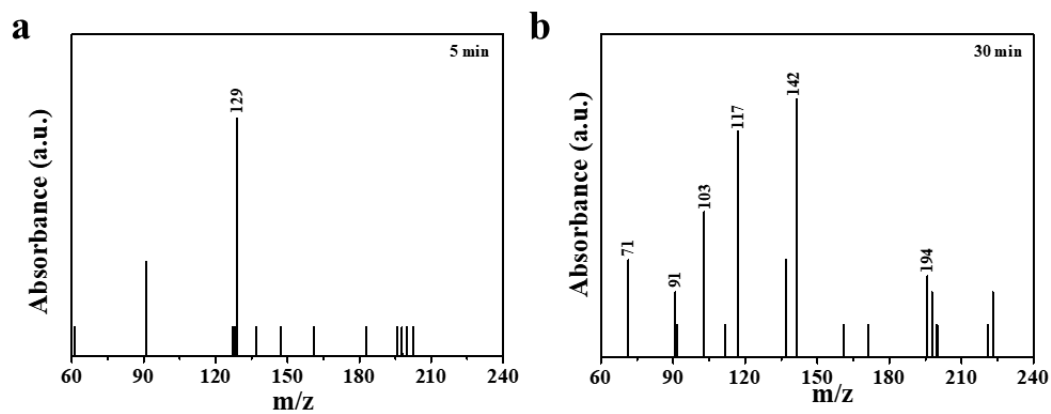


Fig. S20. Ultra-high-performance LC-MS of degradation solution (a) degradation in 5 min and (b) degradation in 30 min

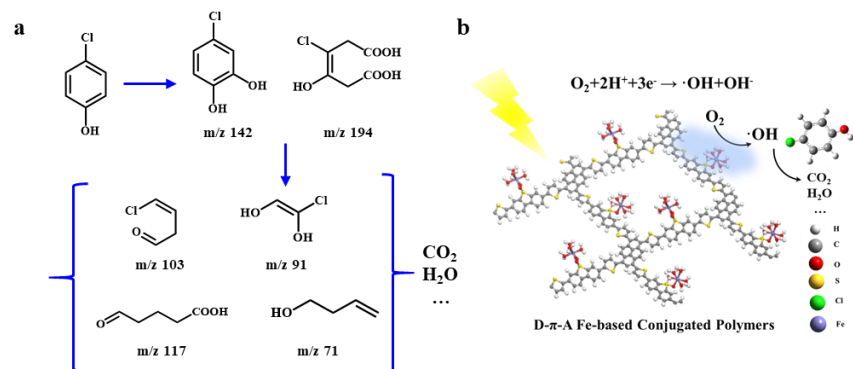


Fig. S21. (a) Possible pathway of 4-chlorophenol degradation; (b) Mechanism of Fe-Py-Tp-BDFO based photocatalysis-self-Fenton degradation of 4-chlorophenol.

3. References

- [1] J.Y. Shao, B. Yu, Y.D. Wang, Z.R. Lan, D. Li, Q. Meng, Y.W. Zhong, In-situ electropolymerized polyamines as dopant-free hole-transporting materials for efficient and stable inverted perovskite solar Cells, *ACS Appl Energy Mater*, 3 (2020), pp. 5058–5066, 10.1021/acsaem.0c00659.
- [2] C. Han, S. Xiang, S. Jin, C. Zhang, J.-X. Jiang, Rational design of conjugated microporous polymer photocatalysts with definite D- π -A structures for ultrahigh photocatalytic hydrogen evolution activity under natural sunlight, *ACS Catal*, 13 (2023), pp. 204–212, 10.1021/acscatal.2c04993.
- [3] K. Kawabata, M. Takeguchi, H. Goto, Optical activity of heteroaromatic conjugated polymer films prepared by asymmetric electrochemical polymerization in cholesteric liquid crystals: structural function for chiral induction, *Macromolecules*, 46 (2013), pp. 2078–2091, 10.1021/ma400302j.
- [4] K.C. Moss, K.N. Bourdakos, V. Bhalla, K.T. Kamtekar, M.R. Bryce, M.A. Fox, H.L. Vaughan, F.B. Dias, A.P. Monkman, Tuning the intramolecular charge transfer emission from deep blue to green in ambipolar systems based on dibenzothiophene-S,S-dioxide by manipulation of conjugation and strength of the electron donor units, *J Org Chem*, 75 (2010), pp. 6771–6781, 10.1021/jo100898a.
- [5] X. Song, N. Li, H. Zhang, L. Wang, Y. Yan, H. Wang, L. Wang, Z. Bian, Graphene-supported single nickel atom catalyst for highly selective and efficient hydrogen peroxide production, *ACS Appl Mater*, 12 (2020), pp. 17519–17527, 10.1021/acsami.0c01278.
- [6] C. Pan, Y. Zhu, New type of BiPO₄ oxy-acid salt photocatalyst with high photocatalytic activity on degradation of dye, *Environ Sci Technol*, 44 (2010), pp. 5570–5574, 10.1021/es101223n.
- [7] H. Wang, C. Yang, F. Chen, G. Zheng, Q. Han, A crystalline partially fluorinated triazine covalent organic framework for efficient photosynthesis of hydrogen peroxide, *Angew Chem Int Ed Engl*, 61 (2022), Article e202202328, 10.1002/anie.202202328.
- [8] J. Yang, J. Jing, W. Li, Y. Zhu, Electron donor-acceptor interface of TPPS/PDI boosting charge transfer for efficient photocatalytic hydrogen evolution, *Adv Sci*, 9 (2022), Article 2201134, 10.1002/advs.202201134.
- [9] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *J Chem Phys*, 110 (1999), pp. 6158–6170, 10.1063/1.478522.
- [10] S. Rayne, K. Forest, Accuracy of computational solvation free energies for neutral and ionic compounds: Dependence on level of theory and solvent model, *Nat Preced*, (2010), 10.1038/npre.2010.4864.1.
- [11] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J Comput Chem*, 32 (2011), pp. 1456–1465, <https://doi.org/10.1002/jcc.21759>.

- [12] M. Nowicki, M. Zaranek, P. Pawluć, M. Hoffmann, DFT study of trialkylborohydride-catalysed hydrosilylation of alkenes – the mechanism and its implications, *Catal Sci Technol*, 10 (2020), pp. 1066–1072, 10.1039/C9CY02261A.
- [13] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys Chem Chem Phys*, 7 (2005), pp. 3297–3305, 10.1039/b508541a.
- [14] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J Comput Chem*, 33 (2012), pp. 580–592, <https://doi.org/10.1002/jcc.22885>.
- [15] W. Humphrey, A. Dalke, K. Schulten, VMD: Visual molecular dynamics, *J Mol Graph*, 14 (1996), pp. 33–38, [https://doi.org/10.1016/0263-7855\(96\)00018-5](https://doi.org/10.1016/0263-7855(96)00018-5).
- [16] Z. Wei, J. Liu, W. Fang, M. Xu, Z. Qin, Z. Jiang, W. Shangguan, Photocatalytic hydrogen evolution with simultaneous antibiotic wastewater degradation via the visible–light–responsive bismuth spheres–g-C₃N₄ nanohybrid: Waste to energy insight, *Chem Eng J*, 358 (2019), pp. 944–954, <https://doi.org/10.1016/j.cej.2018.10.096>.