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Pillararene-Enriched Linear Conjugated Polymer Materials with Thiazolo[5,4-

d]thiazole Linkages for Photocatalysis

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1. Materials and methods

Materials: All reagents and solvents were purchased from commercial suppliers such as Sigma-Alrich and Aladdin Reagents and used as received. Deionized water purified on an Experimental Water System (Lab-UV-20) was used in relevant experiments. Dibenzaldehydefunctionalized pillar[5]arene (P[5](PhCHO)₂) and *p*-terphenyl-dicarboxaldehyde (TPA) were successfully synthesized according to our published procedure.^{S1}

Methods: ¹H NMR spectra were recorded at 298 K on a Bruker AVANCEIII 500MHz instrument. Solid-state cross-polarization magic angle spinning (CP/MAS) ¹³C NMR spectra of polymers were measured on a Bruker Digital Avance III HD 400 WB (400 MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 7.0 kHz. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Vertex 80 V spectrometer. Thermogravimetric (TG) analysis was performed by using a NETZSCH STA 449F3 QMS403D \ Bruker V70 instrument, and each sample was heated up to 800 °C at a rate of 10 °C min⁻¹ under nitrogen atmosphere. Scanning electron microscopy (SEM) images were obtained on a Thermo FEI instrument. Transmission electron microscopy (TEM) images were carried out with a JEM-2100F transmission electron microscope and elemental mapping were taken by a FEI TECNAI F20. Elemental analyses (C, H, O, N, S) were recorded on an Elementar Vario EL cube elemental analyzer. Powder X-ray diffraction (PXRD) analyses of samples were carried out over the 2θ range of 5° to 80° on a PANalytical B.V. Empyrean powder diffractometer. The fluorescence spectra and time-resolved fluorescence decay curves were obtained on a FLS920 instrument (Edinburgh Instrument) with an excitation of 385 nm. The electrochemical measurement was recorded by a CHI 660A workstation with a three-electrode cell.

2. Syntheses



Fig. S1 Synthetic routes to P5Tz-CP and CP.

Synthesis of P5Tz-CP: $P[5](PhCHO)_2$ (0.90 g, 1 mmol) and dithiooxamide (0.12 g, 1 mmol) were heated at reflux in anhydrous DMF (10 mL) with stirring under N₂ protection for 5 days. After the reaction mixture was cooled to room temperature, the precipitate was collected by filtration and purified by washing with H₂O and MeOH three times. The product was dried under vacuum for 24 hours at 150 °C, resulting in an orange powder (870 mg, 85 %).

Synthesis of CP: TPA (0.29 g, 1 mmol) and dithiooxamide (0.12 g, 1 mmol) were heated at reflux in anhydrous DMF (10 mL) with stirring under N_2 protection for 5 days. After the reaction mixture was cooled down to room temperature, the precipitate was collected by filtration and purified by washing with H₂O and MeOH several times. The product was dried under vacuum for 24 hours at 150 °C to give an orange powder (370 mg, 90 %).

3. General procedure for photocatalytic RhB degradation

For the degradation of RhB, P5Tz-CP (20 mg) was dispersed in an aqueous solution of RhB (50 mL, 10 mg/L), and the mixture was stirred for 1 h in the darkness to get adsorptiondesorption equilibrium. Then the mixture was irradiated with a 300 W Xenon lamp (equipped with 420 nm optical filter to filtrate off the ultraviolet light) under stirring at room temperature. The UV-vis absorbance of the solution at 554 nm was measured after a centrifugation process to remove the solid P5Tz-CP catalyst at different intervals. In the case of CP, 5 mg of powder was used with other conditions unchanged. In order to investigate the effect of active species, different scavengers were added into the reaction suspension and other conditions are identical.

4. Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) and electrochemical Mott-Schottky plots were recorded by a CHI 660A workstation with a three-electrode cell, for which, platinum plate electrode was employed as the counter electrode, the as-prepared sample served as the working electrode, and a saturated calomel electrode was used as the reference electrode. The work electrodes were prepared via drop-casting sonicated acetone suspensions onto the surface of glassy carbon electrode to be filmed. Na₂SO₄ solution (0.2 M) was used as the supporting electrolyte.^{S2}

5. Characterization



Fig. S2 ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of P[5](PhCHO)₂.

Compound	P[5](PhCHO) ₂
Empirical formula	C ₁₂₈ H ₁₃₈ Cl ₆ O ₂₀
Formula weight	2209.08
Crystal system	triclinic
Space group	P-1
a/Å	12.0838(7)
b/Å	15.3449(9)
c/Å	16.0627(10)
α/deg.	84.6388(14)
β/deg.	89.2490(14)
γ/deg.	88.2990(12)
V/Å ³	2963.9(3)
Z	1
D _{calcd} /g⋅cm ⁻³	1.238
<i>m</i> /mm ⁻¹	0.212
<i>F</i> (000)	1168.0
Theta range/deg.	3.372 to 52.764
Reflections collected	16545
R(int)	0.0300
R ₁ , wR ₂ [obs I>=2σ (I)]	0.1064, 0.2870
R ₁ , wR ₂ (all data)	0.2327, 0.3827
CCDC number	2065576

Table S1. Details of the X-ray crystal structure analyses of $P[5](PhCHO)_2$



Fig. S3 Crystal structure of P[5](PhCHO)₂ grown by slow evaporation of CHCl₃ and *n*-hexane.



Fig. S4 Illustration of (a) C-H···O and C-H··· π interactions in *n*-hexane \bigcirc P[5](PhCHO)₂ and (b) C-H···O interactions in CHCl₃ \bigcirc P[5](PhCHO)₂.



Fig. S5 Illustration of (a) C-H···O and (b) C-H··· π interactions in P[5](PhCHO)₂.



Fig. S6 FT-IR spectra of CP (red), P5Tz-CP (blue), and dithiooxamide (black).

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	C [%]	H [%]	N [%]	S [%]	O [%]
Found ^a	71.56	5.79	2.60	6.60	13.43
Calculated ^a	72.24	5.30	2.86	6.53	13.06
Found [®]	73.19	4.84	5.62	13.51	2.04
Calculated ^b	71.74	3.26	7.60	17.39	0.00

Table S2. Elemental analysis of P5Tz-CP and CP

Elemental Analysis

^aP5Tz-CP

^bControl polymer



Fig. S7 Thermogravimetric analysis of P5Tz-CP and CP.



Fig. S8 N_2 (blue) and CO₂ (purple) adsorption-desorption isotherms of (a) CP and (b) P5Tz-CP.



Fig. S9 SEM images of P5Tz-CP at different polymerization intervals.



Fig. S10 SEM images of CP.



Fig. S11 TEM images of P5Tz-CP.



Fig. S12 TEM images of CP.



Fig. S13 Fluorescence spectra of P5Tz-CP and CP.



Fig. S14 UV-vis diffuse reflectance spectra (DRS) of P5Tz-CP and CP.



Fig. S15 Photocatalytic degradation of RhB in N_2 in the presence of (a) P5Tz-CP and (b) CP.



Fig. S16 RhB adsorption process of (a, b) P5Tz-CP and (c, d) CP before light irradiation.



Fig. S17 EIS Nyquist plots of P5Tz-CP and CP.



Fig. S18 Mott-Schottky plots of (a) CP and (b) P5Tz-CP at 500, 1000, and 1500 Hz. The interception at potential axis shows the conductive band position.



Fig. S19 Recyclable performance in photocatalytic degradation of RhB (50 mL, 10 mg/L) in the presence of (a) CP (0.1 mg/mL) under irradiation for 1 h and (b) P5Tz-CP (0.4 mg/mL) under irradiation for 2 h.

6. References

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