Supplementary Information

Enhancing photocatalysis in conjugated microporous polymers *via* π -bridge engineering between pyrene and thiazolothiazole

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1. General information

1.1. Reagents and solvents

The 4,4',4",4"'-(pyrene-1,3,6,8-tetrayltetrakis(ethyne-2,1-diyl))tetrabenzaldehyde (AEBPy) was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. The 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (TFPPy), dithiooxamide (DTO), 2-phenyl-1,3,2-dioxaborinane (PhB(OCH₂)₂), and phenylboronic acid (PhB(OH)₂) were obtained from Adamas. The other reagents were purchased from Sigma-Aldrich, TCI, Innochem, Adamas, Alfa Aesar, Sinopharm Chemical Reagent, and J&K Scientific Co., Ltd., etc.

1.2. Syntheses of Py-TzTz-CMP and Py-π-TzTz-CMP

Py-TzTz-CMP and Py- π -TzTz-CMP were synthesized via oxidative cyclization of DTO and an aromatic aldehyde, following our previously reported protocol.¹ Initially, 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (TFPPy, 76.5 mg, 0.12 mmol) or 4,4',4",4"'-(pyrene-1,3,6,8-tetrayltetrakis(ethyne-2,1-diyl))tetrabenzaldehyde (AEBPy, 90.3 mg, 0.12 mmol) were fixed with DTO (29.4 mg, 0.24 mmol) using nitrobenzene as the solvent in a 20 mL Pyrex tube. After dispersion uniformity through 5 min ultrasonication, the mixture was treated by three cycles of degassing. Consequently, the Pyrex tube was sealed under vacuum and heated at 150 °C for 120 h. Naturally cooling to room temperature, the mixture solid was treated by filtering and rinsing with CH₂Cl₂ and *N*,*N*-dimethylformamide in sequence. Soxhlet extractor with CH₂Cl₂ as the solvent was exploited for further purification of the polymer. The Py-TzTz-CMP and Py- π -

TzTz-CMP were obtained as collected brown and brownish-red solids, respectively.

1.3. Procedure for the selective hydroxylation by photocatalysis

In a 20 mL Pyrex vessel, the 2-phenyl-1,3,2-dioxaborinane (PhB(OCH₂)₂) or phenylboronic acid (PhB(OH)₂) (0.6 mmol) was mixed with DIPEA (1.8 mmol) and Py- π -TzTz-CMP (5 mg) using CH₃OH (3 mL) as solvent. After adsorption–desorption equilibrium through 30 min of stirring in the dark, the vessel was exposed to green light-emitting diodes (LEDs, 3 W × 4) with 1500 rpm of magnetic stirring. Finally, the supernatant, obtained by centrifugation, was detected through gas chromatography with a flame ionization detector (GC–FID) for quantitive analysis. Besides, qualitative analysis of the product was performed through gas chromatography–mass spectrometry (GC–MS).

1.4. The recycle experiment

After irradiation, the fresh Py- π -TzTz-CMP underwent centrifugation from the reaction mixture. Subsequently, twice rinsing with CH₃OH and centrifugation were performed to remove residue over Py- π -TzTz-CMP. The reused photocatalyst was directly added to the subsequent runs without additional treatment. The reaction was carried out under green LED irradiation for 1.4 h at room temperature with magnetic stirring.

1.5. Characterizations and instrumentations

Scanning electron microscopy (SEM) images of organic materials were measured

on Zeiss Merlin Compact field emission scanning electron microscope. The highresolution transmission electron microscopy (HRTEM) images of CMPs were estimated on a JEM-F200. The N2 isotherms and specific surface areas were determined at 77 K employing a Micromeritics ASAP 2460 automated system with the Brunauer-Emmet-Teller (BET) model, and the pore size and volume were derived from the sorption curve by using the quenched solid density functional theory (QSDFT) model, the materials were degassed in a vacuum ($<1\times10^{-5}$ bar) at 120 °C for 12 h. The crystal phase composition of solid samples was identified by X-ray powder diffraction (PXRD) using a Rigaku Miniflex 600 diffractometer. The Fourier transform infrared (FTIR) spectra were carried out by NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400–4000 cm⁻¹. Solid-state ¹³C nuclear magnetic resonance spectra were performed on 400 MHz spectrometers (Bruker 400M) at room temperature. The UV-vis diffuse reflection spectroscopy (DRS) was detailed on a Shimadzu UV-3600 UV-VIS spectrophotometer with a diffuse reflectance measurement accessory.

1.6. Electrochemical measurements

Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an electrochemical station. Firstly, 6 mg photocatalysts were dispersed in 3 mL 0.2 wt% Nafion by the ultrasonic instrument. Then the samples were dripped on ITO coated glasses which were placed on the top of a glassy carbon served as the working electrode, and the samples were dried under infrared irradiation. With 0.1 M Na₂SO₄ aqueous solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference electrode and counter electrode, respectively. Meanwhile, the 520 ± 10 nm green LEDs (Shenzhen Ouying Lighting Science and Technology Co., Ltd.) placed at 2 cm away from the photoelectrochemical cell were employed as the light source.

1.7. DFT calculations

Py-TzTz and Py- π -TzTz molecular fragments were optimized using density functional theory (DFT) methods through the Gaussian 16 package (Rev. A.03) at the B3LYP/6-311G(d) level. The excited-state electronic structures of Py-TzTz and Py- π -TzTz were calculated using time-dependent density functional theory (TD-DFT) calculations at the CAM-B3LYP/6-31G level. The localized orbital locator- π , electrons-holes distribution, delocalization index, and exciton binding energy were calculated and mapped using the Multiwfn program.^{2, 3}



2. Results

Fig. S1 The PXRD patterns of TFPPy and Py-TzTz-CMP (a) and AEBPy and Py-π-

TzTz-CMP (b).



Fig. S2 The TEM images of Py-TzTz-CMP (a) and Py- π -TzTz-CMP (b). The TEM images inclusive of selected area electron diffractions of Py-TzTz-CMP (c) and Py- π -TzTz-CMP (d).



Fig. S3 The UV–vis DRS spectra of Py-TzTz-CMP, Py-π-TzTz-CMP, DTO, TFPPy, and AEBPy.



Fig. S4 Calculated frontier molecular orbitals of Py-TzTz-CMP and Py- π -TzTz-CMP.

Table S1 Hydroxylation of PhB(OCH₂)₂ to phenol by Py-TzTz-CMP, Py- π -TzTz-CMP, TzTz-TA, TFPPy, AEBPy, or DTO photocatalysis^a

Photocatalyst, DIPEA, O ₂ Green LEDs, CH ₃ OH						
Entry	Photocatalyst	Conv. (%) ^b	Sel. (%) ^b			
1	Py-π-TzTz-CMP	84	99			
2	Py-TzTz-CMP	46	96			
3	TFPPy	19	99			
4	AEBPy	42	99			
5	DTO	14	99			

^aStandard conditions: CH₃OH (3 mL), O₂ (1 atm), PhB(OCH₂)₂ (0.6 mmol), DIPEA (3.0 equiv.), photocatalyst (5 mg), green LEDs (3 W \times 4), 1.4 h.

^bDetermined by GC–FID using bromobenzene as the internal standard, conversion of PhB(OCH₂)₂, selectivity of phenol.

Table S2 Hydroxylation of phenylboronic acids to phenols by Py-TzTz-CMP or Py-π-TzTz-CMP photocatalysis^a

$R \stackrel{OH}{=} OH \xrightarrow{Py-TzTz-CMP, DIPEA, O_2} R \stackrel{OH}{=} OH \xrightarrow{Green LEDs, CH_3OH} R \stackrel{H}{=} OH$					
Entry	Substrate	Product	Photocatalyst	Yield. (%)	
1	он В он	С	Py-TzTz-CMP	29	
			Py-π-TzTz-CMP	95	
2	он	С	Py-TzTz-CMP	46	
	€) of		Py-π-TzTz-CMP	90	
3	он F	п → ОН	Py-TzTz-CMP	22	
		F	Py-π-TzTz-CMP	79	

^aStandard conditions: CH₃OH (3 mL), O₂ (1 atm), boronic acid (0.6 mmol), DIPEA (3.0 equiv.), photocatalyst (5 mg), green LEDs (3 W \times 4), 1.6 h.



Fig. S5 The influence of the amount of DIPEA for hydroxylation of PhB(OCH₂)₂ to phenol by Py- π -TzTz-CMP photocatalysis. Standard conditions: CH₃OH (5 mL), O₂ (1 atm), PhB(OCH₂)₂ (0.6 mmol), Py- π -TzTz-CMP (5 mg), green LEDs (3 W × 4), 1.4 h.



Fig. S6 The influence of different solvents (a) and the amount of CH₃OH (b) for hydroxylation of PhB(OCH₂)₂ to phenol by Py- π -TzTz-CMP photocatalysis. Standard conditions: O₂ (1 atm), PhB(OCH₂)₂ (0.6 mmol), Py- π -TzTz-CMP (5 mg), DIPEA (3.0 equiv), green LEDs (3 W × 4), 1.4 h. (a) solvent (5 mL), (b) CH₃OH.



Fig. S7 The influence of different LED irradiation for hydroxylation of PhB(OCH₂)₂ to phenol by Py- π -TzTz-CMP photocatalysis. Standard conditions: CH₃OH (3 mL), O₂ (1 atm), PhB(OCH₂)₂ (0.6 mmol), Py- π -TzTz-CMP (5 mg), DIPEA (3.0 equiv), LEDs (3 W × 4), 1.0 h.



Fig. S8 The FTIR spectra of Py-π-TzTz-CMP before and after recycle.

3. ¹H and ¹³C NMR data of isolated phenol products

Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Unless otherwise stated, CDCl₃ (¹H NMR:7.26 ppm; ¹³C NMR:77.16 ppm) was used as the solvent.

Phenol: yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.26–8.01 (m, 2H), 7.72–7.53 (m, 1H), 7.48 (m, 2H), 7.26 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.5, 129.8, 120.9, 115.5.



4-Methoxyphenol: white solid; ¹H NMR (400 MHz, CDCl₃) δ 6.91–6.56 (m, 4H), 5.29 (s, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 149.7, 116.2, 115.0, 56.0.



3-Methoxyphenol: yellowish liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.48 (dd, *J* = 13.1, 5.2 Hz, 3H), 5.98 (s, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 157.2, 130.2, 108.2, 106.3, 101.8, 55.3.

References

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