

Electronic supplementary information

Extending the 2D conjugated microporous polymers linked by thiazolo[5,4-*d*]thiazole for green light-driven selective aerobic oxidation of amines

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1. Instrumentations

NMR measurement

Solid-state ^{13}C CP/MAS NMR measurements of TzTz-CMP-Py and TzTz-CMP-Be were conducted by using a Bruker AVANCE III 400M spectrometer. ^1H and ^{13}C spectra of 1,3,6,8-tetra(4-formylphenyl)pyrene and 1,3,5-tris(4-formylphenyl)benzene were made on a Bruker AVANCE III HD NMR spectrometer.

FTIR spectra

The FTIR spectra of solid samples were carried out by NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400-4000 cm^{-1} .

PXRD

The crystal phase composition of solid samples was identified by X-ray powder diffraction (PXRD) using a Rigaku Miniflex 600 diffractometer.

BET

The nitrogen isotherms were measured at 77 K using an Autosorb-iQ (Quantachrome) surface area size analyzer. The specific surface areas of the TzTz-CMP-Py and TzTz-CMP-Be were calculated by using the Brunauer-Emmett-Teller (BET) method and the pore size and volume were derived from the sorption curve by using the quenched solid

density functional theory (QSDFT) model.

TGA

Thermogravimetric analysis (TGA) of TzTz-CMP-Py and TzTz-CMP-Be were conducted on an SDT Q600 thermogravimeter under N₂ atmosphere with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C.

SEM

Scanning electron microscopy (SEM) images of TzTz-CMP-Py and TzTz-CMP-Be were measured on Zeiss Merlin Compact field emission scanning electron microscope.

HRTEM

High-resolution transmission electron microscopy (HRTEM) images of TzTz-CMP-Py and TzTz-CMP-Be were measured on JEM-2100 transmission electron microscopy.

AFM

Atomic force microscopy (AFM) images were obtained on Bruker Dimension ICON atomic force microscopy.

UV-visible spectra

The UV-visible absorption spectra of the TzTz-CMP-Py and TzTz-CMP-Be were detailed on a Shimadzu UV-3600 UV-VIS spectrophotometer with a diffuse reflectance measurement accessory.

TRPL spectra

Time-resolved photoluminescence (TRPL) spectra of TzTz-CMP-Py and TzTz-CMP-Be were recorded on FLS980 Series of fluorescence spectrometer.

EPR

The EPR experiments were carried out on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300). The sample under standard conditions was irradiated in the light chamber of the EPR spectrometer irradiated by a high-pressure Hg lamp with a filter to select the band of 520 nm visible light.

GC and GC–MS

Gas chromatography (GC) quantitative measurements of the conversions of substrates and the selectivities of products were carried out on a gas chromatograph equipped with a flame ionization detector (GC–FID, Agilent 7890B) using high purity N₂ as the carrier gas and an Agilent J & W DB-5 capillary column (30 m × 0.32 mm × 0.25 μm, 19091 J-413) or an Agilent J&W DB-17 capillary column (30 m × 0.32 mm

× 0.25 μm, 123–1732). GC–FID standard analysis conditions: injector temperature 250 °C, detector temperature 280 °C, and column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C min⁻¹. The results were all obtained using a split mode with a split ratio of 30 : 1. Gas chromatography-mass spectrometry (GC–MS) analysis was performed on an Agilent GC 8890 gas chromatograph equipped with an Agilent 5977B GC/MSD mass spectrometer using an Agilent (HP-5 MS) capillary column (30 m × 0.25 mm × 0.25 μm) with high purity He as the carrier gas. Conversion and selectivity for selective oxidation of the substrate to target product were defined as follows:

$$\text{Conversion (\%)} = [(C_0 - C_r)/C_0] \times 100$$

$$\text{Selectivity (\%)} = [C_p/(C_0 - C_r)] \times 100$$

Where C_0 is the initial concentration of reactant, C_r and C_p are the concentrations of substrate and target product, respectively, at a certain time after the photocatalytic reaction.

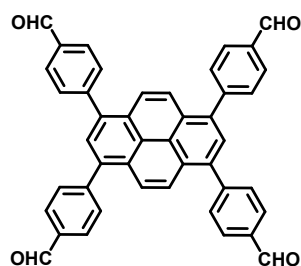
2. Experimental section

2.1 Reagents and solvents

All the reagents without special descriptions were purchased from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J&K Scientific, etc. without further purification. The solvents were obtained by Merck, Fischer Scientific, and

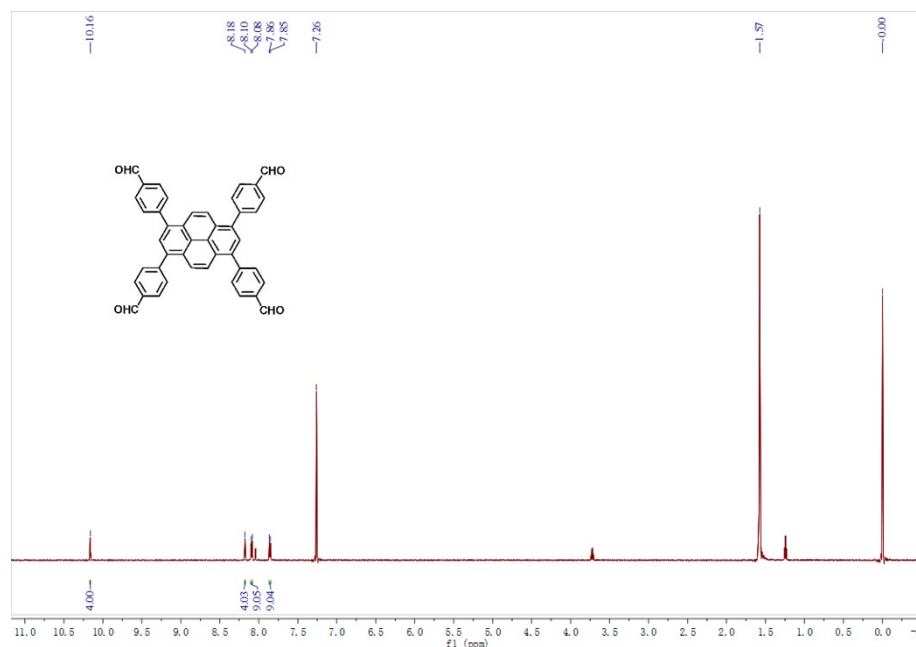
Sinopharm Chemical Reagent Co., LTD. Benzyl- α,α -d₂-amine was obtained by CDN Isotopes, Quebec, Canada. Dithiooxamide was purchased from Fisher Scientific. 1,3,6,8-tetra(4-formylphenyl)pyrene and 1,2,4,5-tetra(4-formylphenyl)benzene were synthesized according to previous reports and the preparation courses were presented as follows.

2.2 Synthesis of 1,3,6,8-tetra(4-formylphenyl)pyrene

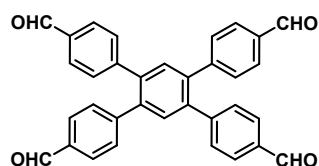


A mixture of 1,3,6,8-tetrabromopyrene (1.0 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol %), and potassium carbonate (2.1 g, 15 mmol) in dry dioxane (30 mL) was stirred under nitrogen for 3 days at 85 °C. The yellow suspension reaction mixture was poured into a solution of ice containing concentrated hydrochloric acid. The yellow solid was filtered and washed with 2 mol/L HCl (20 mL) three times. The product was extracted with CHCl₃ (3 × 100 mL) and dried over MgSO₄. After filtration, the solvent was removed under reduced pressure and the resultant solid residue was recrystallized from hot CHCl₃ to afford 1,3,6,8-tetra(4-formylphenyl)pyrene as a bright yellow powder (0.82 g, 70%).

^1H NMR (600 MHz, CDCl_3) δ 10.16 (s, 4H), 8.18 (s, 4H), 8.09 (d, $J = 8.0$ Hz, 9H), 7.86 (d, $J = 8.1$ Hz, 9H).



2.3 Synthesis of 1,2,4,5-tetra(4-formylphenyl)benzene

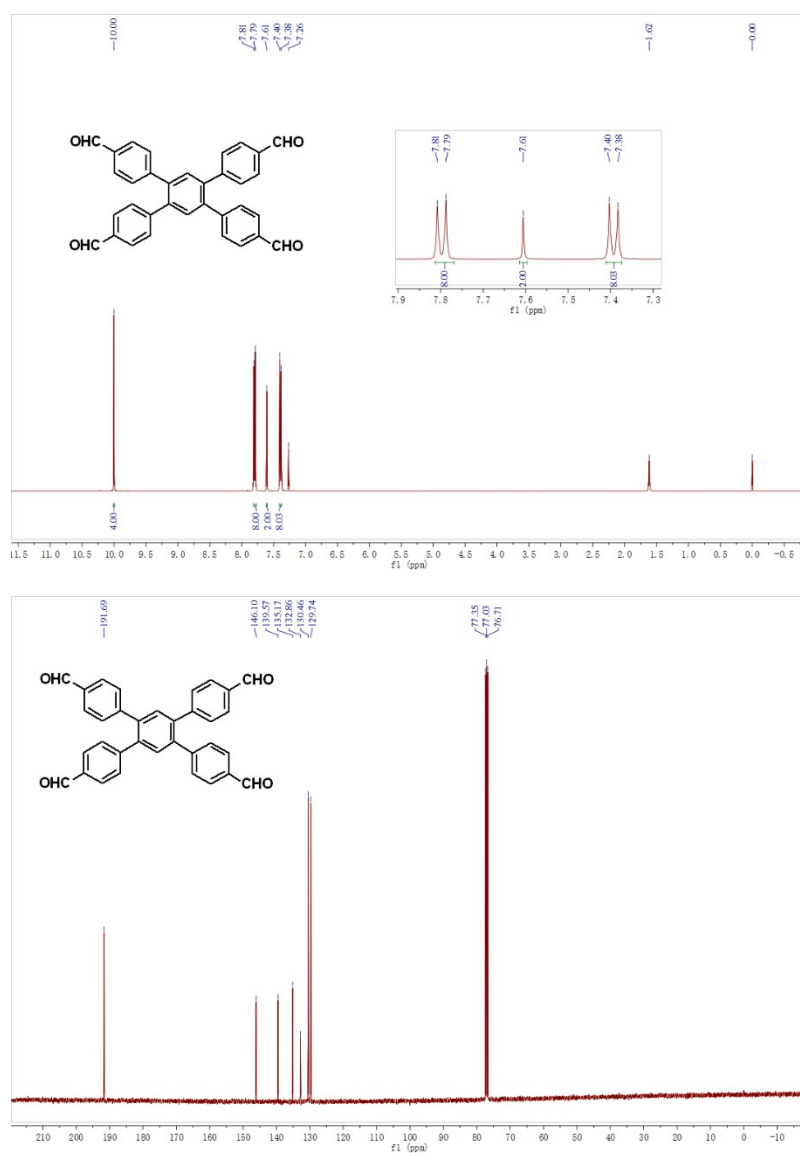


A mixture of 1,2,4,5-tetrabromobenzene (1.5 g, 3.85 mmol), 4-formylphenylboronic acid (3.4 g, 22.7 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol%), and potassium carbonate (4.2 g, 30.4 mmol) in dry 1,4-Dioxane (50 mL) was stirred under nitrogen for 3 days at 90 °C. The white suspension reaction mixture was poured into slurry ice containing 80 mL concentrated hydrochloric acid. The solid product was filtered and washed with water three times. The final product was obtained

after extraction of the crude product with chloroform (4×50 mL). The extracted organic layer was dried over MgSO_4 , filtered, and evaporated under reduced pressure. The resultant solid was recrystallized from hot ethyl acetate to afford (TFPB) as a yellowish powder (1.3 g, 68%).

^1H NMR (400 MHz, CDCl_3) δ 10.00 (s, 4H), 7.80 (d, $J = 8.2$ Hz, 8H), 7.61 (s, 2H), 7.39 (d, $J = 8.1$ Hz, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ 191.69, 146.10, 139.57, 135.17, 132.86, 130.46, 129.74.



2.4 Synthesis of TzTz-CMP-Py and TzTz-CMP-Be

A Pyrex tube was charged with 0.228 mmol dithiooxamide (27.4 mg), 0.114 mmol 1,3,6,8-tetra(4-formylphenyl)pyrene (70.8 mg)/1,2,4,5-tetra(4-formylphenyl)benzene (56.4 mg), and 4 mL nitrobenzene. The mixture was ultrasonicated for 10 min to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze–pump–thaw cycles. The tube was sealed under vacuum and then heated at 150 °C for 120 h. Thereafter, the resulting precipitate was collected by centrifugation, washed with dichloromethane and *N,N'*-dimethylformamide for several times. The resulting powder was purified for 72 h by Soxhlet extraction with dichloromethane as the solvent and then dried under infrared light for 3 h.

2.5 Typical procedure for the selective aerobic oxidation of amines

Typically, 0.5 mmol of benzylamine, 5 mg of TzTz-CMP-Py, and 1 mL of CH₃CN were added into a 10 mL Pyrex reactor. Next, the mixture was stirred for 30 min in the dark to get adsorption-desorption equilibrium. Subsequently, the Pyrex reactor was sealed and filled with 0.1 MPa O₂, which was then irradiated by green light-emitting diodes (LEDs) (3 W × 4, Shenzhen Ouying Lighting Technology Co., Ltd.) and stirred simultaneously at a speed of 1500 rpm at room temperature. After the reaction, the conversion of substrates and selectivity of the products were analyzed by gas chromatography equipped with a flame ionization detector (GC–FID). The products were confirmed by comparing the retention time with authentic samples by GC–FID and further affirmed by gas chromatography-mass spectrometry (GC–MS).

2.6 Typical procedure for photoelectrochemical tests

The Electrochemical impedance spectroscopy (EIS) measurements, Mott–Schottky plots were determined by a Metrohm PGSTAT302N electrochemical workstation in a conventional three-electrode configuration with Ag/AgCl (saturated KCl) as the reference electrode and Pt wire as the counter electrode. A 0.2 mol/L Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 6 mg of the as-prepared photocatalyst was suspended in 3 mL dilute NaFion dispersion to produce a slurry, which was then dropped 10 μL onto an indium tin oxide (ITO) glass electrode and the film was dried by an infrared lamp, then the working electrode was obtained after five cycles.

2.7 Testing the recycled photocatalyst

A recycled photoactivity test on the used photocatalyst was done as the following. Typically, after the reaction of 1.2 h under green light irradiation, the liquid and photocatalyst were separated by centrifugation. The liquid was decanted, while the used photocatalyst was washed 3 times with 1 mL of acetonitrile. Then the used photocatalyst was subjected to the 2nd run photoactivity testing under standard conditions. In analogy, the recycled 3rd run and 4th run photoactivity tests were performed.

3. Results

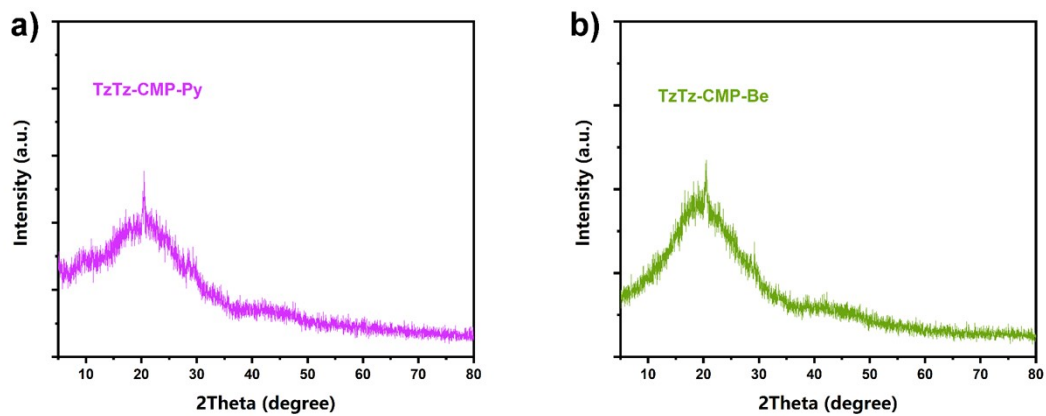


Fig. S1. PXRD patterns of TzTz-CMP-Py and TzTz-CMP-Be.

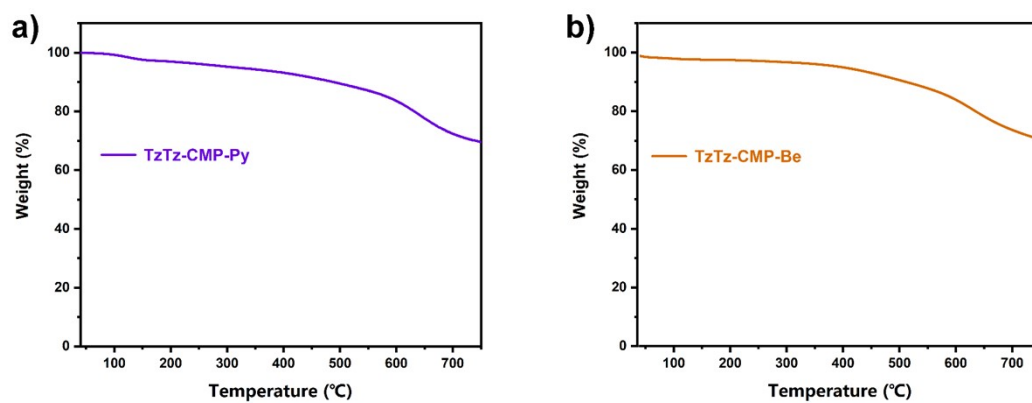


Fig. S2. TGA curves of TzTz-CMP-Py and TzTz-CMP-Be.

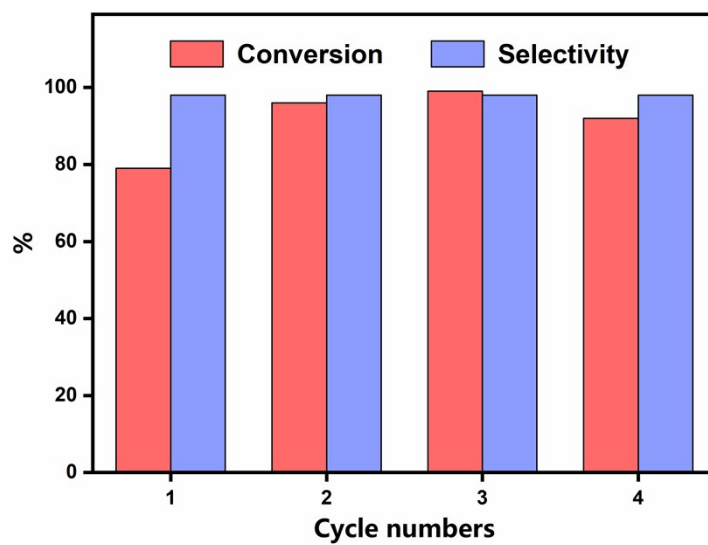


Fig. S3. The recycling experiment of TzTz-CMP-Py for the green light-driven selective aerobic oxidation of benzylamine. Reaction conditions: benzylamine (0.5 mmol), TzTz-CMP-Py (5 mg), green LEDs ($\lambda = 520 \pm 15$ nm), O₂ (0.1 MPa), CH₃CN (1 mL), 1.2 h.