## **Electronic Supplementary Information**

# Phenoxazine-based covalent triazine framework for photocatalytic aerobic hydroxylation of arylboronic Acids to phenols

Yaju Chen,<sup>a</sup> Haowen Chen,<sup>a</sup> Jun Jiang <sup>\*b</sup> and Hongbing Ji <sup>\*c</sup>

<sup>a</sup> School of Chemistry, Guangdong University of Petrochemical Technology,

Maoming 525000, China.

<sup>b</sup> Guangdong Brunp Recycling Technology Co. Ltd, Foshan 528137, China.

<sup>c</sup> Institute of Green Petroleum Processing and Light Hydrocarbon Conversion, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China.

#### 1. Instruments

FT-IR spectra were recorded on a Bruker spectrophotometer using KBr pellets. Liquid <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 MHz spectrometer using CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> as the solvent. Solid-state <sup>13</sup>C CP/MAS NMR spectrum was obtained using a Bruker Avance III 400 MHz spectrometer at a MAS rate of 8 kHz and a CP contact time of 1.5 ms. XPS spectra were conducted in a Thermo Fisher Scientific ESCALab250 using mono AlK $\alpha$  radiation (hv = 1486.6 eV) as the excitation source under a base pressure of  $2 \times 10^{-9}$  mbar. The binding energies were referenced to the C 1s peak at 284.8 eV. Field emission scanning electron microscopy (SEM) images and energy dispersive X-Ray spectroscopy (EDX) were determined by a Regulus 8220 microscopy at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) was performed on JEM-2100F field emission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Powder X-Ray diffraction (PXRD) patterns of the powder samples were obtained with a Bruker AXS D8 Advanced SWAX diffractometer by depositing powder on glass substrate, from  $2\theta = 2^{\circ}$  to  $60^{\circ}$  at 25 °C. Thermogravimetry analysis (TGA) was carried out in a NETZSCH TG 209 F3 Tarsus instrument by heating samples from 40 °C to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. N<sub>2</sub> sorption isotherm was recorded using an ASAP2020M adsorption instrument. Before measurement, the as-prepared sample was outgassed in vacuum at 100 °C for 10 h. UV-Vis-NIR DRS spectra were conducted in a Lambda 950 spectrophotometer in the wavelength range of 200-2000 nm. Room temperature photoluminescence (PL) and Time-resolved photoluminescence (TRPL) spectra were scanned on a FLS980 photoluminescence spectrometer at an excitation wavelength of 350 nm. The Electrochemical Impedance spectroscopy (EIS) and Mott-Schottky analysis were completed on a CHI660E electrochemical station in a standard three-electrode system with a graphite electrode (i.d. = 3 mm) as the working electrode system, a Pt electrode as a counter electrode, and an saturated Ag/AgCl as the reference electrode in aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.2 M). Photocatalysis was carried out on a CEL-LAB200E7 multichannel photochemical reaction system equipped with a circulating cooling water system and ten of white LED lamps (410-760nm, 40 mW/cm<sup>2</sup>), which was provided by Beijing China Education Au-light Co. Ltd. Reaction products were analyzed by Agilent GC7890B equipped with DB-1 capillary column (0.25  $\mu$ m × 250  $\mu$ m × 30 m) and FID detector. Standard analysis condition: oven temperature 50 °C, injector temperature 250 °C, detector temperature 300 °C, heating rate 10 °C/min, final temperature 250 °C and hold time 1 min. ESR measurements were performed on a JEOL JES-FA2000 ESR spectrometer. Catalyst recovery was performed on a centrifugal machine with 4000 r/min for 20 min.

#### 2. Electrochemical measurements

The catalyst (10 mg) was dispersed in 20  $\mu$ L of 5 wt% Nafion and 1 mL of isopropanol to obtain a suspension, and 20  $\mu$ L of the suspension was was dropped on F-doped SnO<sub>2</sub> (FTO) glass, which was used as the working electrode. The Mott-Schottky plots were collected in 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution. The Mott-Schottky plots of sample were measured at frequencies of 500, 1000, and 1500 Hz.

#### **3. ESR measurements**

NP-CTF (5 mg) was dispersed in acetonitrile of 0.5 mL, and bubble with O<sub>2</sub> for 5 min. Next, TEMP (50  $\mu$ L), DMPO (50  $\mu$ L) or DIPEA (50  $\mu$ L) was added to the mixture. The resulting mixture was injected to a Wilmad WG-810-A quartz flat cell with a syringe. ESR analysis was carried out at microwave frequency of 9.22 GHz at room temperature in the dark or under visible light ( $\lambda > 420$  nm).

#### 4. Synthesis

#### Synthesis of 3,7-Di(4-cyanophenyl) 2-Naphthalene-10-Phenoxazine (CNP)

Syntheses of CNP was performed using previously reported procedures.<sup>1</sup>



2-Naphthyl-10-Phenoxazine (NP): Under a N2 atmosphere, to a mixture of phenoxazine (1.83 g, 10 mmol), 2-bromonaphthalene (3.11 g, 15 mmol) and sodium tert-butaoxide (NaOtBu, 2.88 g, 30 mmol) in degassed toluene (100 mL), bis(dibenzylideneacetone)palladum (Pd(dba)<sub>2</sub>, 0.057g, 0.1 mmol) and 0.33 mL of solution of tri-tert-butylphosphine (PtBu<sub>3</sub>) in toluene (1.0 M) were added, respectively. The resulting mixture was stirred at 110 °C for 24 h under a N<sub>2</sub> atmosphere. After reaction, the mixture was cooled to ambient temperature, and then the solvent was removed under reduced pressure. The resulting solid was again dissolved in dichloromethane, and the mixture was washed with deionized water (2  $\times$ 50 ml), followed by brine  $(1 \times 100 \text{ ml})$  and dried over magnesium sulfate. The organic under layer was concentrated reduced pressure. Crystallization from dichloromethane/methanol at -25 °C results in a white precipitate, which was collected and dried at 60 °C in vacuum (2.05 g). Yield: 66%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.9 Hz, 2H), 7.62 - 7.52 (m, 2H), 7.41 (dd, J = 8.6, 2.0 Hz, 1H), 6.72 (dd, J = 7.9, 1.4 Hz, 2H), 6.68 - 6.61 (m, 2H), 6.56 (td, J = 7.8, 1.4 Hz, 2H), 5.95 (dd, J = 8.0, 1.2 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) & 143.97, 136.17, 134.71, 134.41, 132.94, 131.39, 130.04, 127.98, 127.95, 127.90, 126.90, 126.55, 123.23, 121.36, 115.44, 113.41.





3,7-Dibromo-2-Naphthyl-10-Phenoxazine (**BNP**): To of mixture а 2-Naphthyl-10-phenoxazine (1.55 g, 5 mmol) in acetic acid/chloroform (240 mL, 1:1 v/v), N-bromosuccinimide (NBS, 1.96 g, 11 mmol) was added in batches over 20 min. The resulting mixture was stirred at room temperature for 3 h, and then deionized water and saturated sodium bicarbonate solution were added to adjust the pH to 7–8. The reaction mixture was diluted with dichloromethane (100 mL), and then the organic layer was collected, washed with deionized water and brine, and dried over magnesium sulfate. The organic layer was concentrated under reduced pressure. Crystallization from dichloromethane/hexane at -25 °C results in a brown precipitate, which was collected and dried at 60 °C in vacuum (1.98 g). Yield: 85%. <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{CDCl}_3) \delta 8.09 \text{ (d, } J = 8.6 \text{ Hz}, 1\text{H}), 7.95 \text{ (d, } J = 8.0 \text{ Hz}, 1\text{H}), 7.88 \text{ (d, } J = 8.0 \text{ Hz}, 1\text{H})$ 7.9 Hz, 1H), 7.82 (d, J = 1.6 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.34 (dd, J = 8.6, 2.1 Hz, 1H), 6.85 (d, J = 2.2 Hz, 2H), 6.68 (dd, J = 8.6, 2.2 Hz, 2H), 5.80 (d, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.14, 135.27, 134.63, 133.28, 133.06, 131.79, 129.75, 127.99, 127.96, 127.26, 127.15, 126.85, 126.27, 118.67, 114.58, 112.94, 77.27, 77.02, 76.76.



3,7-Di(4-cyanophenyl) 2-Naphthalene-10-Phenoxazine (CNP)

Under a  $N_2$  atmosphere, 3,7-Dibromo 2-Naphthalene-10-phenoxazine (1.17 g, 2.5 mmol) and 4-cyanophenyl boronic acid (1.47 g, 10 mmol) were dissolved in 100 mL of degassed THF. 20 mL of degassed aqueous solution of  $K_2CO_3$  (2 M) was added,

then the resulting mixture was heated to °C. and 80 Subsequently, tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.433 g, 0.375 mmol) was added, and the reaction mixture was heated at 100 °C for 24 h. After reaction, the mixture was cooled to ambient temperature, and then the solvent was removed under reduced The residue purified by silica pressure. was a gel column using dichloromethane/hexane (3:1 v/v) as the eluent to afford a yellow solid, which was further recrystallized using dichloromethane/methanol at -25 °C to give a yellow precipitate. The product was collected and dried at 60 °C in vacuum (0.91 g). Yield: 71%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.68 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 7.4 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.32–7.25 (m, 2H), 7.06–6.96 (m, 11H), 6.55 (dd, J = 8.4, 2.1 Hz, 2H), 5.95 (d, J = 8.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) § 144.22, 144.17, 135.16, 134.66, 134.35, 133.14, 132.61, 131.80, 129.70, 128.02, 127.34, 127.18, 126.94, 126.56, 122.30, 119.00, 114.06, 110.31.





Scheme S1. Synthesis of NP-CMP

## 5. Characterization of NP-TCF and NP-CMP

















Fig. S6 SEM (A and B) and EDS elemental mapping (C) images of NP-CTF; SEM image of reused NP-CTF (D)



Fig. S7 TEM images of fresh (A) and reused (B) NP-CTF



Fig. S8 PXRD patterns of fresh (a) and reused (b) NP-CTF









Fig. S11 TRPL spectra of NP-CTF (A) and CNP (B) (excitation at 350 nm)



Fig. S12 Nyquist plots of electrochemical impedance spectra (EIS) of NP-CTF



Fig. S13 Band gap of NP-CTFS obtained from the UV-Vis-NIR DRS spectrum according to the Kubelka–Munk theory.

### 6. Hydroxylation reaction under nature sunlight

Table S1 Hydroxylation of various arylboronic acids to phenols under nature sunlight <sup>a</sup>				
Entry	Substrate	Product	Time (h)	$\mathbf{Yield}^{b}$
1	он В он	ОН	7	99.2
2	OH Br	Br	7	46.9
3	он Б <sub>3</sub> С	F <sub>3</sub> C OH	7	54.1
4	OH O <sub>2</sub> N	O <sub>2</sub> N OH	7	48.7
5	OH B OH	OH N	7	82.2
6	ОН В ОН	ОН	7	89.5
7	он <sup>В</sup> он	₩ОН	7	91.2

<sup>&</sup>lt;sup>*a*</sup> Reaction conditions: substrate (0.5 mmol), NP-CTF (25 mg), DIPEA (2.5 mmol), acetonitrile (10 mL), air, ambient temperature, dodecane (0.5 mmol) as the internal standard. <sup>*b*</sup>Determined by GC with dodecane as the internal standard, selectivity of all products >99%.



## 7. Standard curves for different products (GC analysis)



## 8. Reference

(1) McCarthy, B. G.; Pearson, R. M.; Lim, C. H.; Sartor, S. M.; Damrauer, N. H.; Miyake, G. M. Structure-Property Relationships for Tailoring Phenoxazines as Reducing Photoredox Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 5088-5101.