## Supplementary Information

# Ultra-low loading porphyrin-incorporated conjugated polymer dots as photocatalysts for scalable aerobic oxidation of sulfides in water

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## Table of contents

1. Materials and methods	3
1.1. Chemicals and instrumentation	3
1.2. Instrumentation and characterizations	3
1.3. Synthesis of polymer dots (Pdots)	5
1.4. Catalytic activity test	5
2. Synthesis of porphyrin and metalloporphyrin monomers	6
3. Supplementary figures	8
4. Supplementary tables	21

#### 1. Materials and methods

#### 1.1. Chemicals and instrumentation

9,9'-dioctylfluorene-2,7-diboronic acid (F-BOH) was purchased from Chemenu. Pd(PPh<sub>3</sub>)<sub>4</sub>, and poly(styrene-*co*-maleic anhydride) (avg.  $M_n \sim 1,900$ ) were purchased from Sigma Aldrich. 9,9'-dioctyl-2,7-dibromofluorene (F-Br<sub>2</sub>), 4,7-dibromo-2,1,3-benzothiadiazole (BT-Br<sub>2</sub>), 2,5-Dibromo-3,4-ethylenedioxythiophene (EDOT-Br<sub>2</sub>), and all sulfide and sulfoxide standards were purchased from TCI Chemical.

All manipulations were carried out using a standard Schlenk line technique under an inert atmosphere of nitrogen. All glass wares were dried at 110 °C for 24 h and cooled under vacuum prior to use. All the regents, analytical grade chemicals, and spectroscopic solvents were used without further purification. All solvents and reagents for the synthesis of polymers were dried on molecular sieves and stored under nitrogen atmosphere before use. Ultrapure water was obtained from Merck Milli-Q® Reference type 1 Type Water Purification System.

#### **1.2. Instrumentation and characterizations**

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and 2D NMR spectra were recorded using a 500 MHz JEOL JNM-ECZ500R/S1 (JEOL, Japan) and a 400 MHz Bruker AVANCE (Bruker, Germany) at ambient temperature. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced internally to residue protio-solvent (<sup>1</sup>H) and are reported relative to tetramethylsilane (TMS). The spectra were analyzed and processed using Mestrenova software (version 14.2.1). Data were reported as following: chemical shift, multiplicity, and coupling constant (s=singlet, d=doublet, dd=doublet of doublets, ddd=doublet of doublets of doublets, t=triplet, q=quartet, p=pentet (quintet), m=multiplet).

Mass spectra of organic compounds and metal complexes were determined by a microTOF-Q II 10355 mass spectrometer with an electrospray ionization (ESI) source type. The condition of nebulizer pressure, dry heater temperature and dry gas flow rate was set at 0.4 Bar, 200 °C and 4.0 L/min. Mass range was scanned from 50 to 1500 m/z.

Solid-state UV–vis diffuse reflectance spectra were recorded on a Shimadzu 2600i UV– Vis–NIR scanning spectrophotometer by using BaSO<sub>4</sub> as a standard, within the range of 200– 1000 nm.

UV-Visible spectra were recorded by a Varian Cary 50 Bio UV-Visible spectrophotometer using a UV Quartz Spectrometer Cuvette cell, path length 1 cm, volume 3.5 mL. Spectra of conjugated polymers were obtained from the polymer solutions at the concentration of 5  $\mu$ g/mL using THF as the solvent. Spectra of Pdots were obtained directly from the solutions as prepared.

Fluorescence spectra were recorded by a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) using a UV Quartz Spectrometer Cuvette cell, path length 1 cm, volume 3.5 mL. The detector voltage and the slit width were set to 590 V and 2.5 nm, respectively. Spectra of conjugated polymers were obtained from the polymer solutions at the concentration of 5  $\mu$ g/mL using THF as the solvent. Spectra of Pdots were obtained directly from the solutions as prepared.

Fourier transform infrared (FT-IR) spectra were tested using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific). The solid samples were mixed with oven dried KBr, pulverized, and pressed into pellet for analysis. The data are reported in wavenumbers range 4000-400 cm<sup>-1</sup>.

Dynamic light scattering (DLS) measurements were conducted using a Zetasizer Nano series instrument (the Malvern Instrument Zen 1600) equipped with He-Ne laser (4 mW at 632.8 nm) at 25 °C. All Pdots were analyzed directly from the solutions as prepared.

Inductively coupled plasma - optical emission spectrometry (ICP-OES) was carried out to determine the amount of cobalt in the metalloporphyrin-incorporated conjugated polymers by using an Inductively coupled plasma-optical emission iCAP 6000 series (Thermospectrometer Scientific). All polymer samples were digested using 9:1 conc.  $HNO_3:35\%$  H<sub>2</sub>O<sub>2</sub> in a Teflon line autoclave under 200 °C for 5 h and adjusted the concentration using Milli-Q water.

Gel permeation chromatography (GPC) was performed to provide molecular weight data of polymers using an Agilent 1260 Infinity II plus RI detector equipped with 2 x PLgel-MIXED-C + Guard column. THF was used as an eluent at a flow rate of 1.00 mL/min at 40 °C.

Transmission electron microscopy (TEM) images were obtained by using a JEM-2100 Transmission Electron Microscope (JEOL, Japan) at an acceleration voltage of 120 kV.

Gas chromatography was carried out to detect reactant and products from photocatalysis study by using a Varian CP-3800 Gas Chromatography using an Agilent Technologies HP-5 GC column (0.32 mm x 30 m) with the following conditions adopted from a previous literature: N<sub>2</sub> was used as the carrier gas at 150 kPa inlet pressure; initial column temperature set to 80 °C; intermediate column temperature set to 150 °C at the progress rate of 10 °C min<sup>-1</sup>; final column

temperature set to 280 °C at the progress rate of 20 °C min<sup>-1</sup>; injection temperature set to 280 °C; detection temperature set to 280 °C. Quantitative analysis was made by calculation from the calibration curves constructed from commercially available chemicals and dodecane as internal standard.

#### **1.3.** Synthesis of polymer dots (Pdots)

Firstly, the solution of conjugated polymer and the solution of poly(styrene-*co*-maleic anhydride) (PSMA), both in THF, were prepared at the concentration of 1.0 mg/mL. Then into a 5-mL of THF was added 250.0  $\mu$ L of conjugated polymer solution and 187.5  $\mu$ L of PSMA solution, and the mixture was quicky injected into 10 mL of Milli-Q water under sonication. THF was then removed by purging the solution with a stream of N<sub>2</sub> under continuous sonication for around 30 min to obtain the clear solution of Pdots.

#### **1.4. Catalytic activity test**

In a 10-mL glass tube equipped with a stir bar was added 2 mL of Pdots solution and sealed with a septum. The solution was sparged with  $O_2$  gas for 10 min, then thioanisole (0.2 mmol)

was added using a syringe. The tube was then equipped with an O<sub>2</sub> balloon and brought to irradiated in the photoreactor, in which the stirring was kept constant and air flow was applied to dissipate heat from the light source. At the end, the reaction mixture was extracted with ethyl acetate (3.5 mL x 3). The organic phase was collected, dried on Na<sub>2</sub>SO<sub>4</sub>, and brought to analysis using gas chromatography.

All photocatalysis experiments were conducted in a homemade photoreactor made from a 15-cm-diameter glass bowl in which a commercial blue LED strip (7.5 W/m x 2.5 m) was adhered to the inside. The reaction test tubes (up to 4 tubes) were held by a wire grid and placed 3 cm away from the light source at the middle height of the bowl. Throughout the experiment, an electric fan was placed above the photoreactor to dissipate heat from the light source, and a stir plate was placed beneath to provide a moderate stir rate.

#### 2. Synthesis of porphyrin and metalloporphyrin monomers



**5-phenyldipyrromethane**. In a round bottom flask containing benzaldehyde (3.12 g, 1.0 eq.) and excess distilled pyrrole (17.7 g, 9.0 eq.) was added trifluoroacetic acid (0.67 g, 0.2 eq.), and the mixture was allowed to stir at room temperature under nitrogen atmosphere for 15 min. After the time, the reaction was stopped by adding 0.1 M solution of NaOH. The resulting mixture was extracted with ethyl acetate and the organic phase was dried on Na<sub>2</sub>SO<sub>4</sub>. The organic solvent and unreacted pyrrole were removed under reduced pressure, leaving a dark crude oil which was subjected to column chromatography (silica gel, 9:1 hexane:ethyl acetate). Solvent removal afforded light-yellow liquid which crystallized upon standing. The obtained product was used in the following step without further purification. Yield 3.20 g (49%). <sup>1</sup>H NMR (500 MHz, *CDCl*<sub>3</sub>)  $\delta$  7.92 (s, 2H, N<u>H</u>), 7.34–7.18 (m, 5H, C<sub>6</sub><u>H</u><sub>5</sub>), 6.70 (d, *J* = 1.6 Hz, 2H, NHC<u>H</u><sub>2</sub>), 6.17 (d, *J* = 3.4 Hz, 2H, NHC=C<u>H</u><sub>2</sub>), 5.93 (m, 2H, NHCH<sub>2</sub>C<u>H</u><sub>2</sub>), 5.48 (s, 1H, C<u>H</u>).

**5,15-bis(4-bromophenyl)-10,20-diphenylporphyrin (TPP-Br<sub>2</sub>)**. In a round bottom flask containing dichloromethane (~300 mL) was added 5-phenyldipyrromethane (1.0 g, 1 eq.) and 4-bromobenzaldehyde (0.83 g, 1 eq). Then, boron trifluoride etherate (BF<sub>3</sub>·Et<sub>2</sub>O, 0.13 g, 0.2 eq.) was added, and the mixture was allowed to stir in the dark for 4 h at room temperature under nitrogen atmosphere. After the time, 2,3-Dichloro-5,6-Dicyanobenzoquinone (DDQ, 1.23 g, 1.2 eq.) was added, and the stirring continued for another 1 h under ambient air. Triethylamine (0.14 g, 0.4 eq.) was then added to neutralize the BF<sub>3</sub>·Et<sub>2</sub>O, followed by filtered through silica pad. Solvent removal afforded dry black solid which was subjected to column chromatography (silica gel, 1:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>). Purple solid was obtained after solvent removal. Yield 0.52 g (30%). <sup>1</sup>H NMR (500 MHz, *CDCl<sub>3</sub>*)  $\delta$  8.87 (m, 8H, NHCCH), 8.22 (m, 4H, *o*-C<sub>6</sub>H<sub>5</sub>), 8.07 (m, 4H,

BrCC<u>H</u>), 7.91 (m, 4H, BrCCHC<u>H</u>), 7.78 (m, 6H, *m*,*p*-C<sub>6</sub><u>H</u><sub>5</sub>), -2.81 (m, 2H, N<u>H</u>). HRMS (ESI–TOF) m/z:  $[M+H]^+$  calc. for C<sub>44</sub>H<sub>29</sub>Br<sub>2</sub>N<sub>4</sub><sup>+</sup> 771.0759, found 771.0748.

**5,15-bis(4-bromophenyl)-10,20-diphenylporphyrin cobalt(II) (CoTPP-Br<sub>2</sub>).** In a round bottom flask equipped with a reflux condenser was added a solution of TPP-Br<sub>2</sub> (0.979 g, 1 eq.) in chloroform (~80 mL). Separately, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (3.16 g, 10 eq.) was dissolved in MeOH (~20 mL) beforehand and then added into the TPPBr<sub>2</sub> solution, then the mixture was brough to reflux under nitrogen atmosphere for 2 h. After cooling down to room temperature, the excess cobalt salt and byproduct was removed by extraction with deionized water, and the organic phase was brough to dried on Na<sub>2</sub>SO<sub>4</sub>. The mixture was then filtered through a silica pad and recrystallized in CHCl<sub>3</sub>/MeOH to afford deep red crystalline powder. Yield 0.90 g (86%). NMR spectrum was unable to obtain due to the paramagnetic nature of Co(II). The success of metalation was confirmed by UV-Visible spectroscopy, IR spectroscopy, and mass spectrometry. HRMS (ESI–TOF) m/z: [M]<sup>+</sup> calc. for C<sub>44</sub>H<sub>26</sub>Br<sub>2</sub>CoN<sub>4</sub><sup>+</sup> 828.9836, found 827.9820.

**5,15-bis(4-bromophenyl)-10,20-diphenylporphyrin zinc(II) (ZnTPP-Br<sub>2</sub>)**. In a round bottom flask equipped with a reflux condenser, TPP-Br<sub>2</sub> (0.077 g, 1 eq.) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.11 g, 5 eq.) were added to the solution mixture of chloroform (~50 mL) and MeOH (~25 mL). The mixture was then refluxed for 2 h. After cooling down to room temperature, the solvent was removed under reduced pressure. The ZnTPP-Br<sub>2</sub> was purified using a column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> as an eluent), concentrated and dried to obtain deep red crystalline powder. Yield 76 mg (91%). HRMS (ESI–TOF) m/z: [M+H]<sup>+</sup> calc. for C<sub>44</sub>H<sub>27</sub>Br<sub>2</sub>ZnN<sub>4</sub><sup>+</sup> 834.9868, found 834.9825.

### 3. Supplementary figures



**Figure S1.** <sup>1</sup>H NMR (499.9 MHz, CDCl<sub>3</sub>) spectra of **PFBT-1%TPP** (Top) and **PFBT-5%TPP** (Bottom). Mole fractions of incorporated TPP units in porphyrin-based polymers are determined by integral ratio of proton signals belonging to methyl substituent of PFBT units ('h') and N-H of TPP rings ('n').



Figure S2. FT-IR spectra of PFBT, PFBT-1%TPP, PFBT-5%TPP, PFBT-1%CoTPP, and PFBT-1%ZnTPP.



**Figure S3.** Absorption spectrums of **PFBT** and porphyrin-based polymers with 5 mol% TPP (**PFBT-5%TPP**) in THF.



**Figure S4.** Emission spectrums of **PFBT** and porphyrin-based polymers with 5 mol% TPP (**PFBT-5%TPP**) in THF (excitation wavelength = 460 nm).



**Figure S5.** Frontier molecular orbitals and calculated energy levels of **PFBT-1%TPP** square planar complex.



Figure S6. Frontier molecular orbitals and calculated energy levels of PFBT chains (n=1-4).



Figure S7. Transmission electron micrographs of representative pdots: PFBT-Pdots and PFBT-1%TPP Pdots.



Figure S8. Hydrodynamic diameter of Pdots measured by DLS.



**Figure S9.** Absorption spectrums of porphyrin-based Pdots with 1 mol% TPP and 5 mol% TPP units in water.



**Figure S10.** Emission spectrums of porphyrin-based Pdots with 1 mol% TPP and 5 mol% TPP units in water (excitation wavelength = 460 nm).



**Figure S11**. Chromatogram of standards showing thioanisole and the corresponding oxidized product from GC-FID. Dodecane was used as an internal standard.



Figure S12. Gram scale synthesis of methyl phenyl sulfoxide using FPBT-1%TPP Pdots.



**Figure S13.** <sup>1</sup>H NMR spectrum of the isolated methyl phenyl sulfoxide from the gram-scale photocatalytic aerobic oxidation of thioanisole using **PFBT-1%TPP Pdots** [<sup>1</sup>H NMR (499.9 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.67 – 7.61 (m, 2H), 7.56 – 7.47 (m, 3H), 2.72 (s, 3H)].





PFBT

b)

20 a)

15

PFBT

Figure S14. Solid-state diffuse reflectance UV-Vis spectra of (a) PFBT, (c) PFBT-1%TPP, (e) PFBT-1%CoTPP, and (g) PFBT-1%ZnTPP. The Tauc plot for determination of the band gap of (b) PFBT, (d) PFBT-1%TPP, (f) PFBT-1%CoTPP, and (h) PFBT-1%ZnTPP.



**Figure S15**. Mott–Schottky plots of (a) **PFBT**, (b) **PFBT-1%TPP**, (c) **PFBT-1%CoTPP**, and (d) **PFBT-1%ZnTPP**.

![](_page_19_Figure_0.jpeg)

**Figure S16.** Optimized structures of porphyrin-based and metal porphyrin-based porphyrin containing PFBTs with pyridinic N and selected frontier molecular orbitals involved in excitations and relaxations of a) **PFBT-1%TPP**, b) **PFBT-1%ZnTPP** and c) **PFBT-1%CoTPP** square planar complexes. Energies are in eV.

## 4. Supplementary tables

Polymers	M <sub>w</sub> (g mol <sup>-1</sup> )	M <sub>n</sub> (g mol <sup>-1</sup> )	Polydispersity index (PDI)
PFBT	135999	47257	2.8779
PFBT-1%TPP	101602	38829	2.6160
PFBT-5%TPP	35075	15268	2.2973
PFBT-1%CoTPP	77989	36656	2.1276
PFBT-1%ZnTPP	59737	27547	2.1685

Table S1. Physical properties of conjugated copolymers by GPC analysis (THF, 40 °C).

**Table S2.** Physical properties of various polymer dots.

Pdots	Emission (nm)	Size (nm)
PFBT Pdots	540	40.1
PFBT-1%TPP Pdots	540, 655, 720	39.8
PFBT-5%TPP Pdots	655, 720	36.1
PFBT-1%CoTPP Pdots	540	31.2
PFBT-1%ZnTPP Pdots	540, 603, 652	53.4

Entry	Catalyst	Solvent	Irradiation power (W)	Catalyst amount	Substrate amount (mmol)	Reaction volume (mL)	Time	Atmosphere	Conversion (%) of sulfide to sulfoxide	ref.	
1 TPP-incorp 1 conjugated								<b>O</b> <sub>2</sub>	99		
	TPP-incorporated conjugated Pdots	TPP-incorporated conjugated Pdots	TPP-incorporated conjugated Pdots	H <sub>2</sub> O	20 W blue light (λ = 456 nm)	0.050 mg (conjugated polymer) 0.0875 mg (Pdots)	0.2-20	2-100	3 h	Air zero	25 (20% sel. sulfoxide) (80% sel. sulfone)
Meso-tetra 2 (4-pyridyl)porphyri + Amberlist-15	Meso-tetra (4-pyridyl)porphyrin)							$O_2$	80–95		
		$H_2O$	20 W white light	94 mg (0.032 mol%)	2	10	3 h	Air	47	1	
	+ Amberlist-15							N <sub>2</sub>	Trace	-	
3	Ir-Zr MOFs	H <sub>2</sub> O	100 W blue light $(\lambda = 460 \text{ nm})$	4 mol% (based on Ir)	0.25	4	6–54 h	O <sub>2</sub>	96–98	2	
4	$Bi_4O_5Br_2$	H <sub>2</sub> O	30 W blue light $(\lambda = 456 \text{ nm})$	20 mg	0.2	1	6–22 h	O <sub>2</sub>	92–99	3	
5	Carbazoyl porphyrin CMP (TCPP-CMP)	MeCN:H <sub>2</sub> O (1:1 v/v)	100 W white light $(\lambda = 410-760 \text{ nm})$	10 mg	0.5	10	16 h	O <sub>2</sub>	99	4	
6	Riboflavin derivative	MeCN:H <sub>2</sub> O (85:15 v/v)	7 W blue light $(\lambda = 450 \text{ nm})$	1.1-22 mg (0.002-0.04 mmol)	2	100	1 min–8 h	O <sub>2</sub>	85–100	5	
7	Carbon nanotube- porphyrin nanohybrid	Tris/D <sub>2</sub> O (25 mM Tris)	white LED strip	0.1 mol%	0.2	1	3 h	Air	25–100	6	
8	TiO <sub>2</sub>	MeCN:H <sub>2</sub> O (97:3 v/v)	500 W Xenon lamp	20 mg	0.01	20	30 min	O <sub>2</sub>	100	7	

## Table S3. Comparative photocatalytic aerobic oxidation of sulfides in water or binary aqueous solvents.

#### 5. References

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