Supporting Information

Porphyrin-based covalent organic polymers connected by imine-bonds: An efficient and recyclable heterogeneous photocatalyst for the oxidation of thioanisole

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Synthesis of 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (H_2THPP).

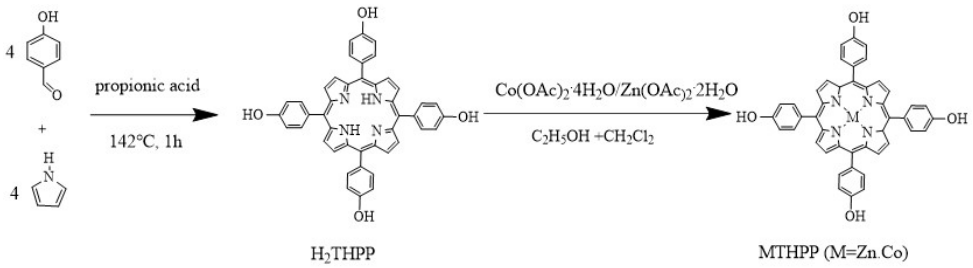
A mixture of 4-hydroxybenzaldehyde (3.0 g, 0.025 mmol) was placed in propionic acid (80 mL), then freshly distilled pyrrole (1.65 mL, 0.025 mol) in 10mL of propionic acid was dropwise added to the mixture with stirring. After the mixture was continuously stirred for 1 h under reflux, the mixture was allowed to distill out of propionic acid. Added 50 ml of dichloromethane, cooled overnight and a purple crude product are collected by filtration. The crude product was purified by SiO_2 column chromatography (CH_2Cl_2 / EtOH =10:1) to give purple porphyrin H_2THPP. Yield: 20 %; MS, (m/z) calcd for $[M + H]^+$: 679.20; UV-vis (C_2H_5OH): λ_{max} / nm: 421 (Soret band), 514, 551, 692, 647 (Q band).

Synthesis of ZnTHPP.

H_2THPP (0.1356 g, 0.2 mmol), zinc acetate (1.317 g, 6mmol) were dissolved in a mixture of ethanol (20 ml) and dichloromethane (20 ml) and stirred for 48 h at room temperature. The aim of a 30-fold amount of zinc acetate to the porphyrin is to ensure full metallization of porphyrin under mild conditions. The crude product was purified by SiO_2 column chromatography (CH_2Cl_2 / EtOH =25:2) to give porphyrin ZnTHPP. Yield: 38 %; MS, (m/z) calcd for $[M + H]^+$: 743.2; UV-vis (C_2H_5OH): λ_{max} / nm: 428 (Soret band), 539, 587 (Q band).

Synthesis of CoTHPP.

H_2THPP (0.1356 g, 0.2 mmol), cobalt acetate (1.494 g, 6 mmol) were dissolved in a mixture of ethanol (20 ml) and dichloromethane (20 ml) and refluxed for 48 h by heating. The crude product was purified by SiO_2 column chromatography (CH_2Cl_2 / EtOH =25:2) to give porphyrin CoTHPP. Yield: 27 %; MS, (m/z) calcd for $[M + H]^+$: 736.3; UV-vis (CH_2Cl_2): λ_{max} / nm: 418 (Soret band), 533 (Q band).



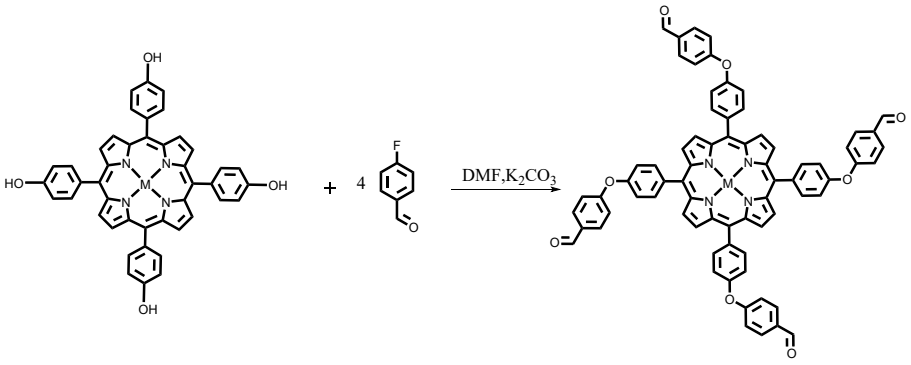
SCHEME S1 Synthesis of MTHPP

Synthesis of 5,10,15,20-[4-(4-Formyl) phenoxy] phenyl porphyrin (H_2Pp)

H2THPP (0.136 g, 0.2 mmol) and 4-fluorobenzaldehyde (1.46 g, 2 mmol) were dissolved in N,N dimethylformamide (150 ml) and heated with a constant stirring under a nitrogen atmosphere. After that, K2CO3 (0.691 g, 5 mmol) was added to the solution when the reaction reached reflux temperature. TLC was checked at the conclusion of the reaction. The crude product was purified by SiO_2 column chromatography (CH2Cl2/EtOH = 10:1) to give purple porphyrin H2Pp.

Synthesis of ZnPp and CoPp

ZnPp and CoPp was synthesized in the same route as the preparation of H2Pp, only changed ZnTHPP and CoTHPP as the start material.



MTHPP (M = H_2, Zn, Co) MPp (M = H_2, Zn, Co)

SCHEME S2 Synthesis of MPp

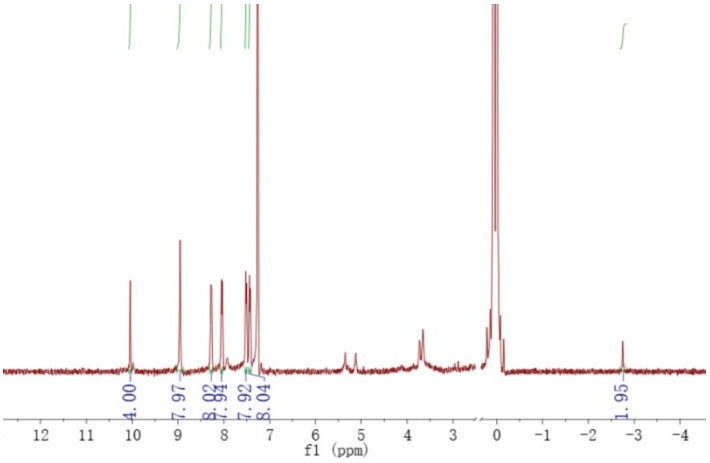


FIGURE S1 ^{1}H NMR spectra of H_2Pp taken at 400 MHz in $CDCl_3$

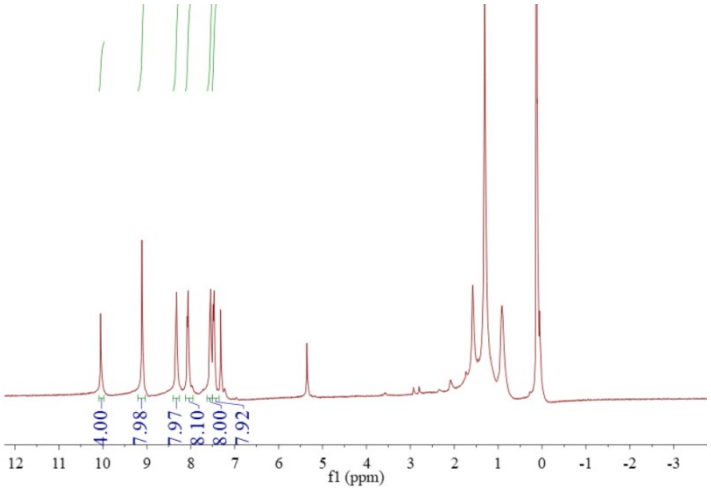


FIGURE S2 ^{1}H NMR spectra of ZnPp taken at 400 MHz in $CDCl_3$

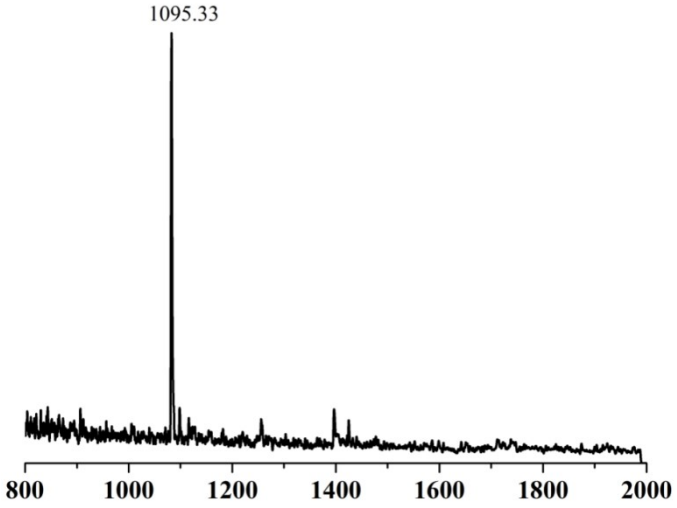


FIGURE S3 MS of H_2Pp

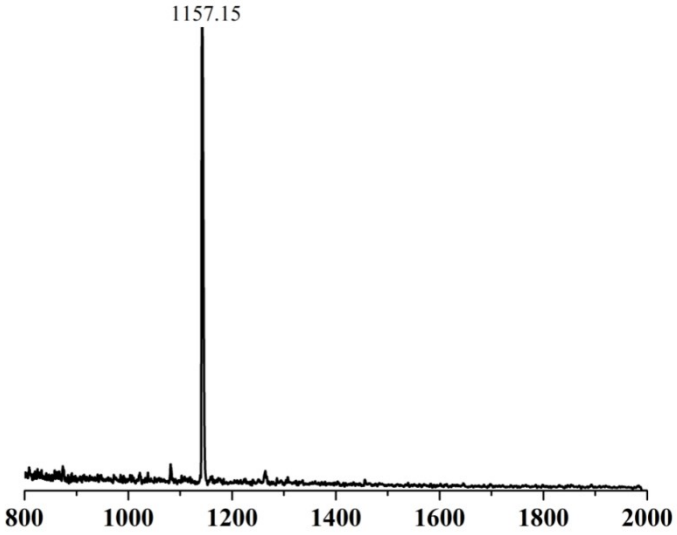


FIGURE S4 MS of ZnPp

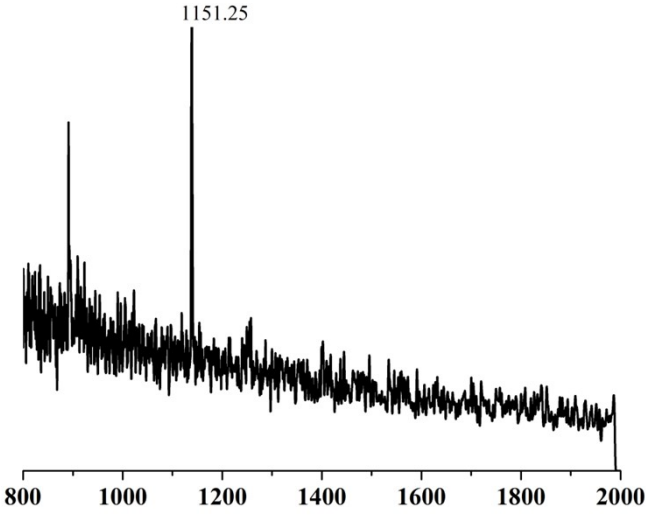


FIGURE S5 MS of CoPp

Table S1 UV-vis spectroscopy data of H_2Pp、ZnPp and CoPp

porphyrin	Soret band（nm）	Q band（nm）
H_2Pp	420	515，551，590，647
CoPp	412	529
ZnPp	422	549，587

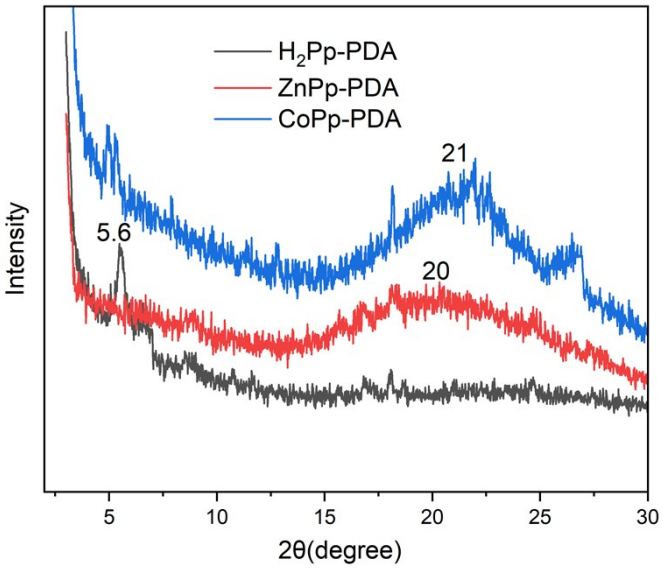


FIGURE S6 PXRD patterns of H_2Pp-PDA (black curve), ZnPp-PDA (red curve) and CoPp-PDA (blue curve)

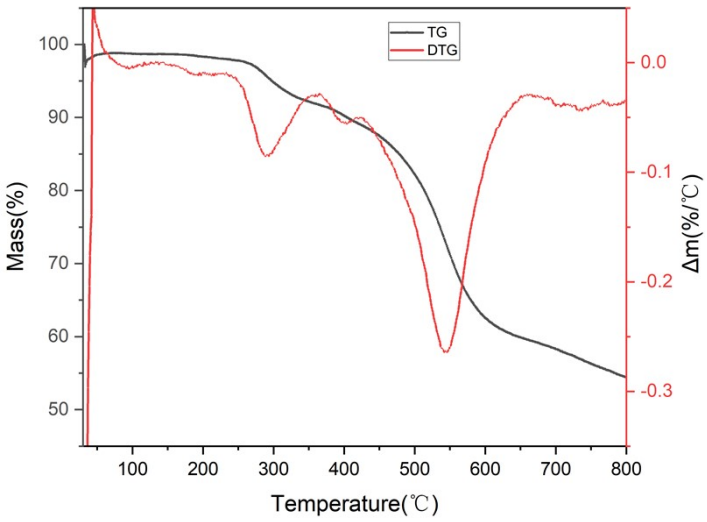


FIGURE S7 DTG curves of H_2Pp-PDA

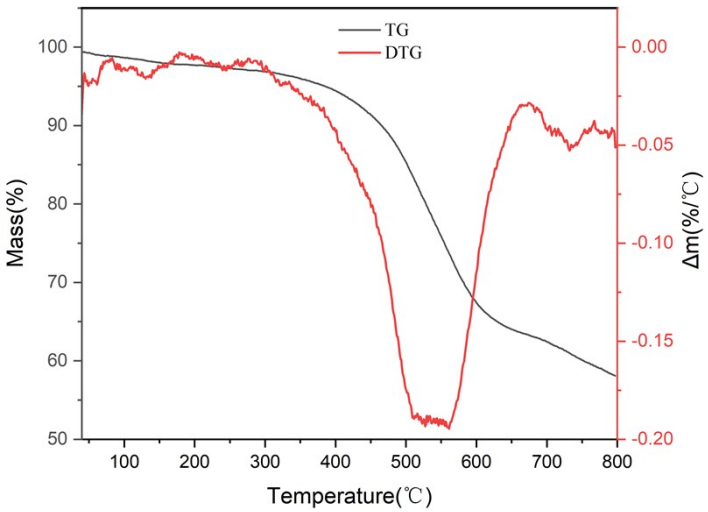


FIGURE S8 DTG curves of ZnPp-PDA

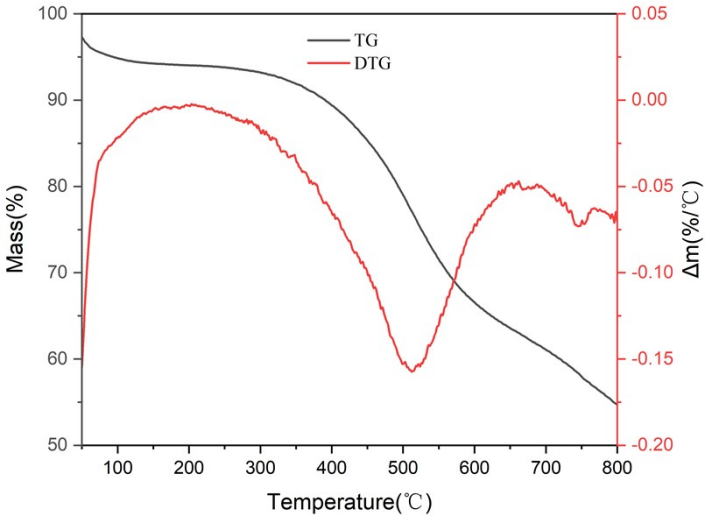


FIGURE S9 DTG curves of CoPp-PDA