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Electronic Supplementary Information

Two-dimensional porous porphyrin materials composed of robust tin(IV)-porphyrin linkages for photocatalytic wastewater remediation

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1.1 Synthesis of 5,10,15,20-tetraphenylporphyrin (H_2TPP)

Freshly distilled pyrrole (2.7 g, 2.8 mL, 40 mmol) and benzaldehyde (4.3 g, 4.1 mL, 40 mmol) were dissolved in propionic acid (400 mL) and refluxed for 2 h. After that, the reaction mixture was kept overnight at 10 °C. The crude product was then filtered and washed with MeOH, followed by water. The resulting purple solid was then dried under reduced pressure. Yield: 1.48 g (24%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.83 (s, 8H, *β*-pyrrole), 8.20 (d, *J* = 7.6 Hz, 8H, *meso-O*-phenyl), 7.70-7.78 (m, 12H, H3, H4, H5-phenyl), –2.81 (s, 2H, NH).

1.2 Synthesis of trans-dichloro[5,10,15,20-tetraphenylporphyrinato]tin(IV) ($SnCl_2$TPP)

H_2TPP (470 mg, 0.77 mmol) and $SnCl_2{\cdot}2H_2O$ (390 mg, 1.72 mmol) were mixed with pyridine (100 mL) and refluxed for 12 h. After that, pyridine was removed under reduced pressure. The solid product was dissolved in dichloromethane (100 mL) and filtered through a Celite pad. After that, *n*-hexane (100 mL) was added to the above solution with constant stirring. The resulting solid was then filtered, dried in an oven, and then recrystallized from 100 mL of CH_2Cl_2/*n*-hexane (1:1). Yield: 0.52 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.19 (s, 8H, *β*-pyrrole), 8.32 (d, *J* = 7.6 Hz, 8H, *meso-O*-phenyl), 7.82-7.88 (m, 12H, H3, H4, H5-phenyl).

1.3 Synthesis of trans-dihydroxo[5,10,15,20-tetraphenylporphyrinato]tin(IV) (SnP)

$SnCl_2$TPP (0.5 g, 0.62 mmol) dissolved in THF (40 mL) was mixed into a solution of K_2CO_3 (0.415 g, 3.0 mmol) in H_2O (10 mL) and refluxed with constant stirring. After 6 h, the THF was removed under reduced pressure. The resulting purple precipitate was filtered and washed with excess hot water, then dried in air. The crude solid was recrystallized from 100 mL of CH_2Cl_2/*n*-hexane (1:1). Yield: 0.38 g (80%). mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 9.11 (s, 8H, *β*-pyrrole), 8.33 (d, *J* = 7.6 Hz, 8H, *meso-O*-phenyl), 7.78-7.84 (m, 12H, H3, H4, H5-phenyl), –7.48 (s. 2H, Sn-OH). UV–visible ($CHCl_3$): λ_{nm} (log *ε*), 424 (5.57), 518 (3.12), 558 (4.32), 598 (3.96). Emission ($CHCl_3$, λ_{ex} = 550 nm): 623 nm and 675 nm.

2. **Synthesis of [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin] (H_2TCPP)**

Pyrrole (2.68 g, 2.8 mL, 40 mmol) and 4-formylbenzoic acid (6.0 g, 40 mmol) were mixed in propionic acid (400 mL) and refluxed. After 2 h, the reaction mixture was cooled to 10 °C and maintained at that temperature overnight. The solid residues were then filtered, washed with cold MeOH, and then dried in air. After that, the crude product was dissolved in 0.1 N NaOH, and the insoluble impurities were removed by filtration; the remaining filtrate was then neutralized with 0.1 N HCl. Finally, the purple precipitate was filtered and dried. Yield: 2.05 g (26%). Melting point > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 13.22 (s, 4H, CO_2H), 8.86 (s, 8H, *β*-pyrrole), 8.22 (d, *J* = 7.6 Hz, 8H, *meso*-*O*-phenyl), 7.85 (d, *J* = 7.6 Hz, 8H, H3, 5-phenyl), −2.94 (s, 2H, NH). UV–visible (THF): λ_{nm} (log *ε*), 418 (5.62), 513 (4.24), 548 (3.89), 591 (3.69), and 646 (3.57). Photoluminescence (THF, λ_{ex} = 550 nm): 672 nm and 733 nm.

3. Synthesis of [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]zinc(II) (ZnTCPP)

A mixture of H_2TCPP (1.0 g, 1.26 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (1.1 g, 5.04 mmol) were added into DMF (140 mL) and heated at 100 °C. After 2 h, the solution was cooled to 10 °C and maintained at that temperature overnight. The solid residue was filtered and washed with DMF, followed by deionized water. The crude product was then dissolved in 0.1 N NaOH solution, and the insoluble solid impurities were removed by filtration. The product was then re-precipitated by neutralizing the filtrate with 0.1 N HCl. Finally, the purple precipitate was filtered and dried. Yield 0.97 g (90%); melting point > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 12.86 (s, 4H, -CO_2H), 8.79 (s, 4H, *β*-pyrrole), 8.36 (d, *J* = 8.8 Hz, 8H, *meso*-*O*-phenyl), 8.30 (d, *J* = 7.2 Hz, 8H, H3, 5-phenyl). UV–visible (H_2O): λ_{nm} (log *ε*), 426 (5.41), 562 (3.88), and 601 (3.52). Photoluminescence (H_2O, λ_{ex} = 550 nm): 629 nm, and 677 nm.

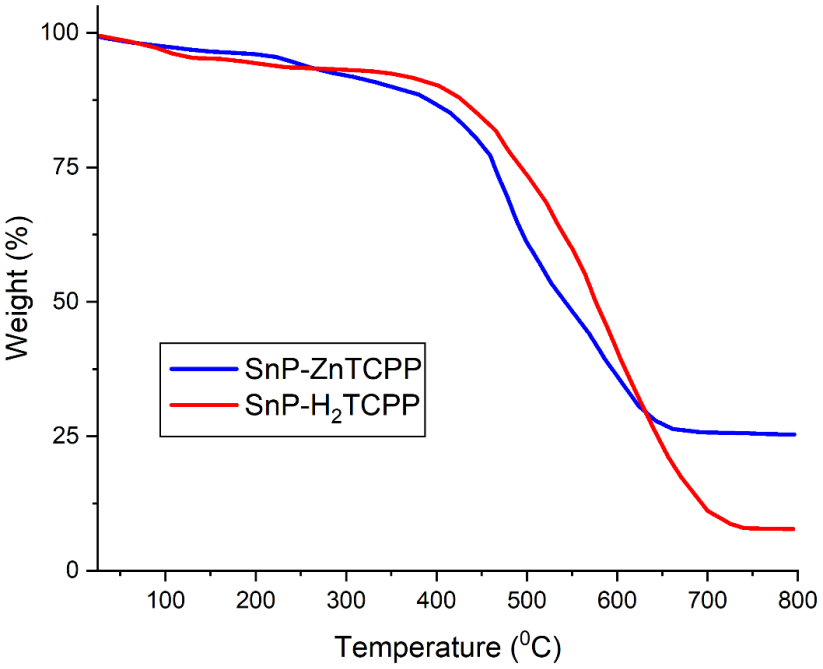


Fig. S1 TGA thermogram of **SnP-H$_2$TCPP** and **SnP-ZnTCPP**.

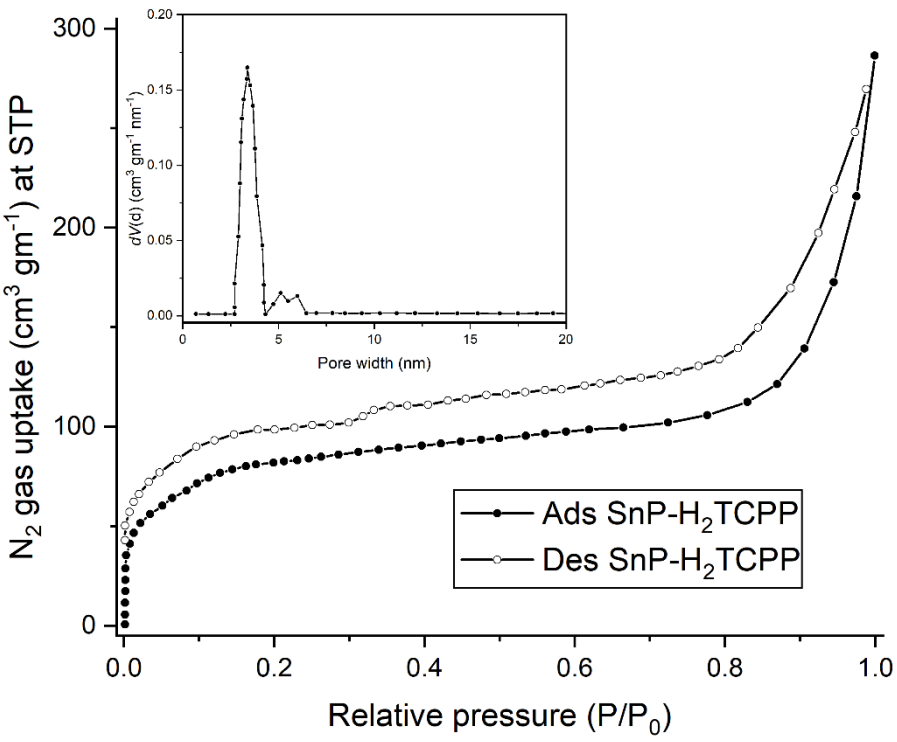


Fig. S2 Adsorption and desorption isotherms of N_2 for **SnP-H$_2$TCPP**.

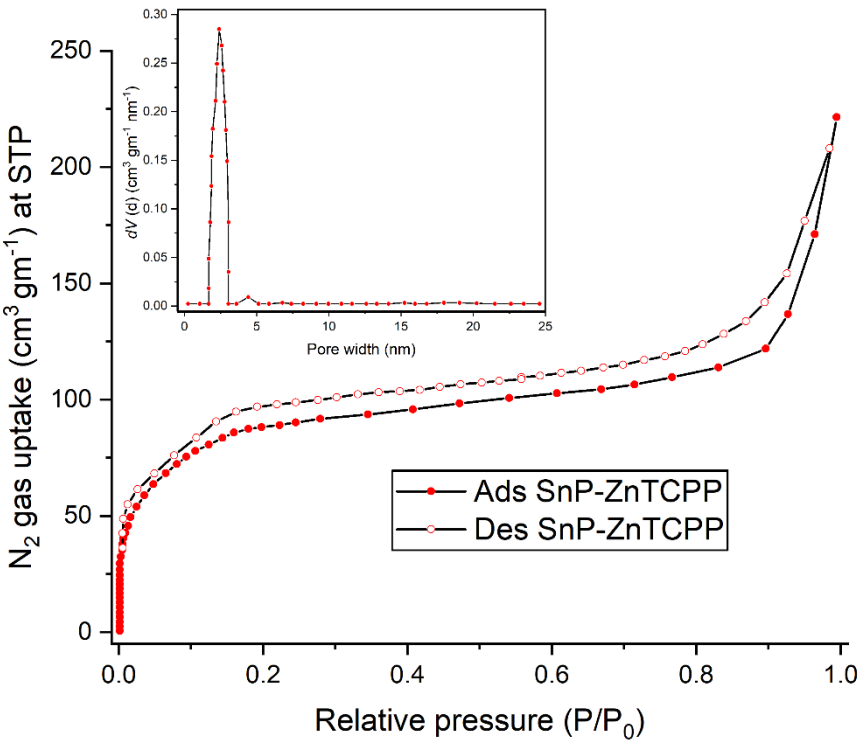


Fig. S3 Adsorption and desorption isotherms of N_2 for **SnP-ZnTCPP** at 77 K.

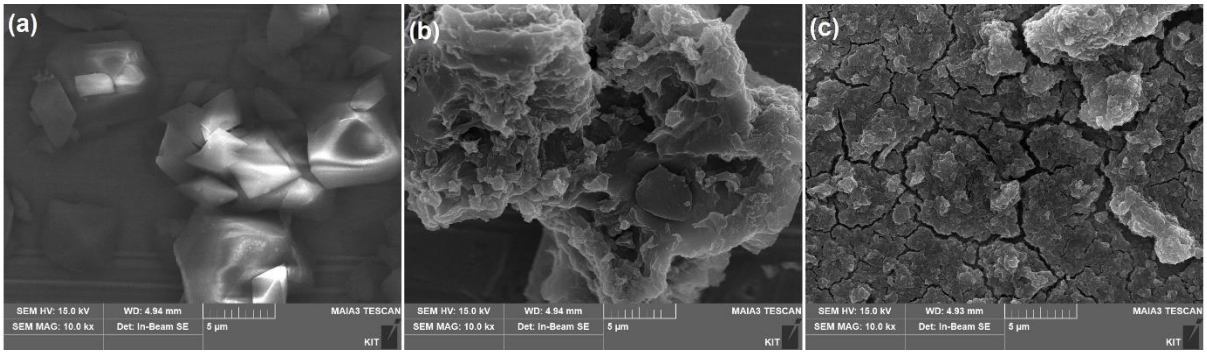
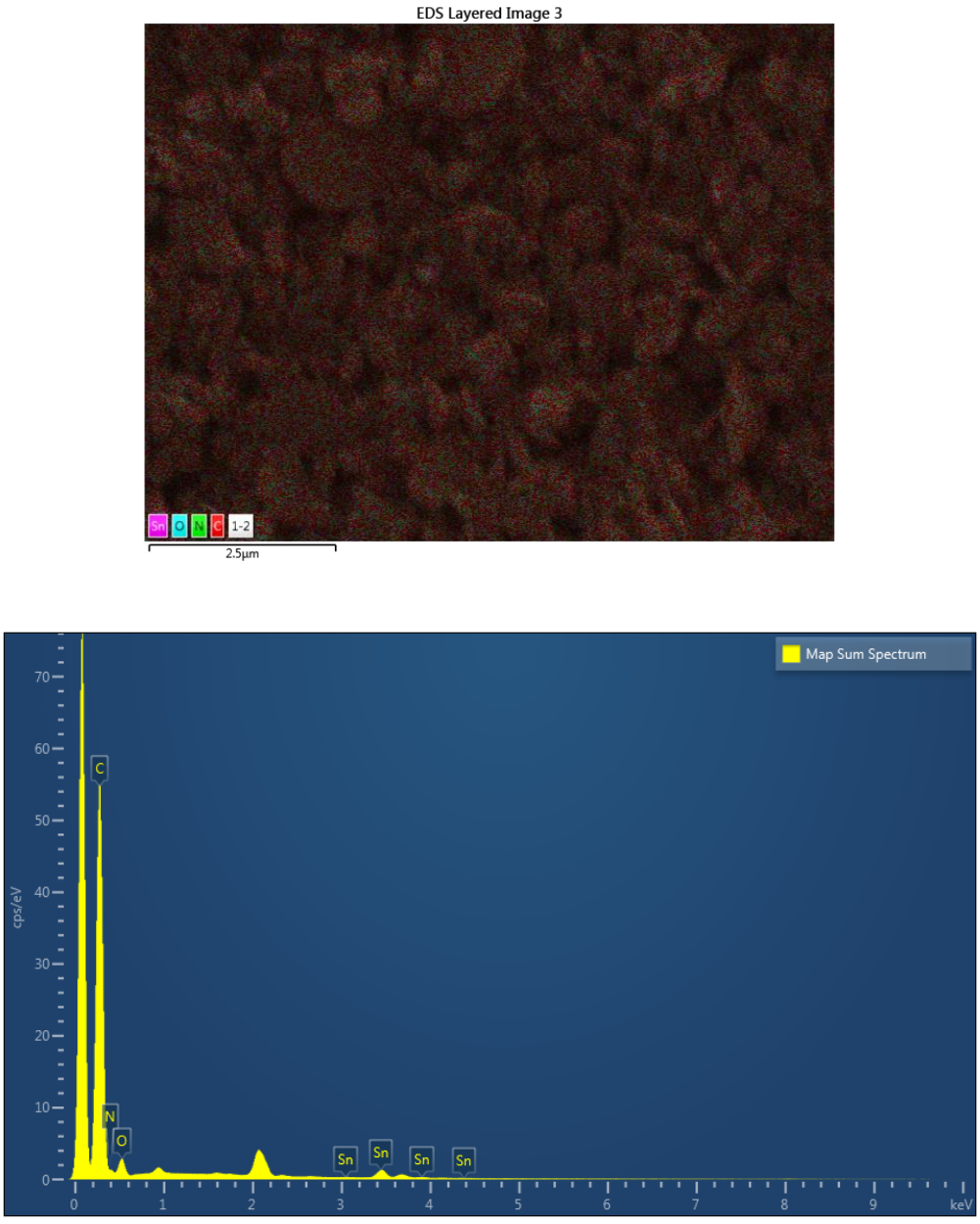
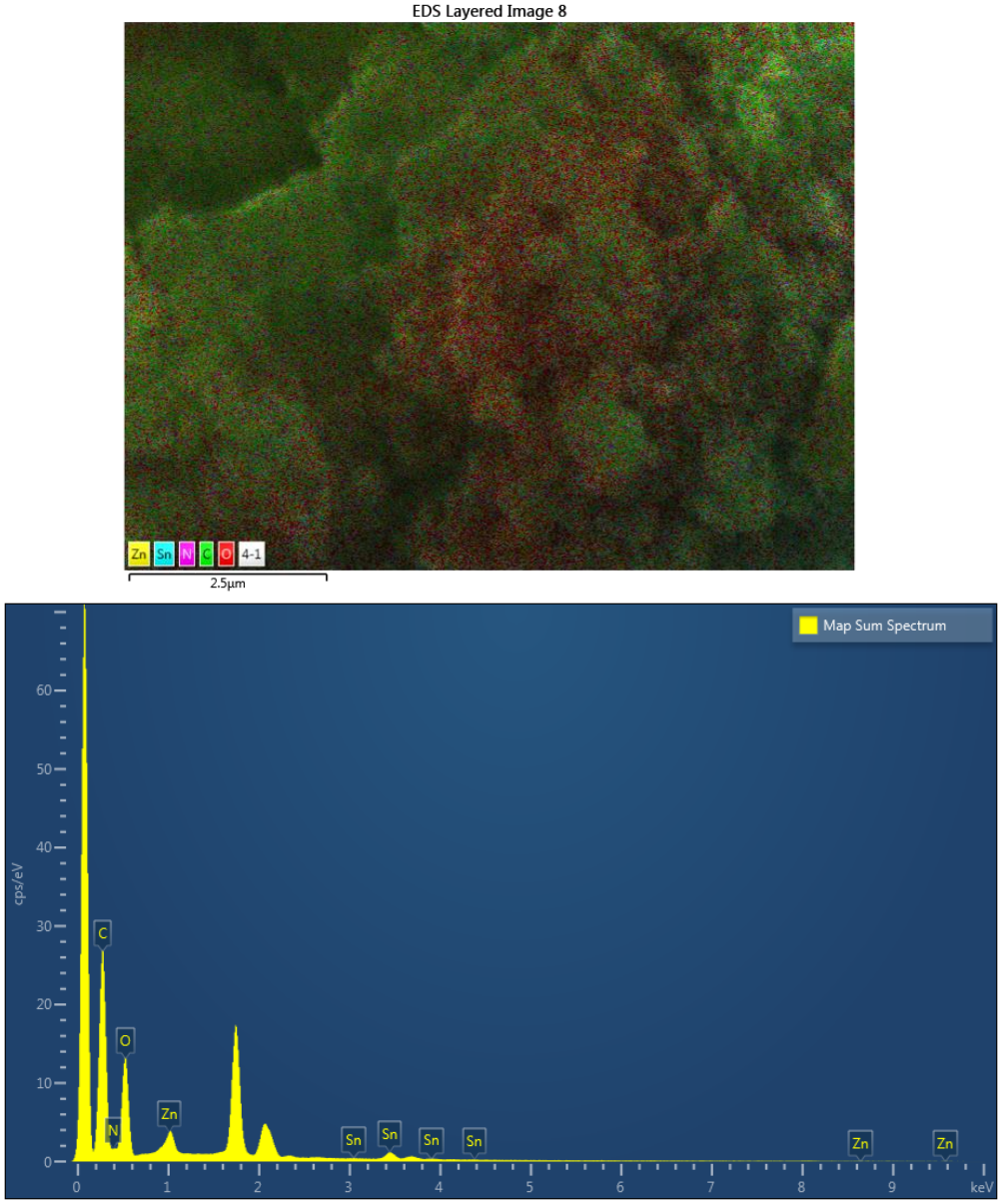


Fig. S4 FE-SEM images of (a) SnP, (b) H_2TCPP, and (c) ZnTCPP.



Element	Wt%	Atomic %
C	73.11	84.44
N	7.74	7.66
O	7.55	6.54
Sn	11.60	1.36
Total:	100.00	100.00

Fig. S5 Energy dispersive X-ray spectroscopy (EDS) for **SnP-H_2TCPP**.



Element	Wt%	Atomic %
C	71.23	83.80
N	7.42	7.48
O	7.72	6.81
Zn	2.97	0.64
Sn	10.66	1.27
Total:	100.00	100.00

Fig. S6 Energy dispersive X-ray spectroscopy (EDS) for **SnP-ZnTCPP**.

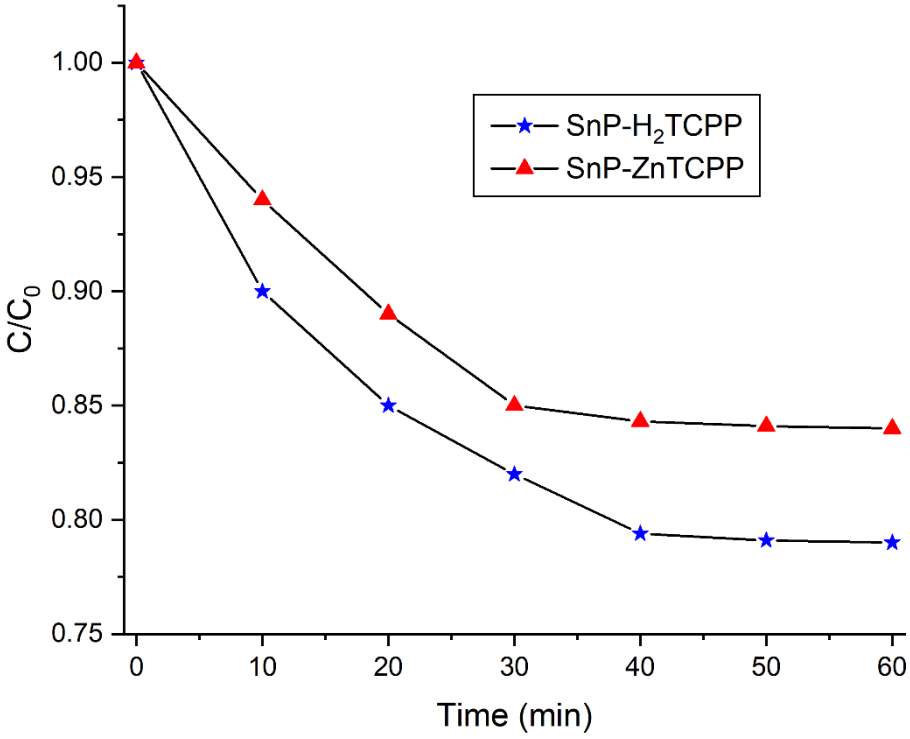


Fig. S7 MB dye adsorption tests for **SnP-H_2TCPP** and **SnP-ZnTCPP**.

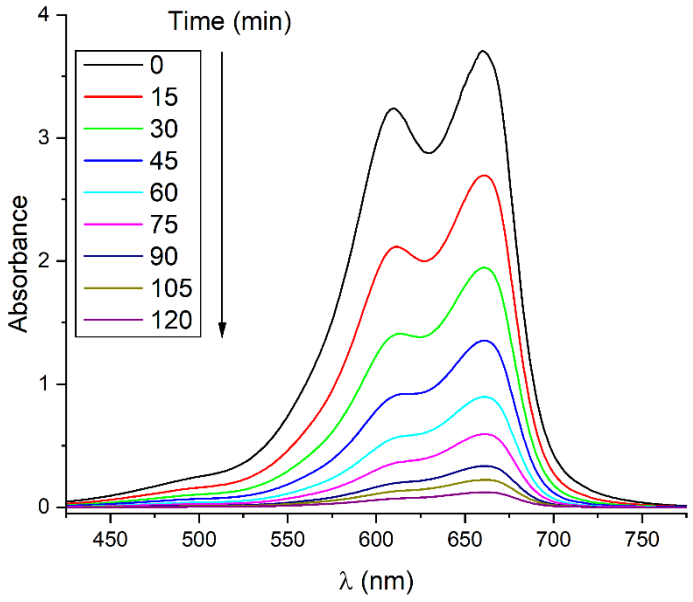


Fig. S8 Time dependent absorption spectra of MB dye in the presence of **SnP-ZnTCPP** under visible light irradiation.

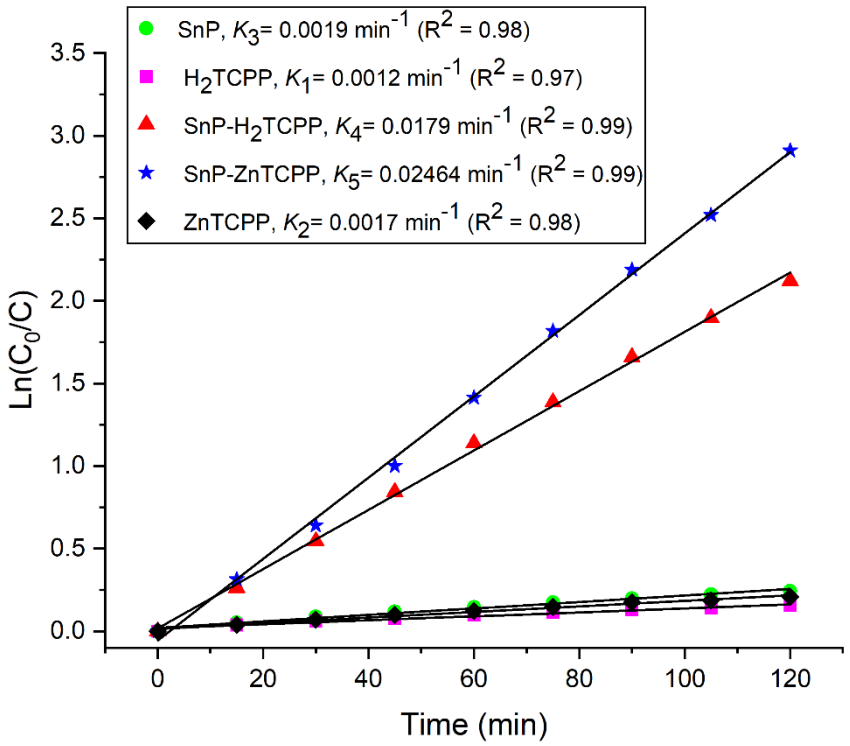


Fig. S9 Kinetics of the photocatalytic degradation of MB under visible light irradiation.

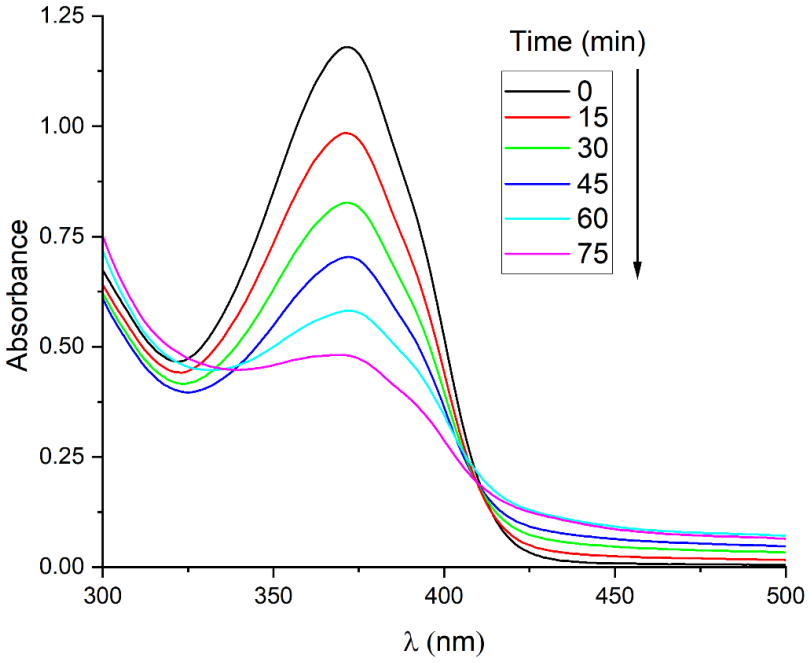


Fig. S10 Absorption spectra of TC in the presence of **SnP-ZnTCPP** under visible light irradiation.

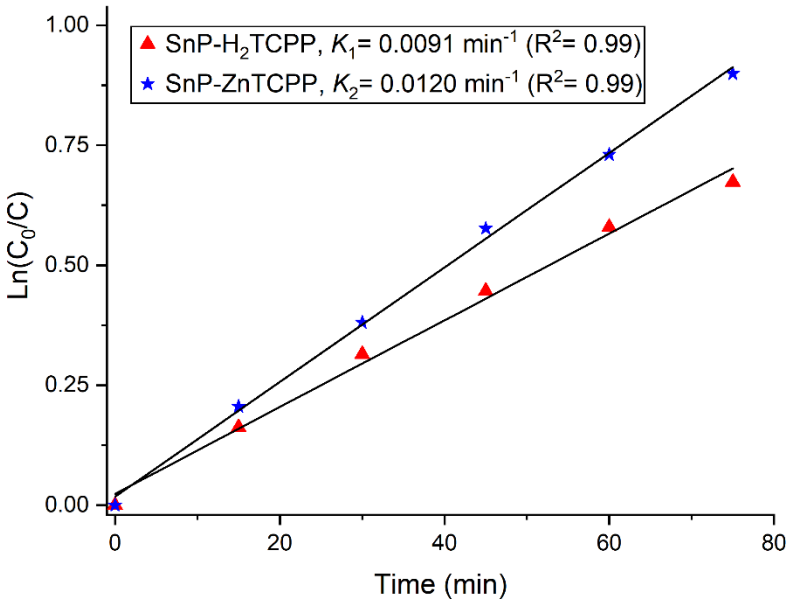


Fig. S11 Kinetics of the photocatalytic degradation of TC under visible light irradiation.

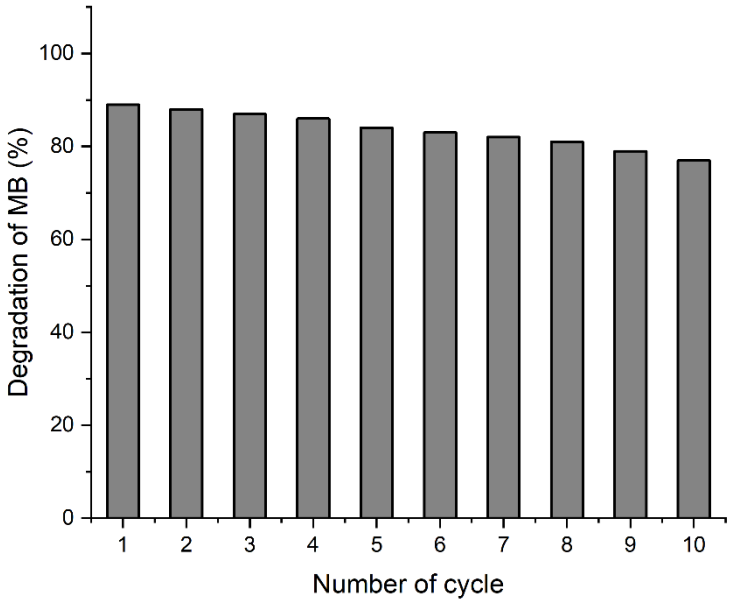


Fig. S12 Recyclability of the photocatalyst **SnP-H₂TCPP** towards the degradation of MB dye.

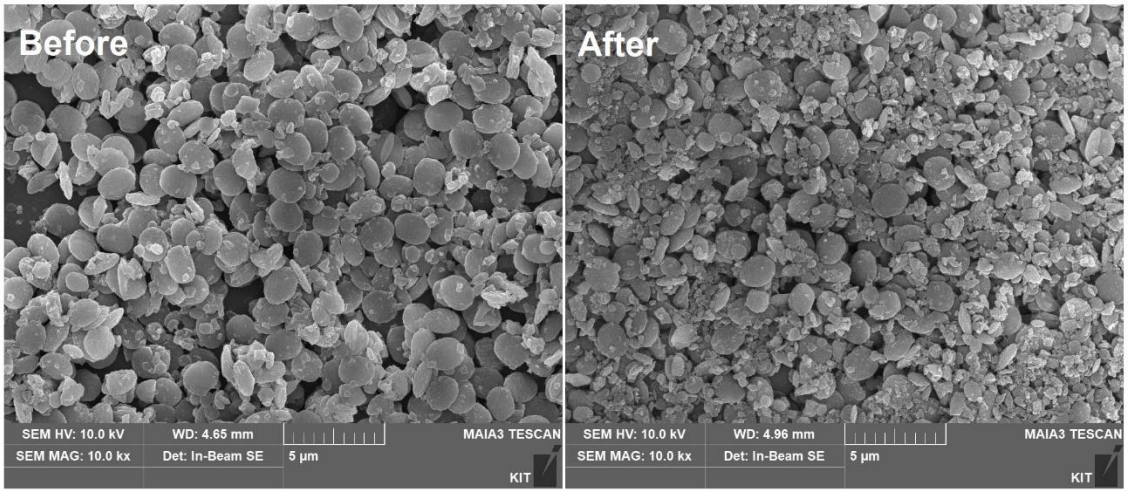


Fig. S13 FE-SEM images of **SnP-H_2TCPP** (before and after the degradation of MB).

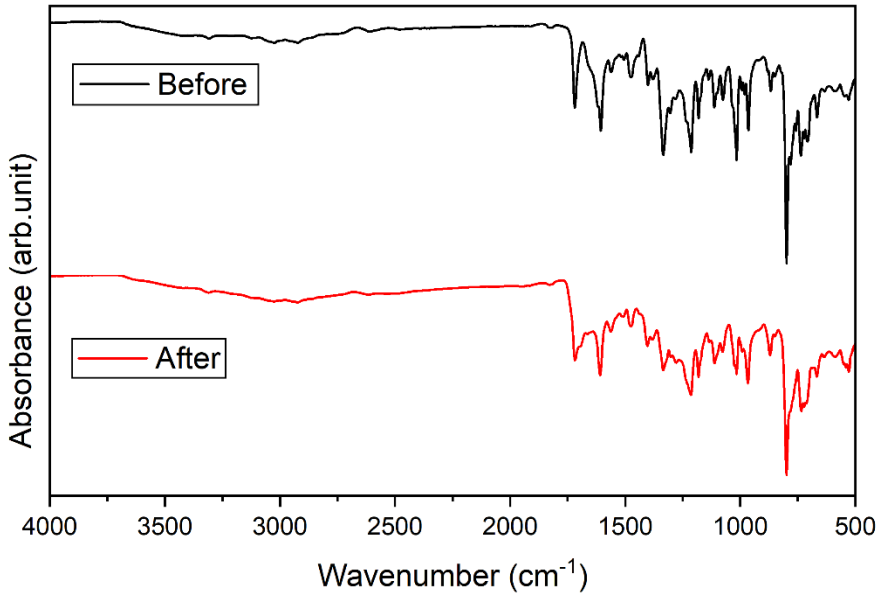


Fig. S14 FT-IR spectra of **SnP-H_2TCPP** (before and after the degradation of MB).

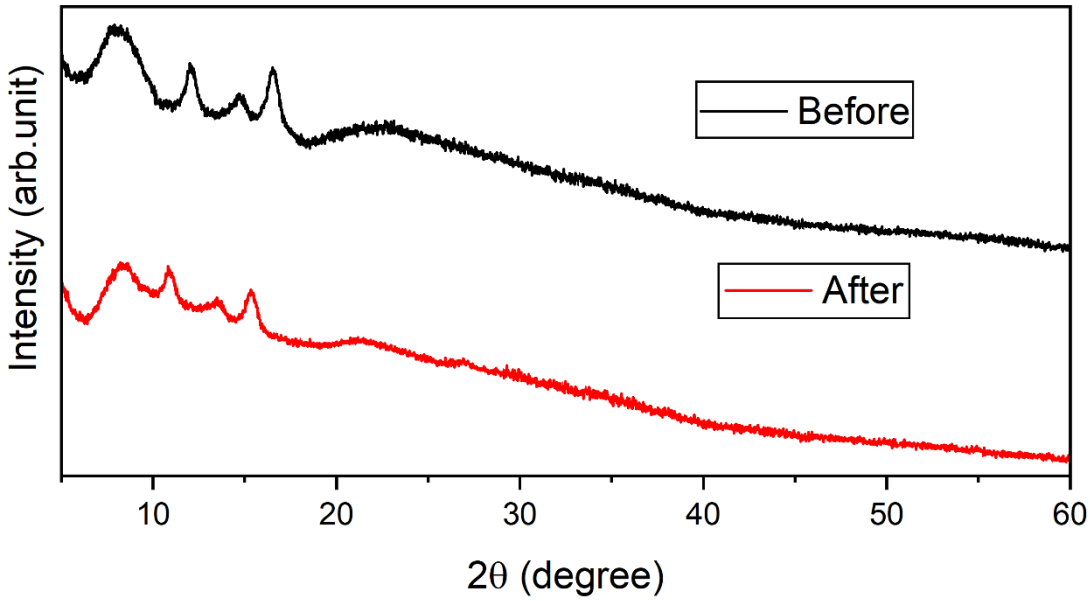


Fig. S15 PXRD patterns of **SnP-H_2TCPP** (before and after the degradation of MB).

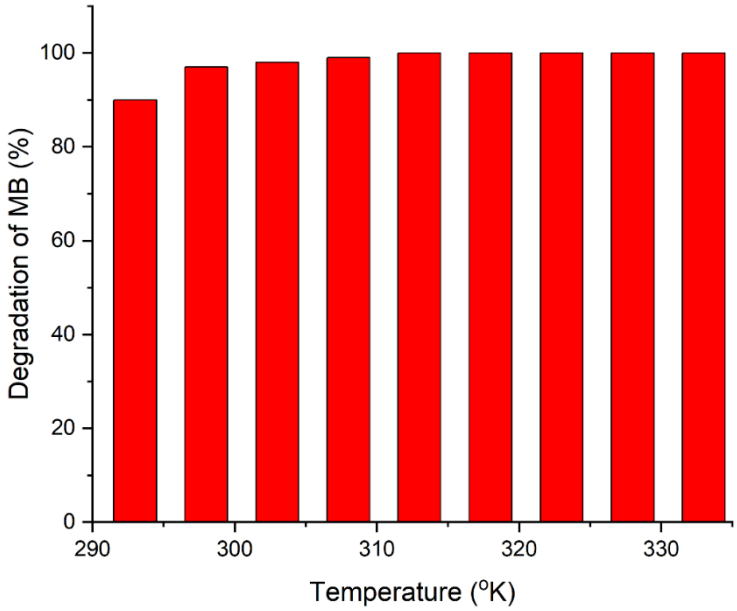


Fig. S16 Effect of temperature on the photocatalytic degradation of MB dye in the presence of **SnP-ZnTCPP**.

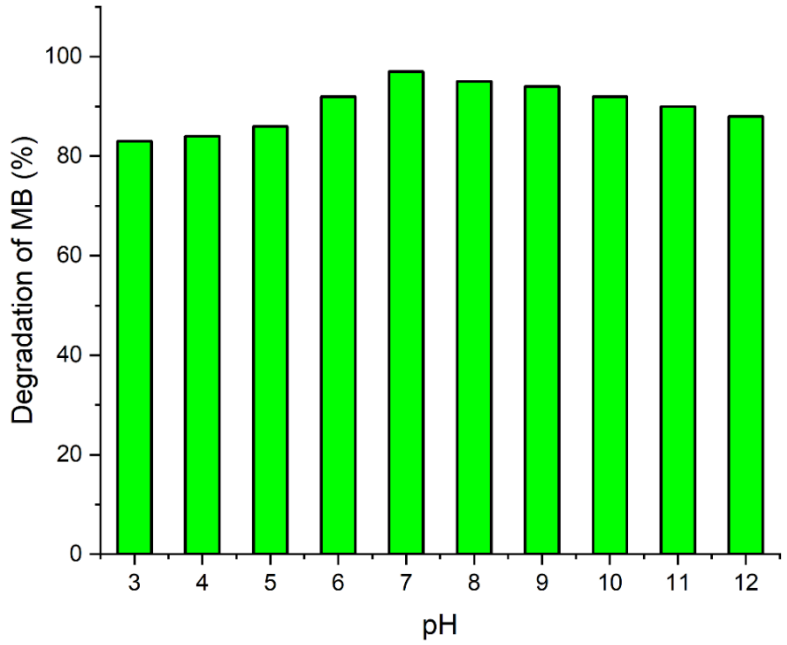


Fig. S17 Effect of pH on the degradation of MB dye solution in the presence of **SnP-ZnTCPP**.

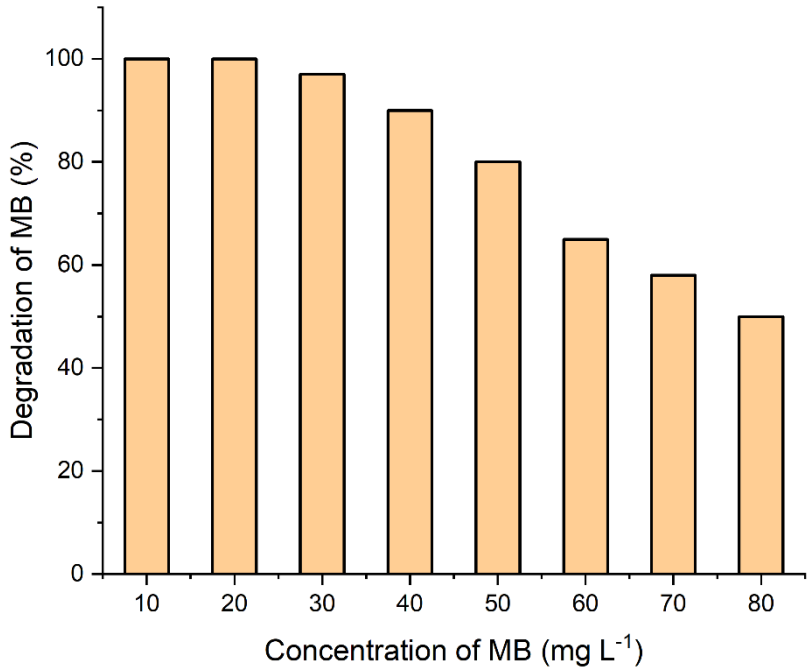


Fig. S18 Effect of dye concentration on the photocatalytic degradation of MB dye in the presence of **SnP-ZnTCPP**.

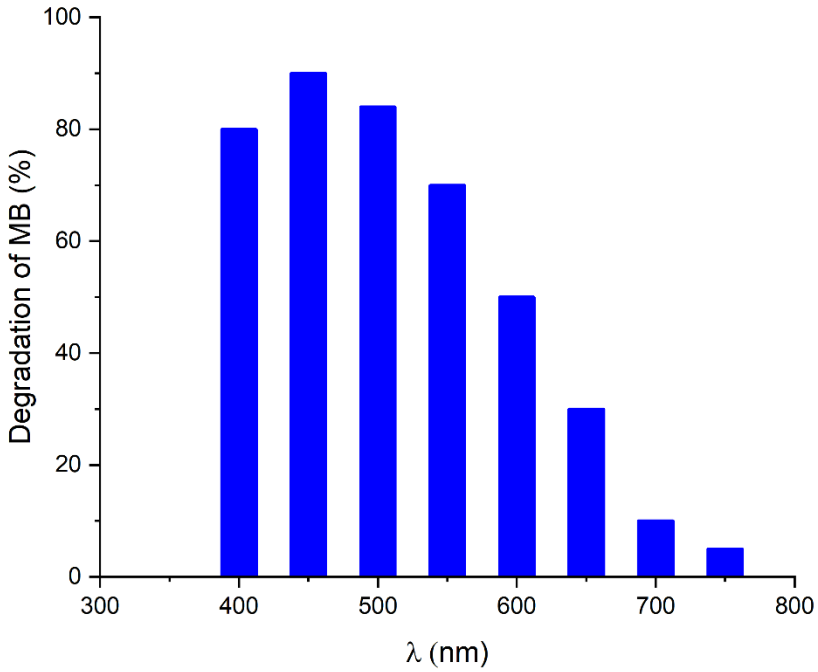


Fig. S19 Effect of wavelength on the photocatalytic degradation of MB dye in the presence of **SnP-H_2TCPP**.

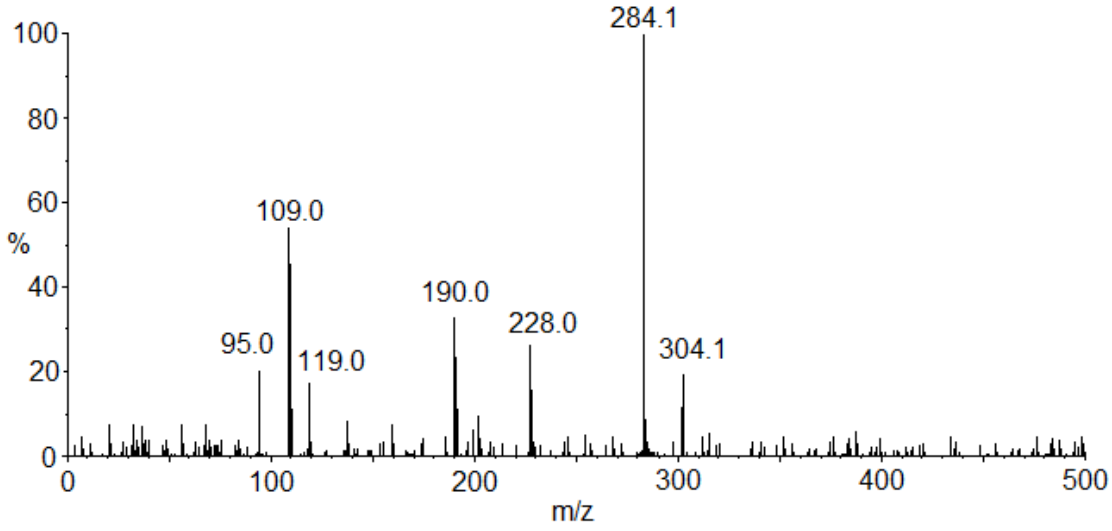


Fig. S20 Positive ion mode ESI-MS spectrum for the MB dye degradation reaction by **SnP-H_2TCPP** after 60 min of visible light irradiation.

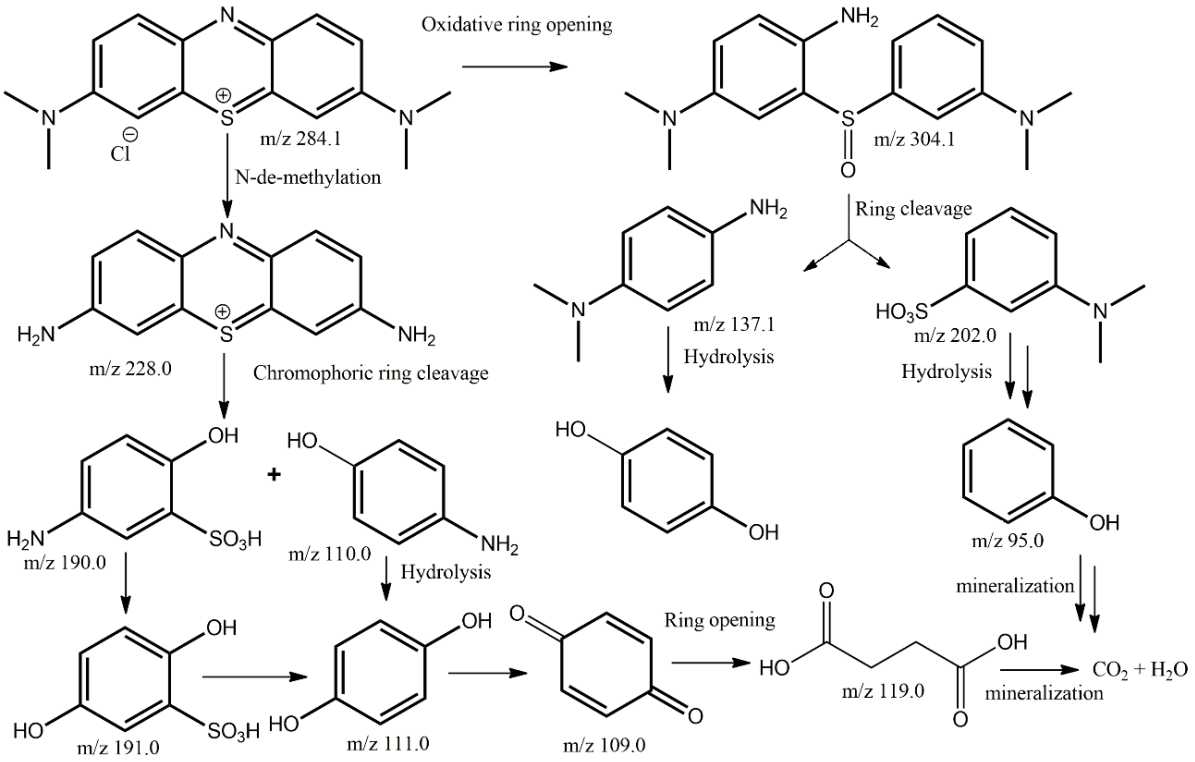


Fig. S21 Possible intermediates formed during MB dye degradation in the presence of **SnP-H_2TCPP** after 60 min of visible light irradiation.

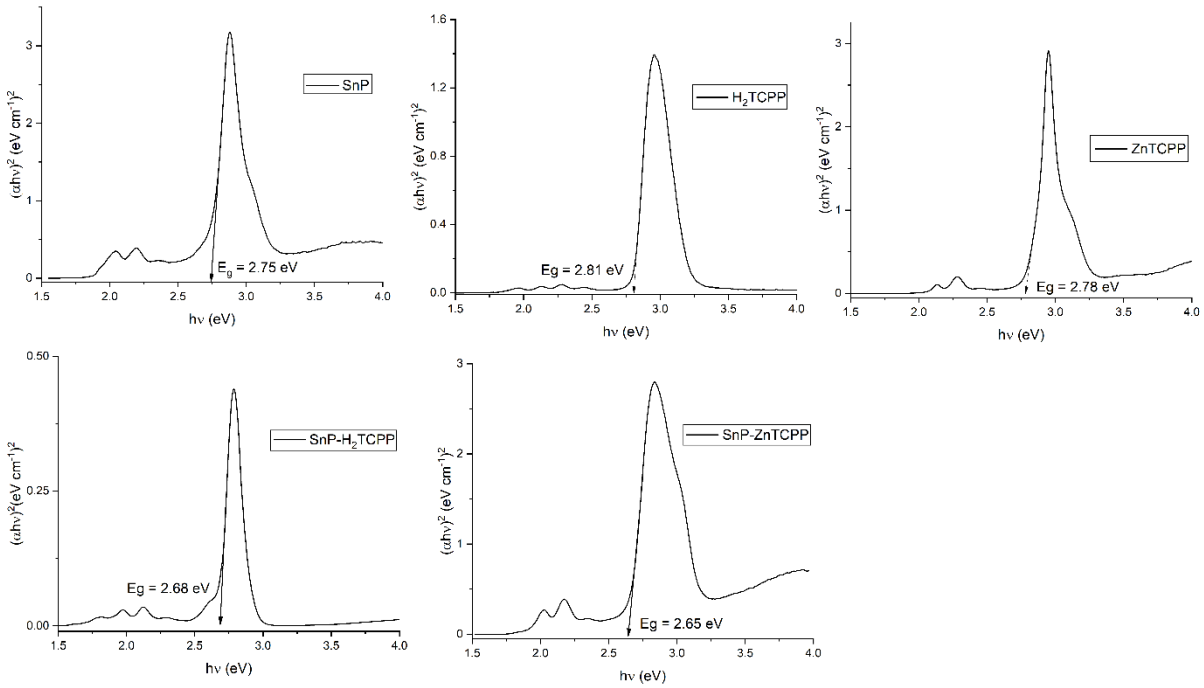


Fig. S22 Band gap energy of SnP, H_2TCPP, ZnTCPP, **SnP-H_2TCPP**, and **SnP-ZnTCPP**, calculated from Tauc Plots using UV-vis absorption spectral data.

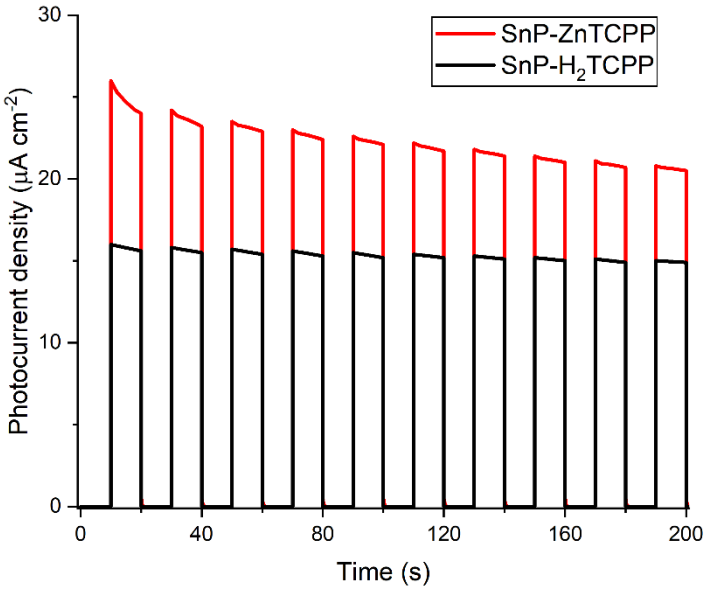


Fig. S23 Photocurrent responses for **SnP-H_2TCPP** and **SnP-ZnTCPP** under visible light.

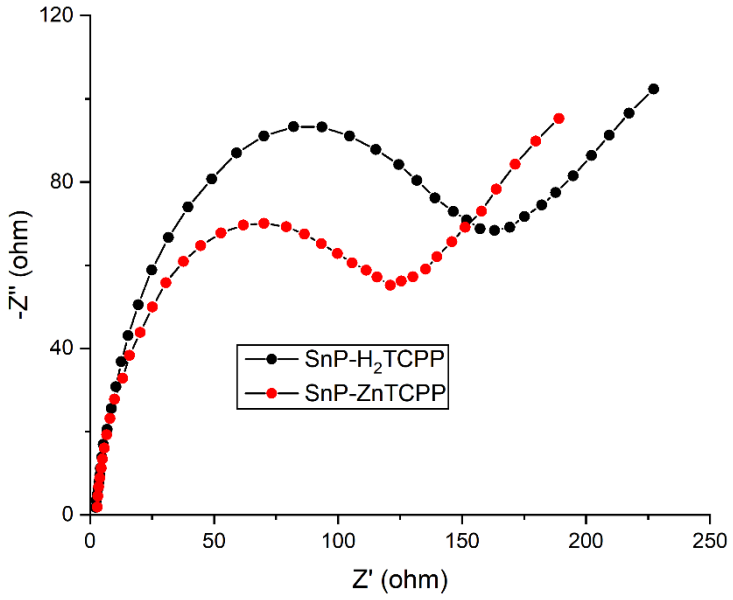


Fig. S24 EIS Nyquist plots for **SnP-H_2TCPP** and **SnP-ZnTCPP** under visible light.

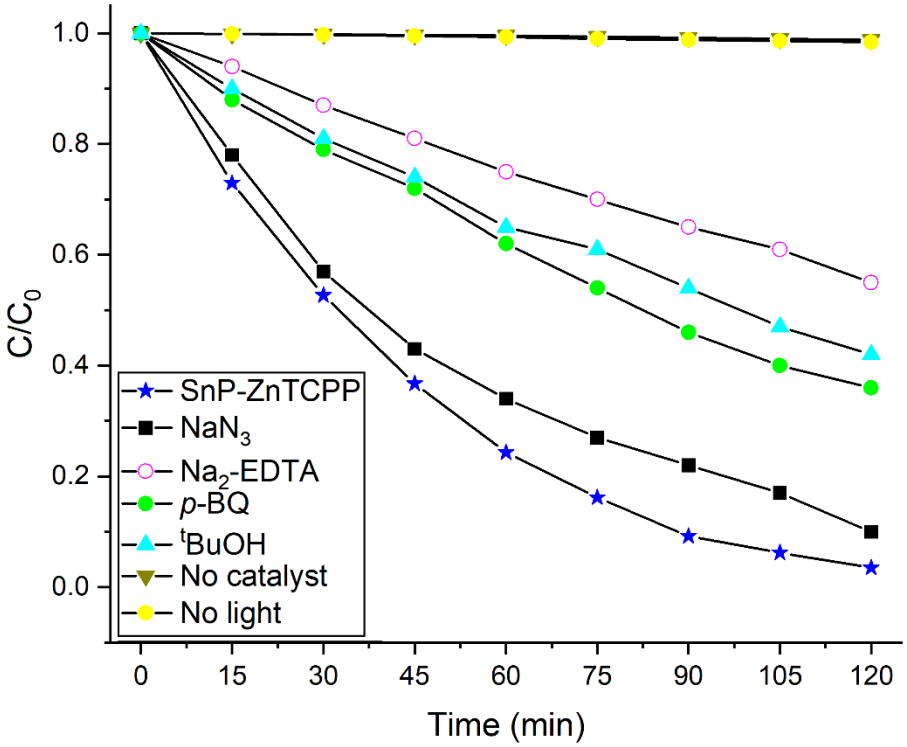


Fig. S25 Visible light MB dye degradation activity of **SnP-ZnTCPP** in the presence of various scavengers.