Synthesis of Star Poly(*N*-isopropylacrylamide) with Two Zinc-porphyrins as Core and End-groups Respectively *via* ATRP and "CLICK" Chemistry and Photocatalytic Performance Study

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EXPERIMENT

Synthesis of THPP P-hydroxybenzaldehyde (6.1 g, 50 mmol) was dissolved in propionic acid (200 mL) and DMSO (6 mL), heated to complete dissolution. And pyrrole (3.5 ml, 50 mmol) was added with stirring at 140 °C. Blue crystals was got by filtering and recrystallization. The product was purified by column chromatography. (Fig S1)

^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.97 (s, 4H, -O*H*), 8.87 (s, 8H, pyrrole-*H*), 8.00 (d, J = 8.3 Hz, 8H, Ar-*H*), 7.21 (d, J = 8.3 Hz, 8H, Ar-*H*), -2.89 (s, 2H, -N*H*-). (Fig S3)

Synthesis of TPP-OH P-hydroxybenzaldehyde (1.5 g, 12.5 mmol) and benzaldehyde (4 g, 37.5 mmol) was dissolved in propionic acid (200 mL), heated to complete dissolution. And pyrrole (3.5 ml, 50 mmol) was added with stirring at 140 °C. The product was purified by column chromatography. (Fig S1)

^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 8.85 (d, J = 13.6 Hz, 8H, pyrrole-*H*), 8.22 (d, J = 6.6 Hz, 6H, Ar-*H*), 8.06 (d, J = 8.3 Hz, 2H, Ar-*H*), 7.75 (m, 9H, Ar-*H*), 7.17 (d, J =

8.3 Hz, 2H, Ar-*H*), 5.11 (s, 1H, -O*H*), -2.78 (s, 2H, -N*H*-). (Fig S4)

Syntheses of ZnTHPP and ZnTPP-OH THPP (100mg, 0.15 mmol) and zinc acetate (90 mg 0.75 mmol) was dissolved in DMF. The mixture was stirred on 120 ℃ for 2 h. The product is poured into water and allowed to stand for filtration. The resulting solid is dried at 70-80 ° C. ZnTPP-OH is prepared in the same way. (Fig S1)

ZnTHPP: ^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.87 (s, 4H, -O*H*), 8.82 (s, 8H, pyrrole-*H*), 7.97 (d, J = 8.2 Hz, 8H, Ar-*H*), 7.18 (d, J = 8.2 Hz, 8H, Ar-*H*). (Fig S3)

ZnTPP-OH: ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 8.96 (d, J = 17.6 Hz, 8H, pyrrole-*H*), 8.22 (d, J = 6.6 Hz, 6H, Ar-*H*), 8.08 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.76 (m, 9H, Ar-*H*), 7.20 (d, J = 8.0 Hz, 2H, Ar-*H*), 5.19 (s, 1H, -O*H*). (Fig S4)

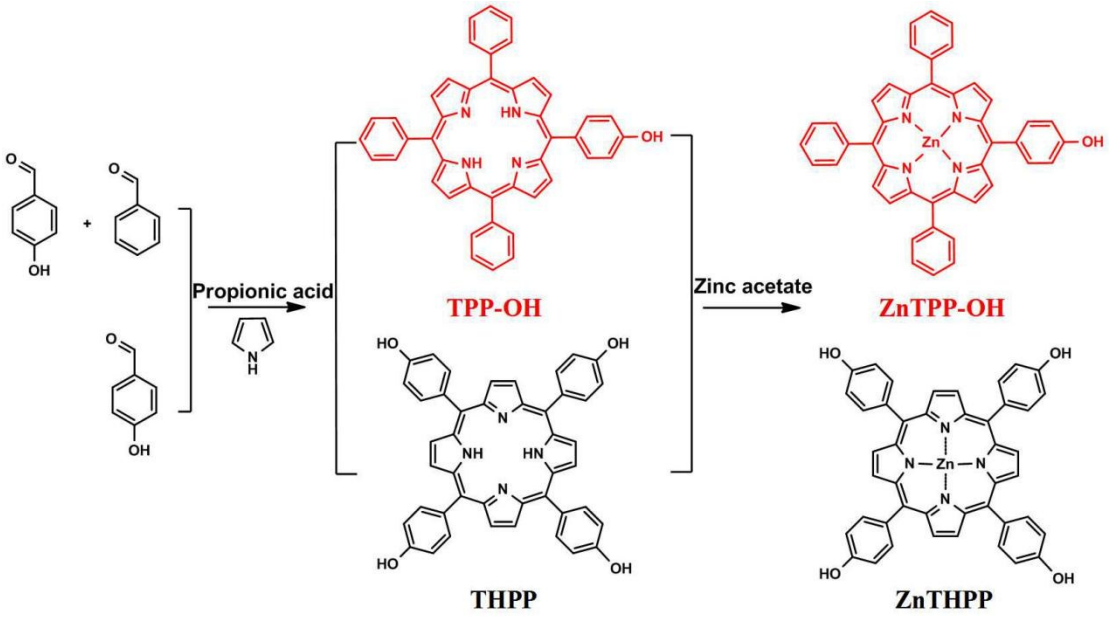

Fig. S1 Synthesis route of ZnTHPP and ZnTPP-OH.

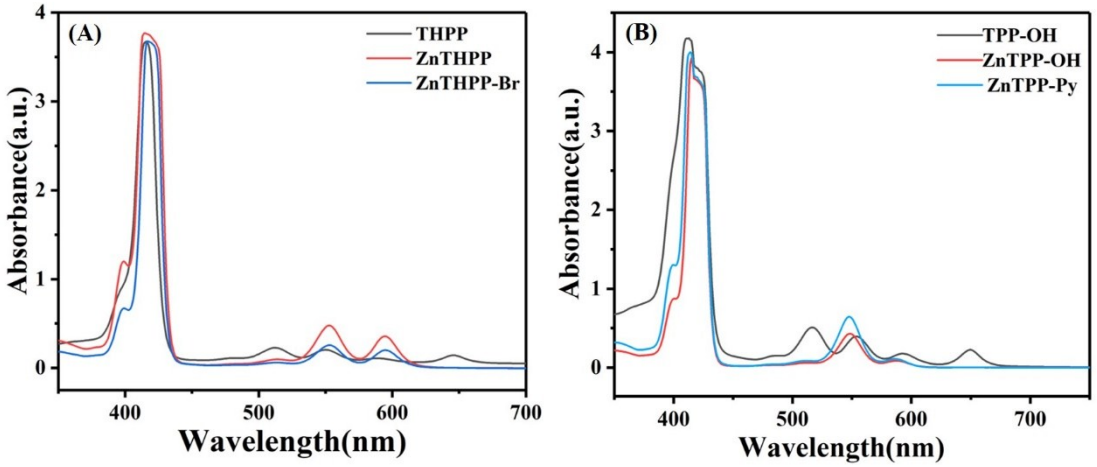

Fig. S2 [1] **(B):** UV-Vis spectra of THPP, ZnTHPP and ZnTHPP-Br. **(B):** UV-Vis spectra of TPP-OH, ZnTPP-OH, ZnTPP-Py.

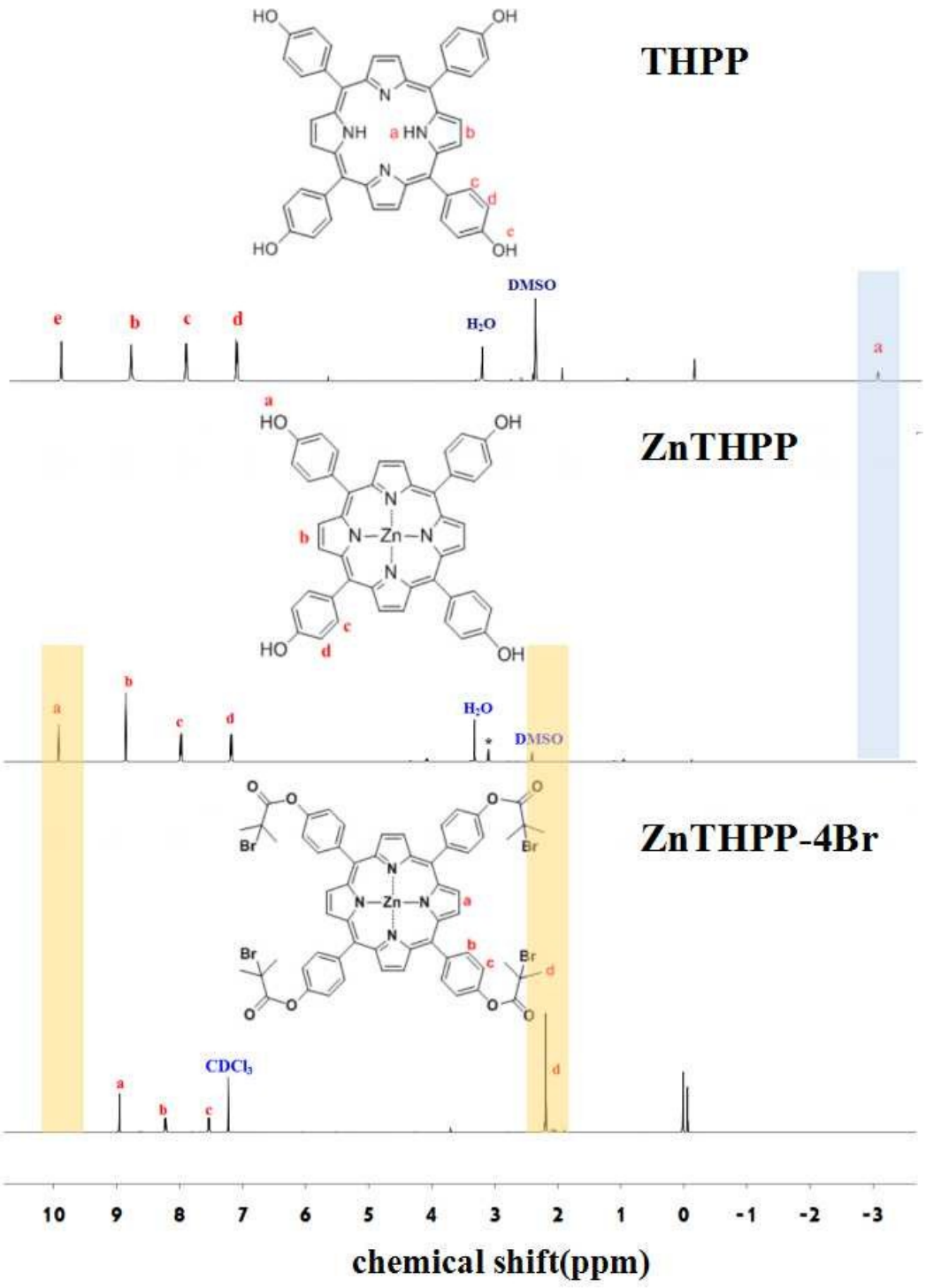

Fig. S3 ^{1}H NMR spectrum of THPP, ZnTHPP and ZnTHPP-Br.

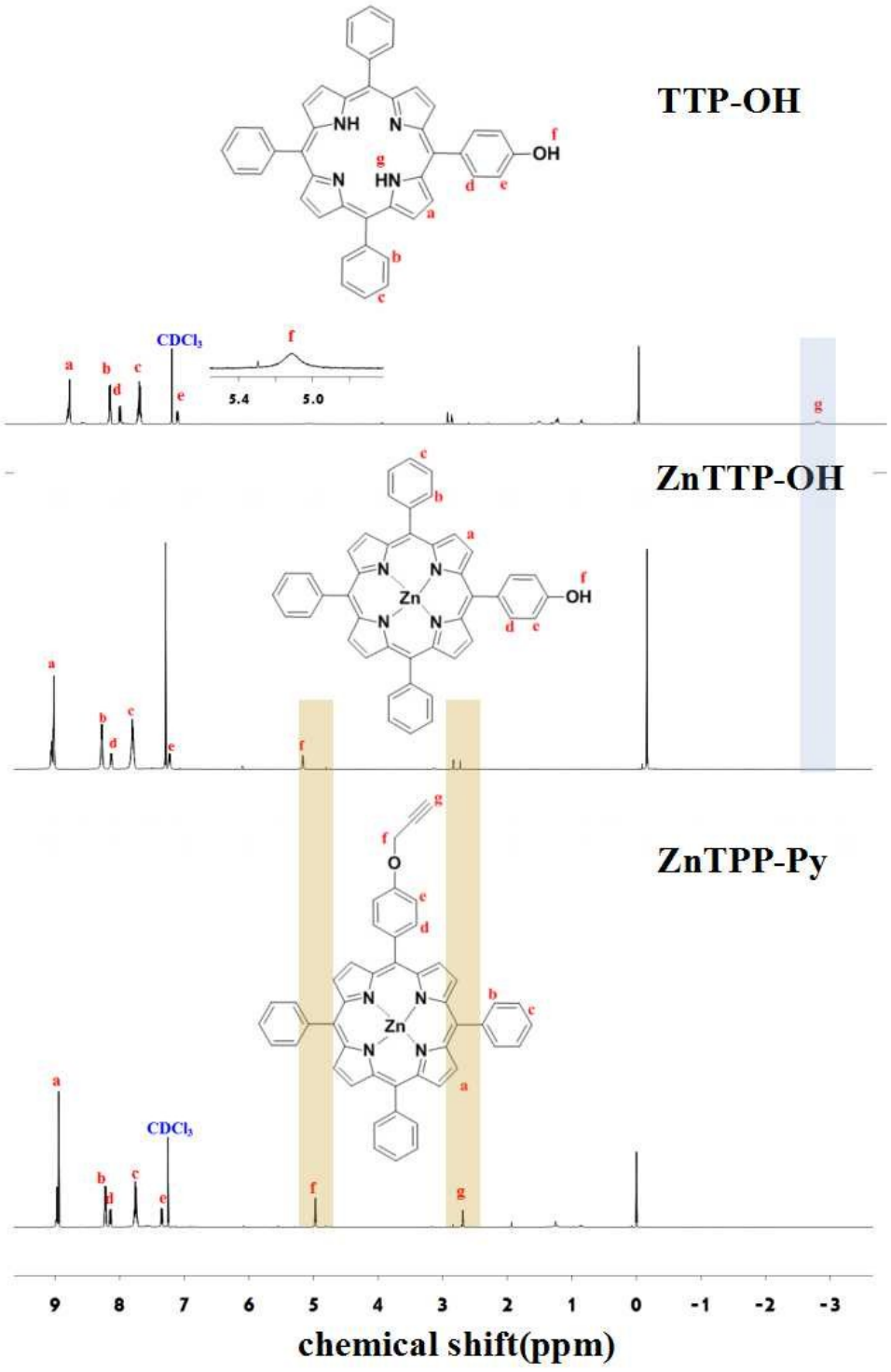

Fig. S4 ^{1}H NMR spectrum of TPP-OH, ZnTPP-OH and ZnTPP-Py.

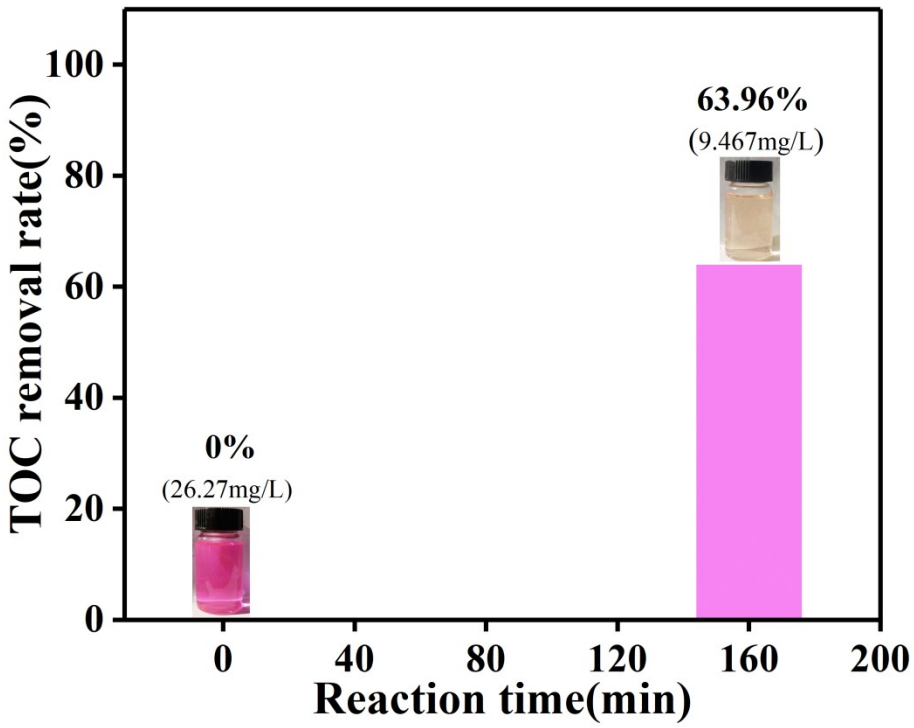

Fig. S5 Initial and final TOC changes during the course of RhB degradation in the presence of ZnTHPP-(PNIPAM-ZnTPP)$_4$ and H_2O_2 under visible light radiation.

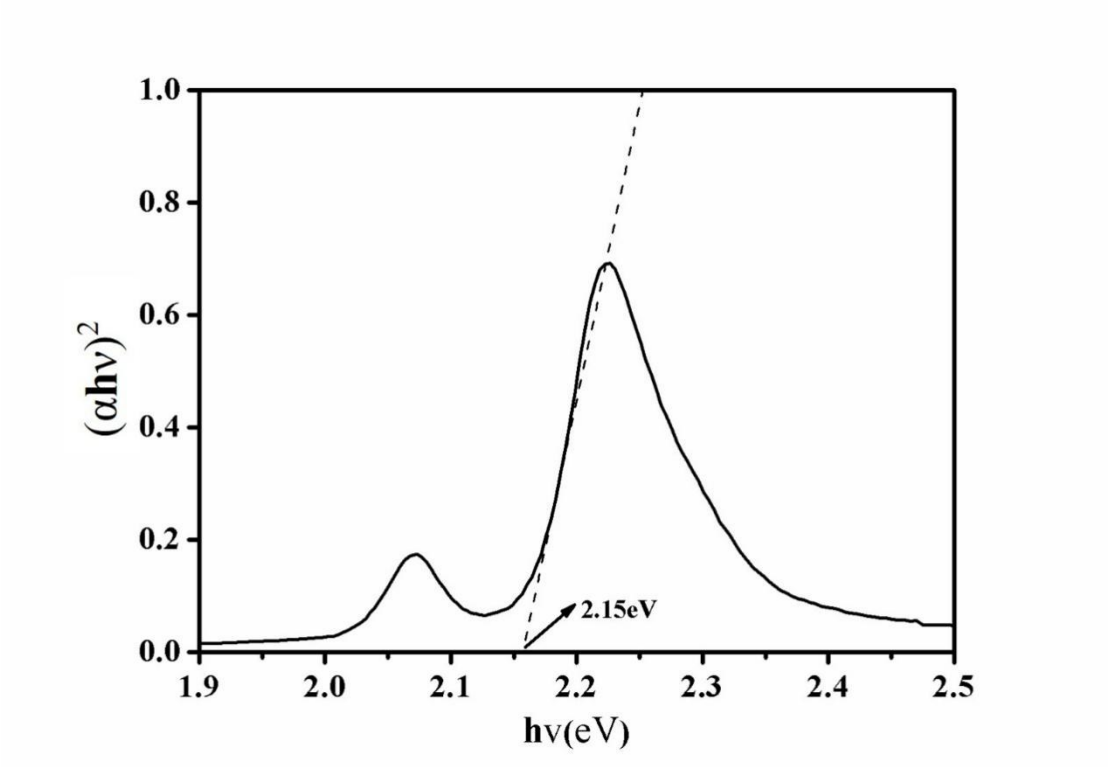

Fig. S6 Optical band gaps of ZnTHPP-(PNIPAM-ZnTPP)$_4$ obtained from UV-vis absorption spectra.

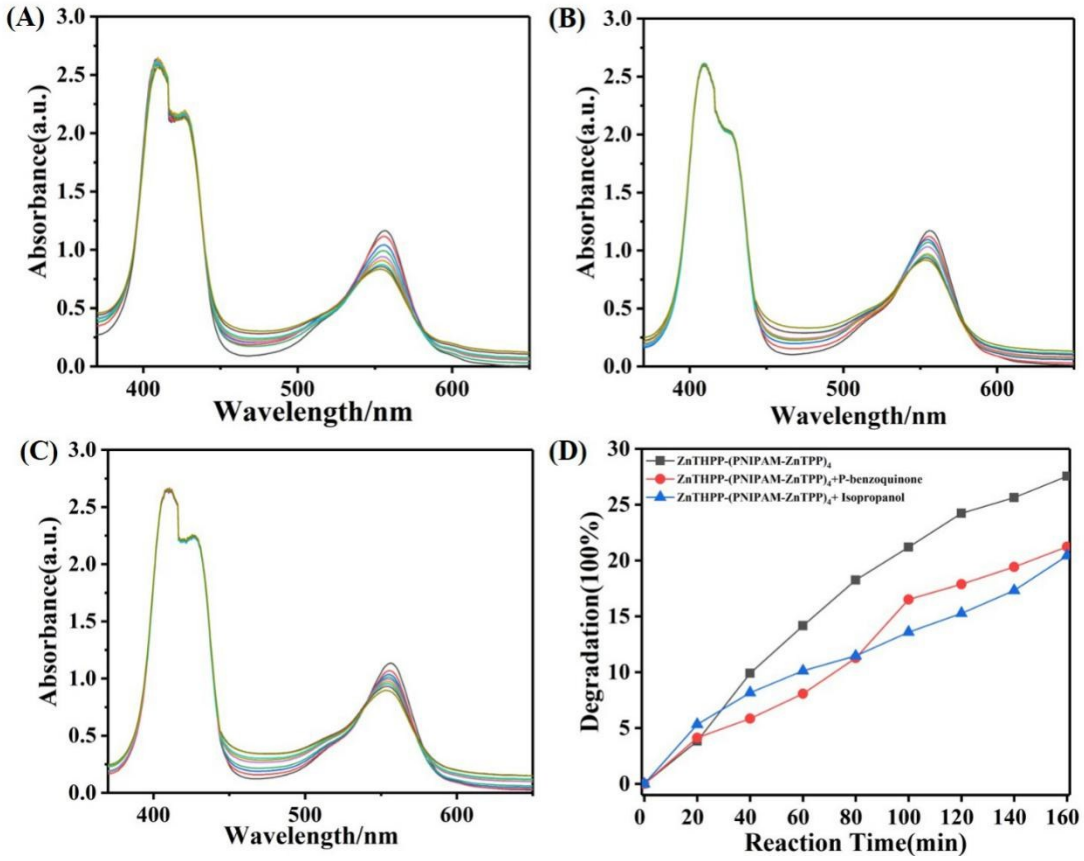

Fig. S7 UV-vis absorbance spectra of RhB degraded by photocatalytic upon visible light irradiation in the respective presence of **(A)** ZnTHPP-(PNIPAM-ZnTPP)$_4$, **(B)** ZnTHPP-(PNIPAM-ZnTPP)$_4$ and p-benzoquinone, **(C)** ZnTHPP-(PNIPAM-ZnTPP)$_4$ and isopropanol **. (D)** The RhB degradation rates of ZnTHPP-(PNIPAM-ZnTPP)$_4$, ZnTHPP-(PNIPAM-ZnTPP)$_4$+p-benzoquinone and ZnTHPP-(PNIPAM-ZnTPP)4 + isopropanol.

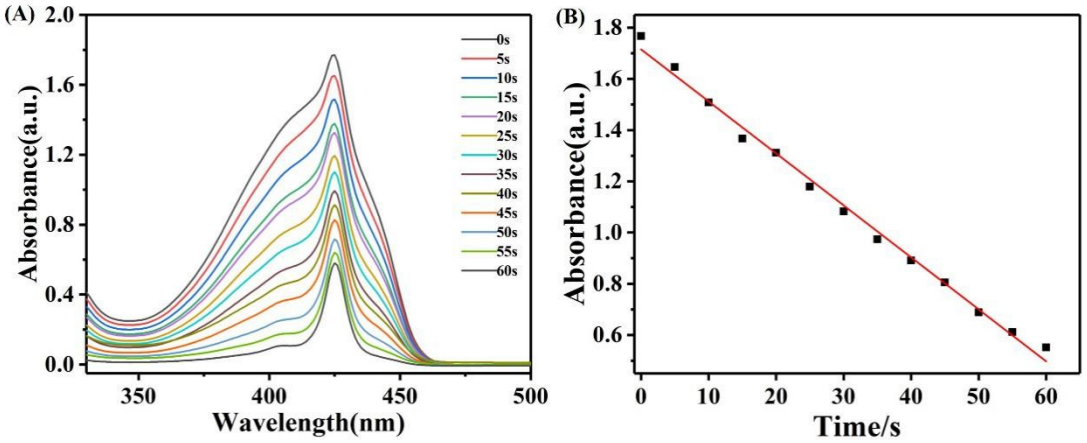

Fig. S8 **(A)** Time-dependent absorption spectra of DPBF in the presence of ZnTHPP-(PNIPAM-ZnTPP)$_4$ **(B)** The comparation of absorption at 410 nm and time.