Supplementary Information (SI) for Nanoscale.

Electronic Supplementary Material (ESI†)

Band Gap-Engineered Phenanthrenequinone-Based Donor–Acceptor Conjugated Microporous Polymers for Ultrafast Photocatalytic Removal of Tetracycline

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1. Experimental Section

1.1. Materials and Methods. All the chemicals and reagents were purchased from commercial sources and used directly as raw materials without further treatment. Thin-layer chromatography (TLC) on silica gel GF_{254} was used for the determination of R_f values, and the visualization was performed by irradiation with a UV lamp at 254 nm. Column chromatography was performed on Merck silica gel (100-200 mesh) with eluent as mentioned. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded in a Bruker Avance-500 NMR spectrometer in deuterated solvent at ambient temperature (300 K). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as the internal standard ($CDCl_3$ δ 7.26 ppm for ^1H and 77.0 ppm for ^{13}C). Solid-state ^{13}C CPMAS NMR spectra were recorded in a Bruker Ultrashield-500 NMR spectrometer. Fourier transform Infrared spectra (FTIR, 4000-600 cm^{-1}) were performed on a Nicolet 6700 FT-IR spectrometer (Thermo Fischer) Instrument, and the wave numbers of the recorded IR signals are reported in cm^{-1}. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond TG DTA (PerkinElmer) instrument. The as-synthesised D-A CMPs were observed under a scanning electron microscope (SEM) model ZEISS SUPRA 40. The samples were prepared on gold stubs by adding powder polymers and mounting them on top of double-sided tape. UV-Vis-NIR diffuse reflection spectrum (DRS) was acquired with a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent). X-ray diffraction patterns of the powder organic polymer samples were obtained using a Bruker AXS D-8Advanced SWAX diffractometer using Cu-Kα (0.15406 nm) radiation. The N_2 adsorption/desorption isotherms of the sample were recorded on a Micromeritics 3-Flex Surface Characterization Analyzer at 77 K. The information related to the excited-state lifetime of CMPs has been obtained from the TCSPC setup from DeltaFlex TCSPC (HORIBA) in reverse mode. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer. The specific measurement details regarding reactive oxygen species (ROS) trapping are as follows: In 3 mL air-saturated CH_3CN, 5 mg photocatalyst and 5 mg of N,N,N',N'-tetramethylphenylenediamine (NTPD) were added. Then O_2 was purged into that mixture, and the whole mixture was stirred under white light irradiation (100 W white LED) for 2 h. Then, the polymer was filtered out, and the filtrate portion was submitted for UV analysis. A Bruker ELEXSYS 580 spectrometer was used to record the EPR spectra. The specific measurement details regarding reactive oxygen species (ROS) trapping are as follows: the modulation frequency = 100.00 kHz, modulation amplitude = 5.000 G. The samples were prepared by adding 1 mg of photocatalyst to a 1 mL 0.1 M air-saturated methanol solution of 5,5-dimethyl-1-pyrrolineN-oxide (DMPO).

1.2. Electrochemical measurements

Cyclic voltammetry (CV) measurement was carried out by using a CH instrument with a three electrode-cell [CMPs-coated glassy carbon electrode as a working electrode, platinum wire as a counter electrode, and Ag/Ag^+ in acetonitrile (+0.49 V vs NHE)[1] as a reference electrode. A scan rate of 0.1 V/s was used. A solution of 0.1 (M) tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte. 2 mg of well-dried POPs was well dispersed in a binder solution of 25 wt% of polyvinylidene fluoride (PVDF) and 500 µL of ethanol through ultrasonication for 1 h to obtain a stable suspension. Then, the pre-polished glassy carbon electrode was coated with 20 µL of the prepared polymeric dispersion. The electrode was dried for 1 day at room temperature, and then prior to the CV experiment. The electrode potential values are given with respect to $E_{Ag/AgCl}$ = 0.197 vs NHE.[2] The LUMO energy levels of the POPs were determined by using the empirical equations, $E_{LUMO} = (E_{onset/red}+0.49-0.197)V$ (vs Ag/AgCl).[3, 4] EIS was determined over the frequency range of 10^2–10^6 Hz with an ac amplitude of 10 mV at the open circuit voltage under room-light illumination by using 0.5 M Na_2SO_4 aqueous solution as supporting electrolyte.

1.3. Photocurrent measurements

Photoelectrochemical measurements were conducted in a three-electrode system using a CH instrument under a 20 W white LED. The working electrodes are prepared as follows: 2 mg of well-dried CMPs is separately ground with 0.5 mg of polyvinylidene fluoride (PVDF) and 50 µL of ethanol to make a slurry. The slurry is then coated onto FTO glass electrodes with an active area of 1 cm^2, and these electrodes were dried at 80 °C for 1 h to evaporate the solvent. An aqueous solution of 0.5 M Na_2SO_4 was used as the supporting electrolyte. The photocurrent intensity of the as-prepared electrodes was measured at 0.3 V versus s-Ag/AgCl with the light on and off.

Synthetic Procedure

Synthesis of D-A CMP, TRZ-PHQ:

In a 100 mL two-necked round-bottom flask, 300 mg (0.436 mmol) of monomer **1**, 240 mg (0.655 mmol) of 2,7-dibromophenanthrene-9,10-dione, 25 mg (5 mol%) of $Pd(PPh_3)_4$, and 963.8 mg (6.984 mmol) of K_2CO_3 were added under an argon atmosphere. A degassed mixture of 9 mL toluene and 3 mL water was injected into the reaction mixture, which was then purged with argon for 40 minutes. The reaction mixture was stirred vigorously at 95 °C for 5 days. The resulting precipitate was collected by filtration and thoroughly washed with water, methanol, and chloroform. Further purification was carried out by washing the precipitate with methanol, acetone, and chloroform in a Soxhlet apparatus. Finally, the polymer was dried under vacuum, yielding a reddish-brown product (238 mg) with an 89 % yield. Characterization data: FT-IR (cm^{-1}): 1672, 1572, 1501; ^{13}C CPMAS NMR (ppm): ~180, ~171, ~140, ~135-127; TGA: 5% weight loss at 330 °C.

2. Characterizations

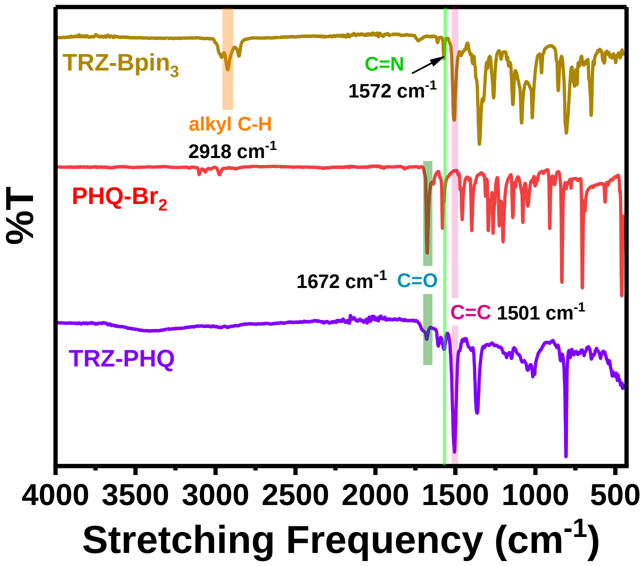


Figure S1. FT-IR spectra of monomer PHQ-Br2 (red), monomer TRZ-Bpin3 (yellow), and polymer **TRZ-PHQ** (blue)

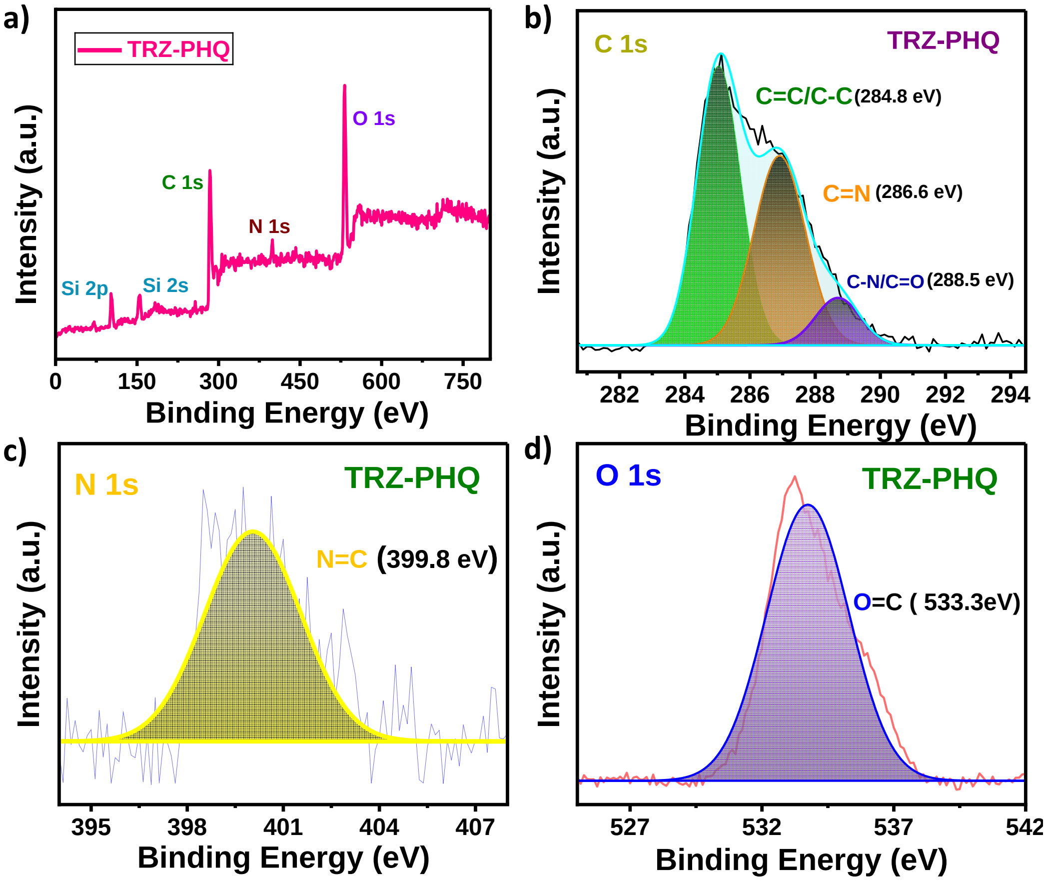
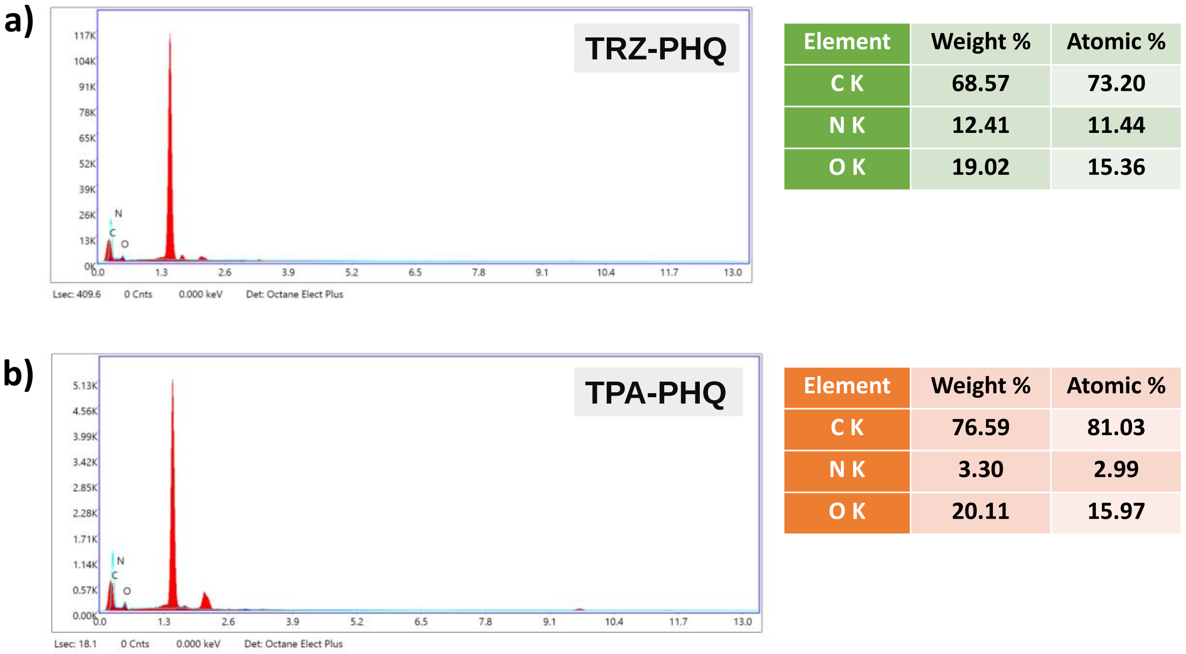


Figure S2. a) Full-range XPS spectrum of **TRZ-PHQ;** high-resolution deconvoluted XPS spectra of b) C 1s, c) N 1s, and d) O 1s for **TRZ-PHQ**



Element	Weight %	Atomic %
C K	68.57	73.20
N K	12.41	11.44
O K	19.02	15.36

Element	Weight %	Atomic %
C K	76.59	81.03
N K	3.30	2.99
O K	20.11	15.97

Figure S3. Energy dispersive X-ray (EDX) analysis of a) **TRZ-PHQ** and b) **TPA-PHQ**; inset: tabular representation of different elements in atomic % and weight % present in the polymer.

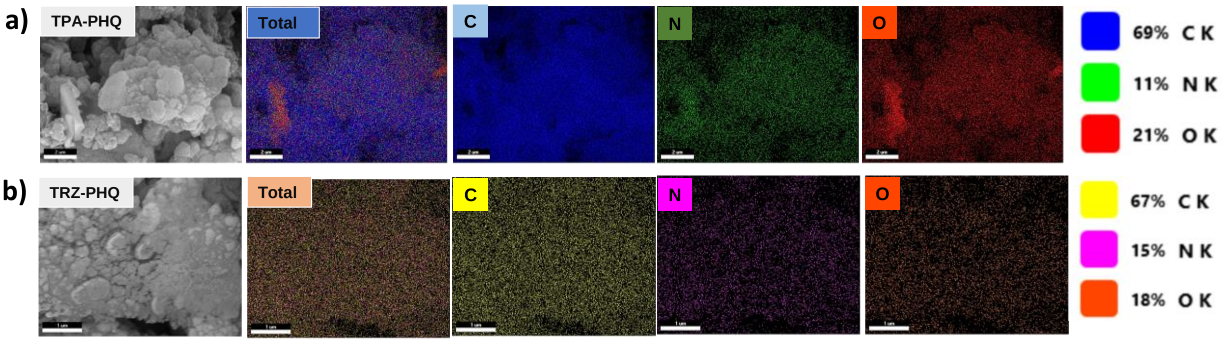
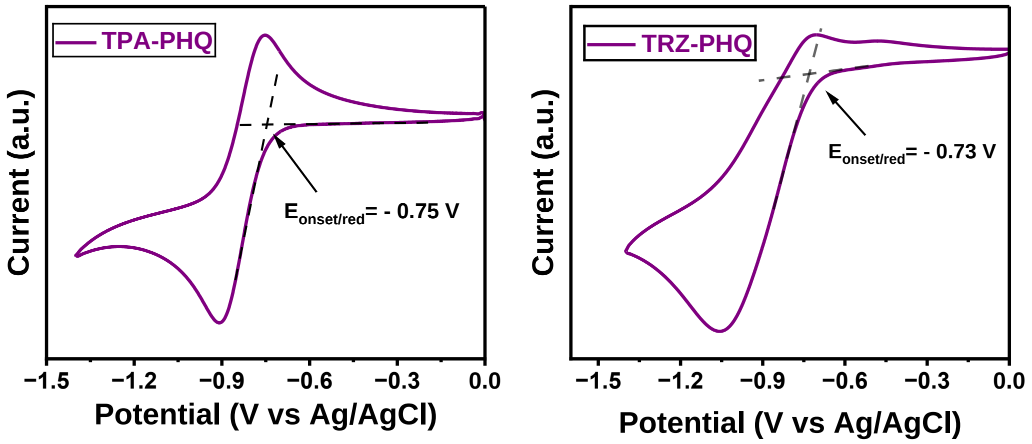


Figure S4. Elemental mapping analysis of a) **TPA-PHQ** and b) **TRZ-PHQ**.

Table S1. BET surface area, pore volume, and average pore diameter of the CMPs.

CMPs	BET Surface area	BJH Adsorption cumulative volume of pores	BJH Adsorption average pore diameter
TRZ-PHQ	42 m^2/g	0.047 cm^3/g	1.78 nm
TPA-PHQ	35 m^2/g	0.037 cm^3/g	2.02 nm



E_{LUMO} = -0.75 V vs Ag/AgCl
= -0.55 V vs NHE
E_{HOMO}= 1.56-0.55
= 1.01 V

E_{LUMO} = -0.73 V vs Ag/AgCl
= -0.53 V vs NHE
E_{HOMO}= 2.06-0.53
= 1.53 V

Figure S5. CV plots of **TPA-PHQ** and **TRZ-PHQ**.

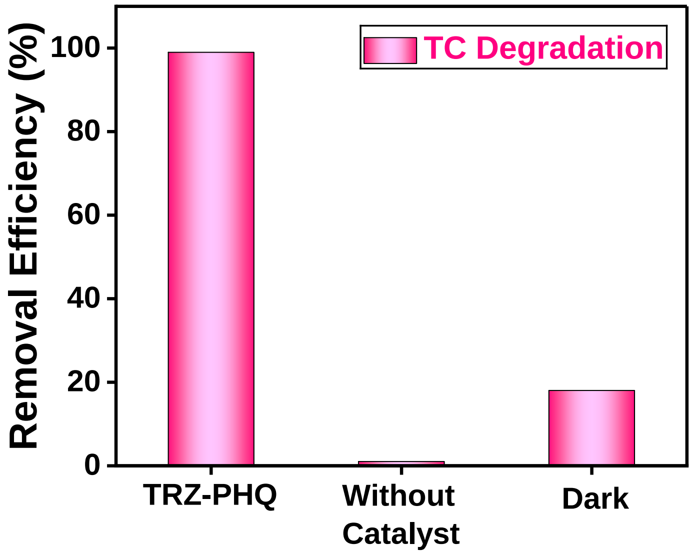


Figure S6. Control tests for photocatalytic degradation of Tetracycline(TC) by **TRZ-PHQ**.

3. Photocatalytic Application

3.1. Photocatalytic degradation of tetracycline

Table S2. Comparison of photocatalytic degradation efficiencies of tetracycline for various photocatalysts.

Catalyst	Light source	Initial conc. TC (mg/L)	Photocatalyst loading (mg)/conc. (g/L)	Solution volume (mL)	pH	Degradation rate (%)	Time	Kinetic constants	Ref.
TRZ-PHQ	**100 W ($\lambda > 420$ nm)**	**20**	**5 / (0.5)**	**10**	**6.5**	**99%**	**15 min**	**0.1924 min^{-1}**	**This work**
N-COF/BOB	300 W ($\lambda > 420$ nm)	60	5 / (0.1)	50	7	81.2%	120 min	0.0137 min^{-1}	5
Tz-CMP-3	300 W ($\lambda > 420$ nm)	15	20 / (0.2)	100	7	95.6%	30 min	0.1122 min^{-1}	6
Sp^{2}c-COF	300 W ($\lambda < 400$ nm)	20	20 / (0.2)	100	4.2	73.5%	90 min	0.0387 min^{-1}	7
ATBT-POP	300 W ($\lambda > 420$ nm)	10	30 / (0.6)	50	---	92.12%	120 min	0.0471 min^{-1}	8
ID-PIP	300 W ($\lambda > 420$ nm)	20	15 / (0.15)	100	7	96 %	30 min	0.0545 min^{-1}	9
BMTA-TAPT	300 W ($\lambda > 420$ nm)	10	50 / (0.5)	100	7	93.6 %	45 min	0.079 min^{-1}	10
0.5 CCM3	350 W ($\lambda > 420$ nm)	20	30 / (0.6)	50	---	88.4 %	90 min	0.0231 min^{-1}	11
MSTO5	250 W ($\lambda > 420$ nm)	10	100 / (1)	100	---	66.7%	60 min	0.0166 min^{-1}	12
CMP-HS-S/TiO_2-2	500 W ($\lambda > 420$ nm)	10	10 / (0.33)	30	---	90 %	180 min	0.011 min^{-1}	13
CNBTC-50	250 W ($\lambda > 420$ nm)	10	25 / (0.5)	50	7.4	91.6 %	60 min	0.0388 min^{-1}	14
3D-PDI	5 W ($\lambda > 420$ nm)	20	25 / (0.5)	50	5	80%	150 min	0.0073 min^{-1}	15
EdtTz-CMP	300 W ($\lambda > 420$ nm)	15	20 / (0.2)	100	7	94.6%	90 min	0.0405 min^{-1}	16
Sol-10BP/BiOBr	300 W ($420<\lambda>780$ nm)	50	100 / (1)	100	---	85 %	90 min	0.021 min^{-1}	17
3BCN	500 W ($\lambda > 420$ nm)	5	20 / (0.2)	100	7	88.6 %	120 min	0.0222 min^{-1}	18

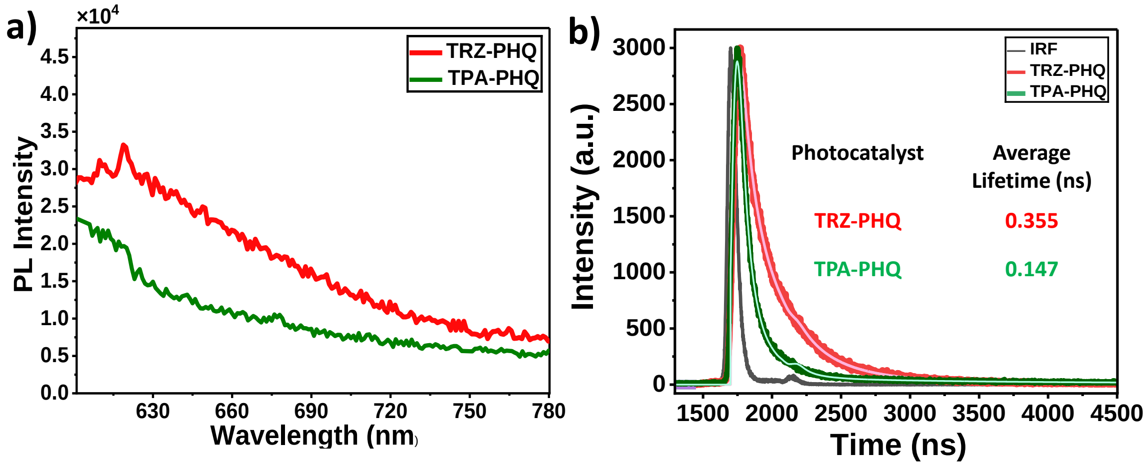


Figure S7. a) PL spectra of the as-prepared CMPs, recorded at excitation wavelengths of 470 nm for **TRZ–PHQ** and 570 nm for **TPA–PHQ**. b) TRPL decay profiles of the corresponding CMPs.

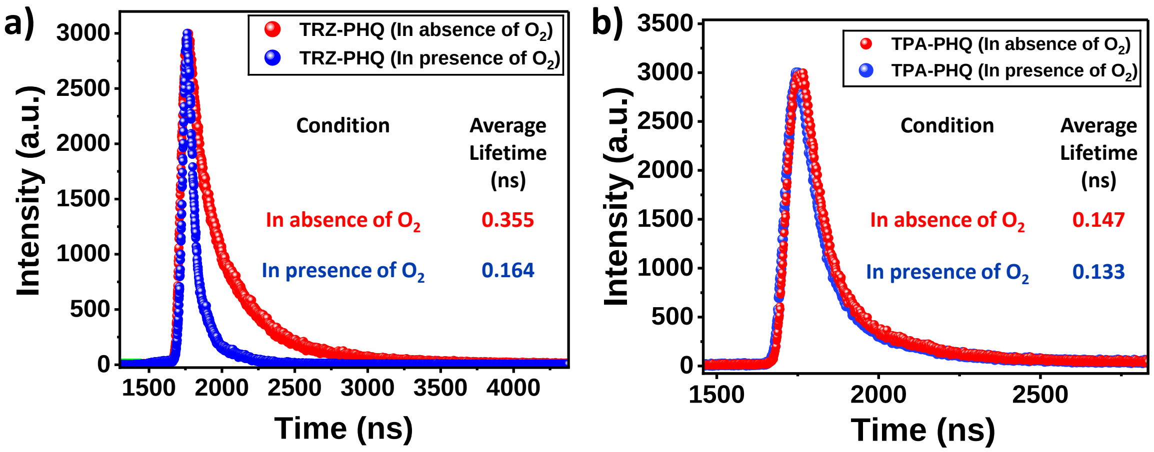


Figure S8. TRPL decay profiles of a) **TRZ-PHQ** and b) **TPA-PHQ** measured in the presence and absence of oxygen.

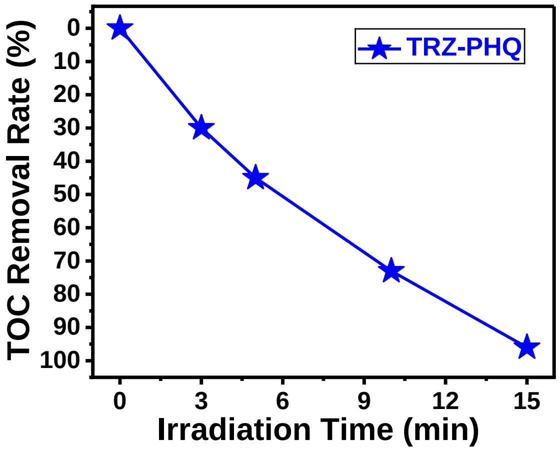


Figure S9. TOC analysis of TC degradation over **TRZ-PHQ** under visible light irradiation.

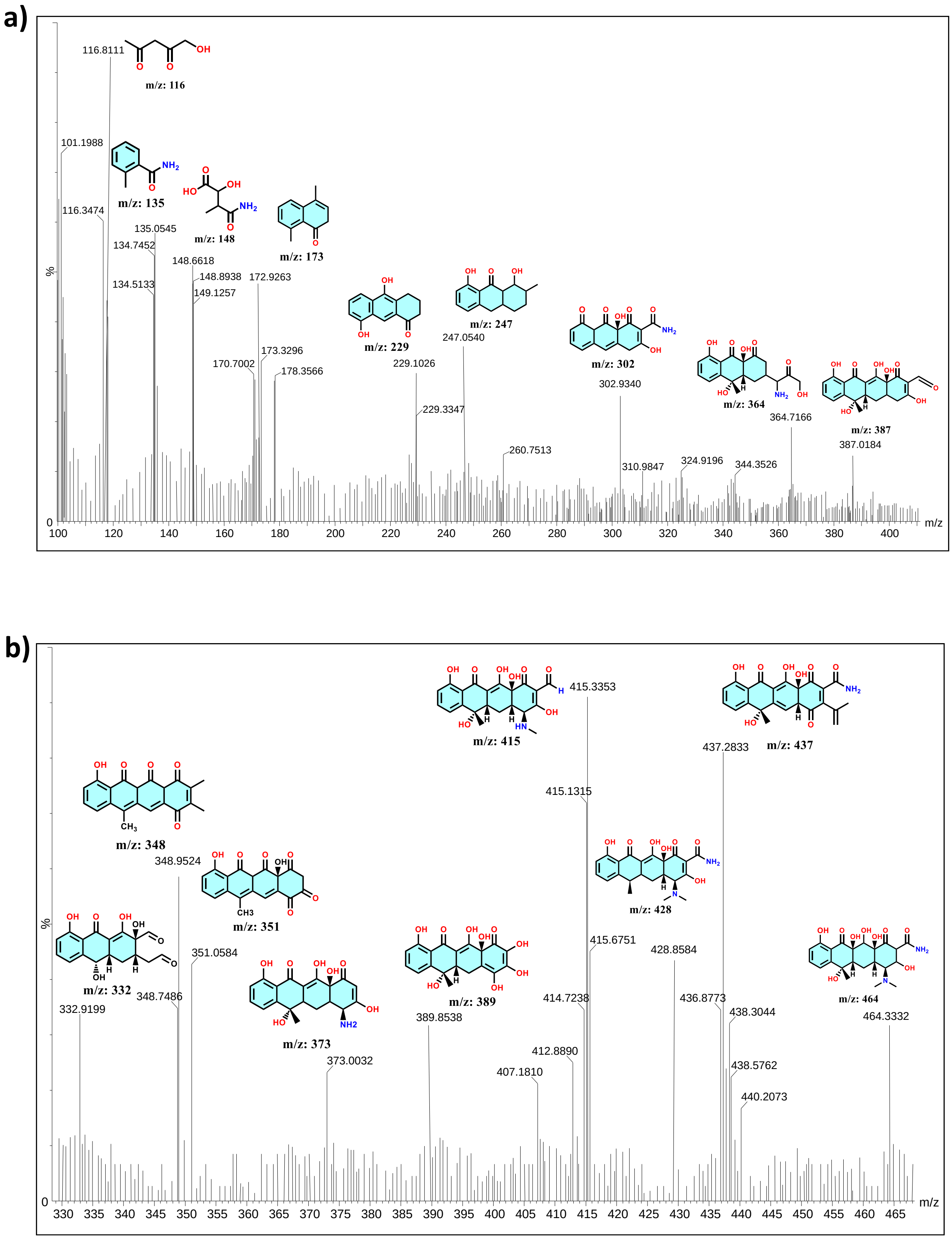


Figure S10. a) and b) LC-MS spectra of tetracycline solutions after photocatalysis by **TRZ-PHQ.**

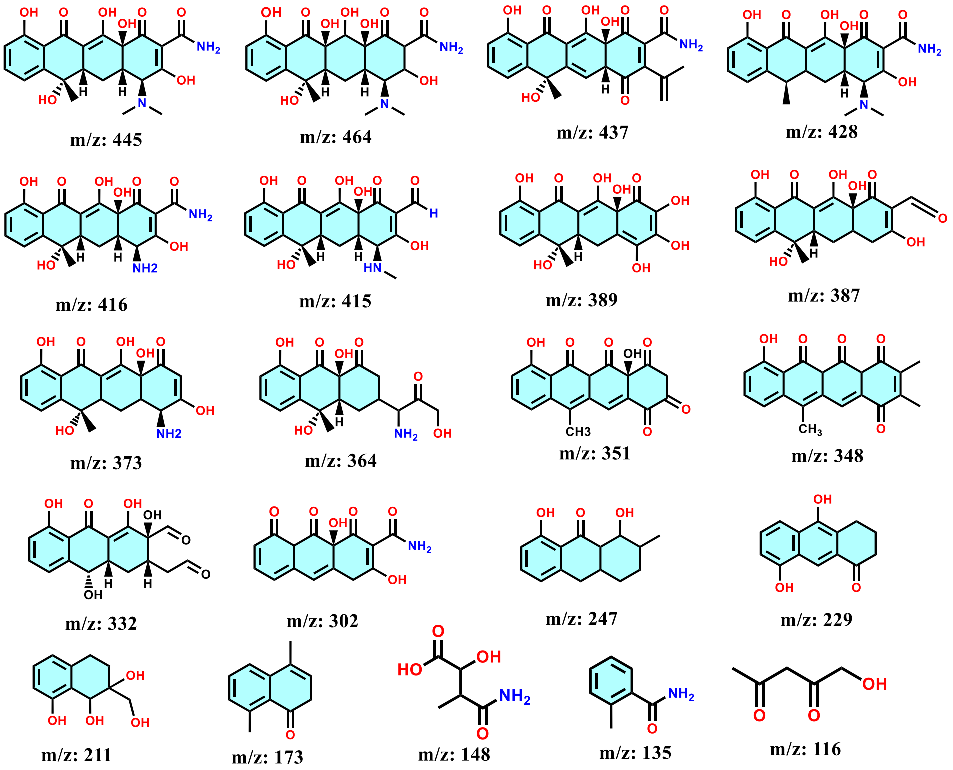


Figure S11. Reaction intermediates for tetracycline degradation with **TRZ-PHQ**.

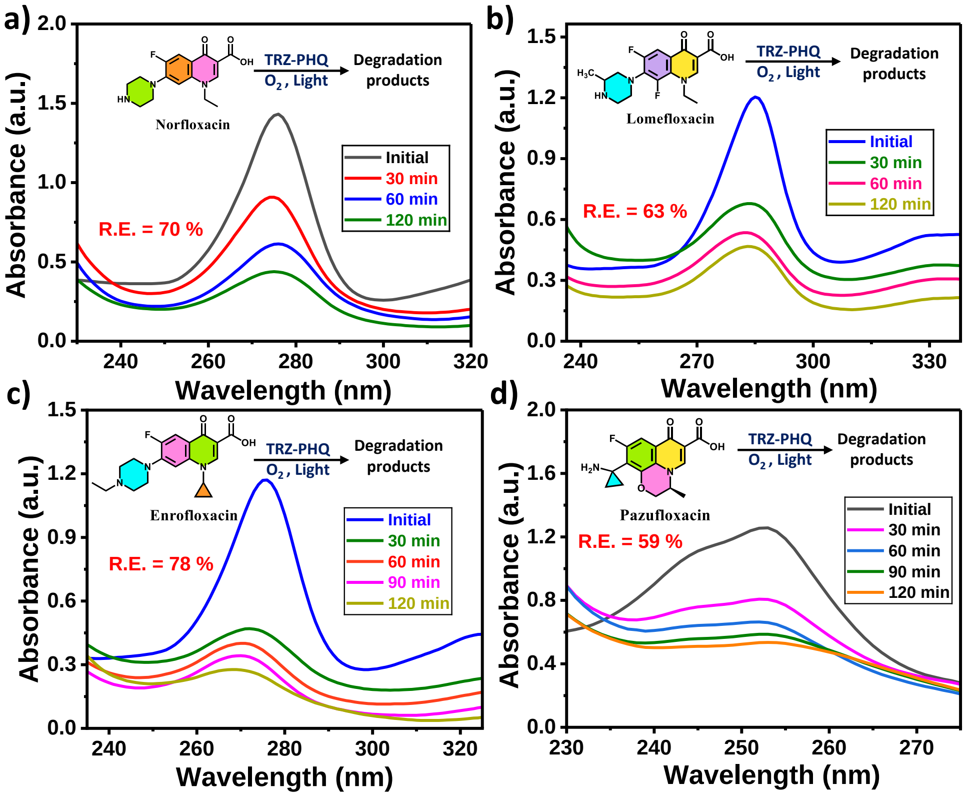


Figure S12. UV-visible spectra of a) Norfloxacin, b) Lomefloxacin, c) Enrofloxacin, and d) Pazufloxacin over time in the presence of the photocatalyst **TRZ-PHQ.**

Table S3. Recovery rate of polymer catalyst, **TRZ-PHQ,** for photocatalytic Tetracycline (TC) degradation.

Cycle number	Catalyst recovery (%)
Run 1	100
Run 2	99
Run 3	97
Run 4	95
Run 5	92
Run 6	91
Run 7	88

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