Supplementary Information (SI) for EES Catalysis.

Electronic Supplementary Information

Three-in-One Approach to Fabricate a Porous Porphyrin-Heptazine Polymer for Highly Efficient Visible Light Photocatalysis

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Experimental Procedures

Methods

All reagents were purchased in high purity grade from Fisher Scientific, Sigma-Aldrich, Alfa and used without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieves. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. Gas sorption isotherms were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. UV-Vis analysis were performed on a Varian CARY50 spectrophotometer. The transmission electron microscope (TEM) image was recorded on a JEM-2100 electron microscope (2.0 kV). The scanning electron microscope (SEM) image was obtained on a Hitachi S4800 FE-SEM system (200 kV). Solid-state ^{13}C and ^{15}N nuclear magnetic resonance (NMR) was performed on a Bruker Advance III 400 WB spectrometer equipped with a 9.4 T magnet. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on a TA Instrument TGA Q50, starting at room temperature to 800 °C at a 20 °C/min heating rate. The steady-state photoluminescence (PL) emission spectra were recorded on an LS-55 fluorescence spectrometer made by PerkinElmer. The time-resolved PL data were collected on an Edinburgh FLS920 fluorescence spectrometer. Electron paramagnetic resonance (EPR) was measured on a Magnettech Miniscope MS200 spectrometer. Conditions for spin trap EPR: DMPO (10 mM), TEMPO (10 mM), PHP (1.2 mg) in 6 mL DMF, under irradiation, $\lambda > 420$ nm. The mixture was separated by filtration and the supernatant was subjected to the ESR measurement. 6 mg of PHP was added to a solution of tetramethylphenylenediamine (TMPD) (100 mM in 3 mL CH_3CN), benzylamine (10 mM in 3 mL CH_3CN), and irradiated with visible light. 0.1 mg of PHP was added to a solution of 1,3-diphenylisobenzofuran (DPBF) (50 μM in 2.5 mL DMF) and irradiated with visible light. The resulting reaction mixture was analyzed qualitatively by UV-vis.

Electrochemical Analysis

The working electrode was prepared on fluoride tin oxide (FTO) glass substrates. First, 50 mg powder was mixed with 2 mL of acetone under sonication for 30 min to get a slurry. The slurry was then spread onto the FTO. After air-drying, the electrode was annealed at 300 °C for 30 min in air to improve the adhesion. The electrochemical properties were performed in a conventional three-electrode cell using an electrochemical analyzer (CHI-633C, Shanghai Chenhua, China). The working electrode was immersed in a sodium sulfate electrolyte solution (0.1 M), using a Pt sheet and an Ag/AgCl electrode as the counter and reference electrodes, respectively. For Mott-Schottky experiments, the perturbation signal was 10 mV with the frequency at 1.5 and 2.0 kHz. The photocurrents were detected by using a standard three-electrode cell with Ag/AgCl as reference electrode and Pt wire as the counter electrode in KCl solution (3 M).

Representative Synthesis of PHP

Meso-tetra(4-nitrophenyl)porphyrin (TNPP). TNPP were synthesized according to the procedures in the references.[1]

Heptazine. Heptazine were prepared by a published procedure with a modification.[2] Melamine is sealed in glass tube. Then, a temperature of 425 °C is maintained for 90 h. Subsequently, the colorless rod crystal mixture at the top of ampule is identified by single-crystal *X-ray* diffraction (Table S1 and Fig. S1). After suspended in water and boiled under reflux for 48 h, the resulting crystal product is dried at room temperature.

Notice: Carefully open the ampule, after the ampule was opened, the typical smell of ammonia was detected!!

Typical synthetic procedure of PHP. TNPP (0.3176 g, 0.40 mmol) and heptazine (0.116 g, 0.53 mmol) were dissolved in DMF (20 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and magnetic stirrer. KOH (0.22 g, 3.94 mmol) was added to this solution while stirring. The temperature of the reaction mixture was increased slowly up to 150 °C with vigorous stirring under Ar atmosphere and stirred at this temperature for 72 h. The reaction mixture was cooled to room temperature, added to 80 mL of distilled H_2O and stirred for 1 h. Purple precipitate was filtered off, immersed in DMF for 1 day and then washed with warm distilled H_2O (x5), Me_2CO (x5) and THF (x5). Subsequently, purple precipitates were dried at 150°C under vacuum for 8 h to yield PHP in 63 % yield. No noticeable physical changes were observed with PHP upon exposure to air, humidity, or organic solvents (DMF, DCM, THF, ethanol and methanol).

General Procedure for the Photooxidation of CEES

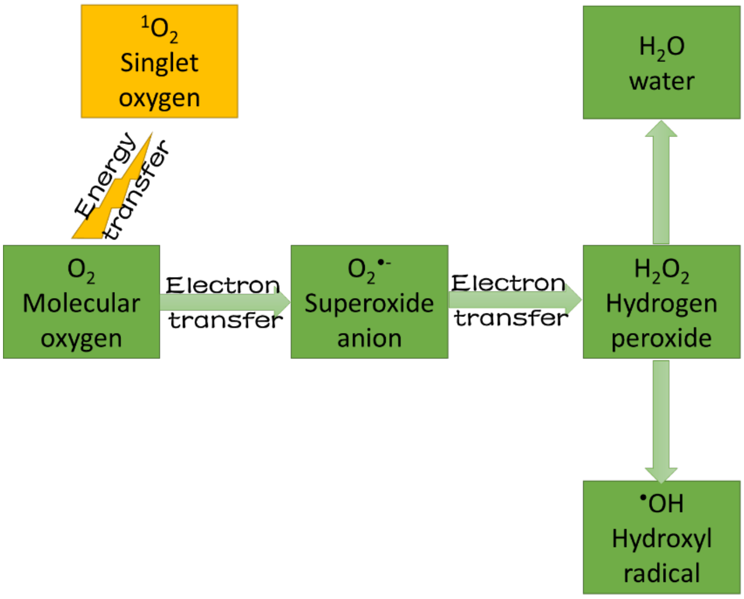
In a typical setup, the catalyst was added to a microwave vial. To the vial, 3 mL of solvent was dispensed. The vial was cringe-capped and purged with O_2 for 10 min under LED irradiation. The suspensions were then placed in a 25 °C water bath to maintain the temperature, to which 0.6 mmol of CEES was added. Then, to take an initial time point, a 20 μL aliquot was taken, diluted with 750 μL of chloromethane, filtered, and analyzed by GC-MS, ^{1}H NMR and ^{13}C NMR.

General Procedure for the Photooxidative Coupling of Benzylamine and Derivatives

PHP (20 mg) was placed in the reaction together with CH_3CN (30 mL) and benzylamine (1 mmol), and the reactor was closed. The autoclave was then flushed three times with O_2, and then maintained at 25 °C under 1 atm O_2. To carry out the photochemical reaction, a 300 W Xenon lamp together with a 420 nm cut-off filter was used as a visible light source for the irradiation of the reaction system. The reaction mixture was filtered through a porous membrane (20 um in diameter) and then injected into the GC equipped with FID detector (Agilent Technologies, GC6890) for analysis. The chemical structures of products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC6890N, MS 5975). Samples were also determined by ^{1}H NMR using DMSO as solvent.

Computational Details

All the theoretical investigations were conducted by using the Gaussian 16 C.01 software package.[3] The geometries were optimized under B3LYP/Def2-SVP level of theory and no imaginary frequencies were found to ensure the energy minima.[4,5] The excited states were calculated under the B3LYP/Def2-TZVP level of theory.[5] Electron density difference (EDD) maps were generated by using Multiwfn 3.8(dev) software.[6,7]



Scheme S1. Schematic representation of generation of reactive oxygen species (ROS) in plants.

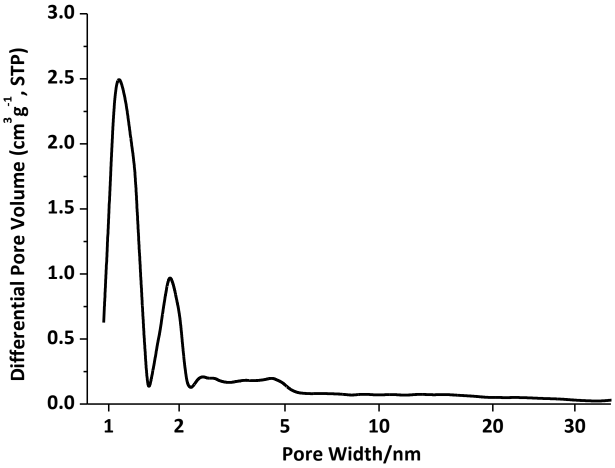


Fig. S1. Pore size distribution of PHP sample calculated using DFT model.

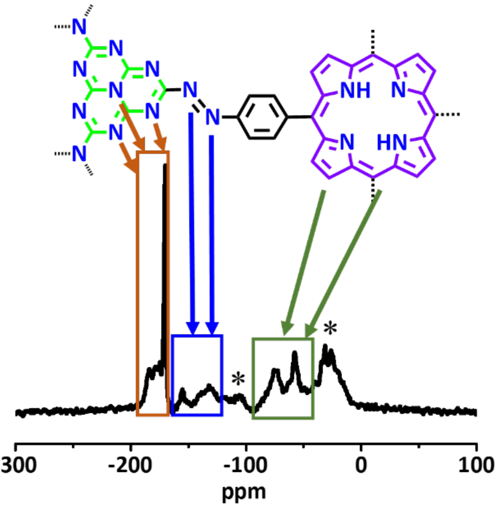


Fig. S2. ^{15}N MAS NMR spectra of for PHP catalyst. Signals with * are side bands.

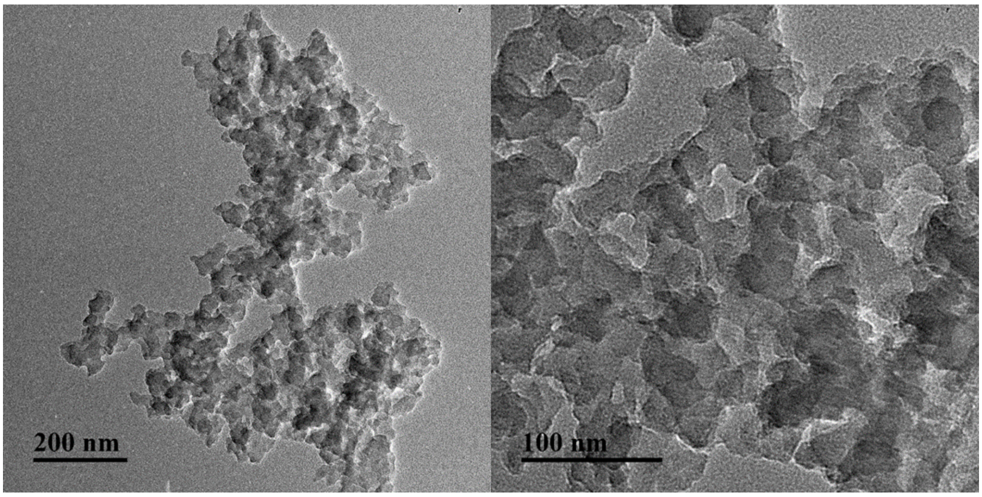


Fig. S3. TEM images of PHP sample.

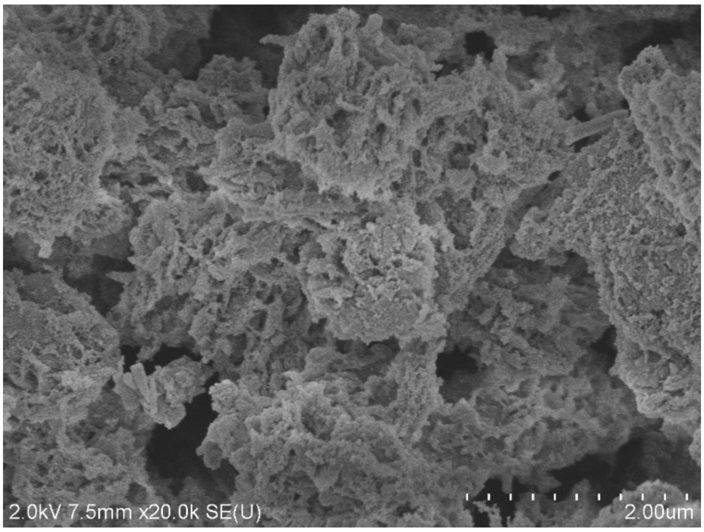


Fig. S4. SEM image of PHP.

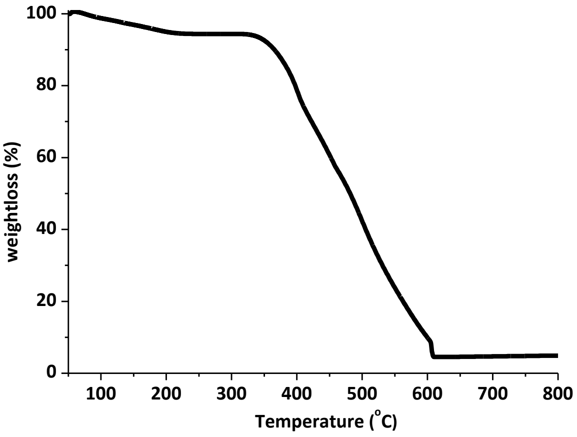


Fig. S5. TGA trace for PHP heated under a nitrogen atmosphere.

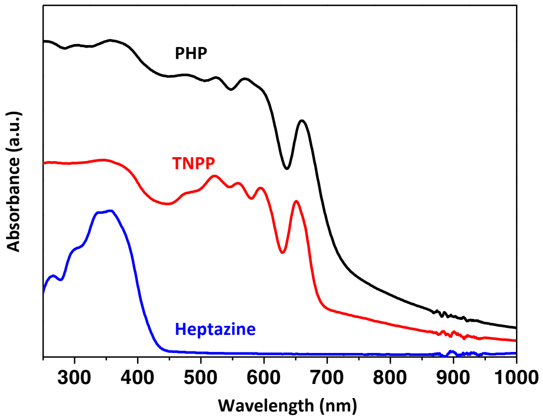


Fig. S6. UV-Vis diffuse reflectance spectra of: PHP (black line), TNPP (red line), heptazine (blue line).

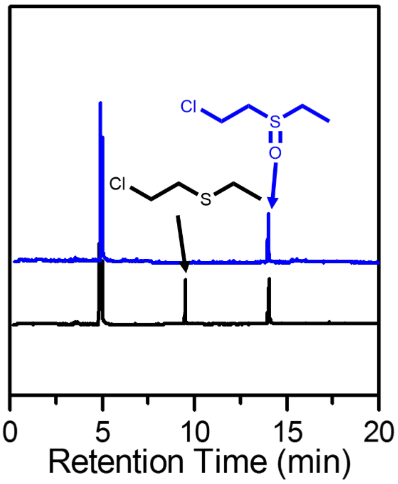


Fig. S7. GC signals indicating the progress of the oxidation of CEES (9 min) to CEESO (14 min) in the presence of PHP.

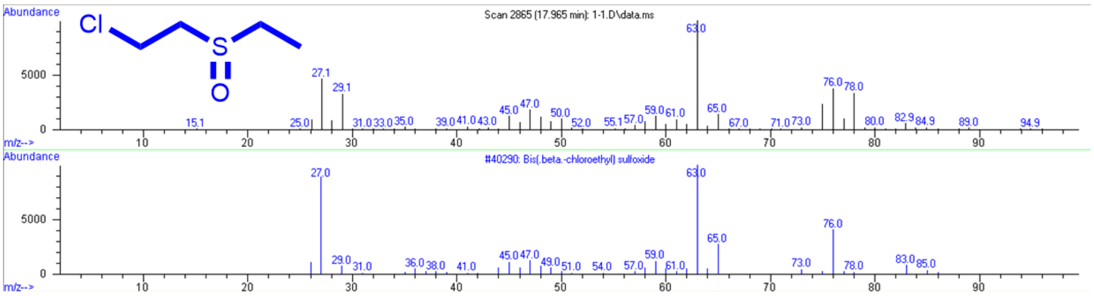


Fig. S8. MS signals of CEESO.

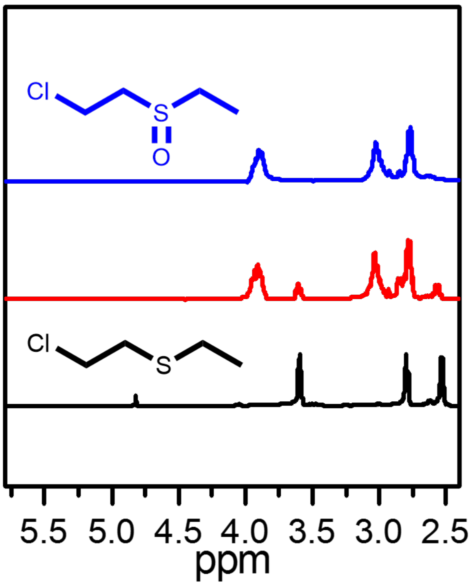


Fig. S9. ^{1}H NMR spectrum measured 7.5 min and 12 min after oxidation started in $CDCl_3$, indicating that the oxidation was complete and only one oxidation product, CEESO, was obtained.

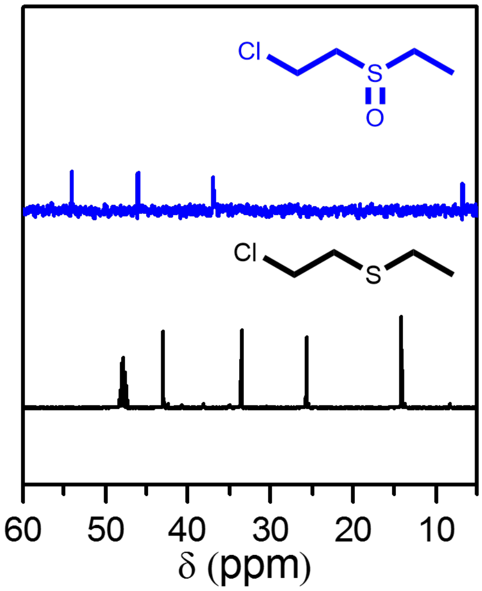


Fig. S10. ^{13}C NMR spectrum measured 12 min after oxidation started in $CDCl_3$, indicating that the oxidation was complete and only one oxidation product, CEESO, was obtained.

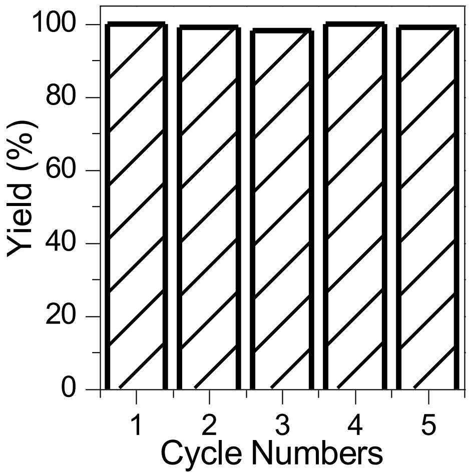


Fig. S11. Recyclability of PHP in photocatalytic oxidative conversion of CEES into CEESO.

Table S1. Photocatalytic oxidative conversion of sulfides by PHP. [a]

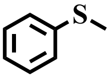
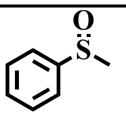
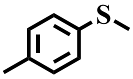
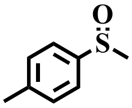
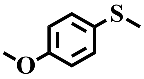
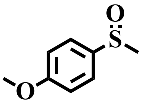
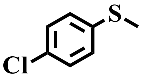
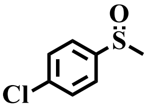
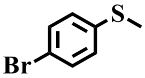
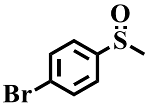
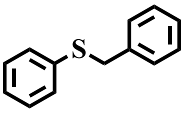
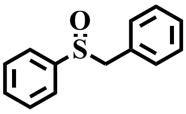
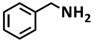
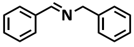
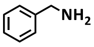
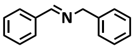
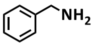
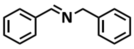
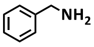
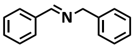
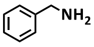
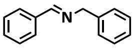
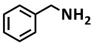
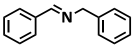
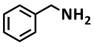
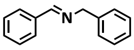
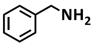
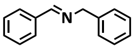
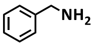
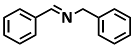
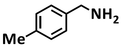
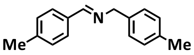
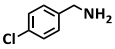
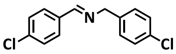
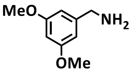
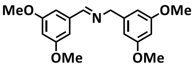
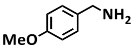
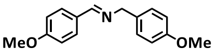
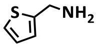
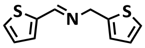
Entry	Amine	Product	Conv. (%)	Sel. (%)
1 (b)			99	>99
2 (c)			99	>99
3 (d)			99	>99
4 (e)			80	>99
5 (f)			82	>99
6 (g)			90	>99

Table S2. Photocatalytic oxidative conversion of amines into imines by PHP. (a)

Entry	Amine	Product	Conv. (%)	Sel. (%)
1 (b)			0	0
2 (c)			0	0
3 (d)			27	>99
4 (e)			13	>99
5 (f)			10	>99
6 (g)			72	>99
7			>99	>99
8 (h)			99	>99
9 (i)			99	>99
10			96	98
11			>99	96
12			90	98
13			93	>99
14			93	>99

(a) Reaction conditions: amine (1.0 mmol), O_2 (1 atm), cat. PHP (20 mg), CH_3CN (30.0 mL), λ > 420 nm, 3 h, 25 °C. (b) Glassware was covered with Al foil under irradiation, λ > 420 nm. (c) No PHP used under irradiation, λ > 420 nm. (d) TNPP as catalyst. (e) g-C_3N_4 as catalyst. (f) Heptazine as catalyst. (g) Reaction time 1.5 h. (h) The recovered catalysts were used. (i) Under solar radiation, 6 h, 25 °C.

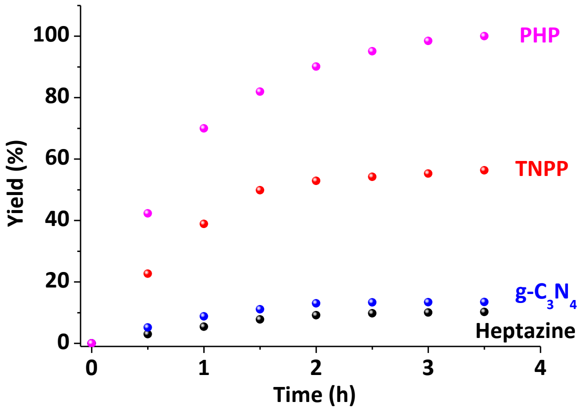
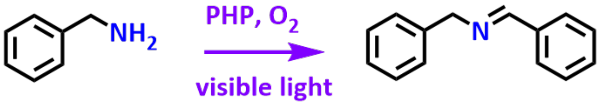


Fig. S12. Plot of yield versus time with catalysts PHP (pink squares), TNPP (red circles), g-C_3N_4 (blue stars), and heptazine (black triangles).



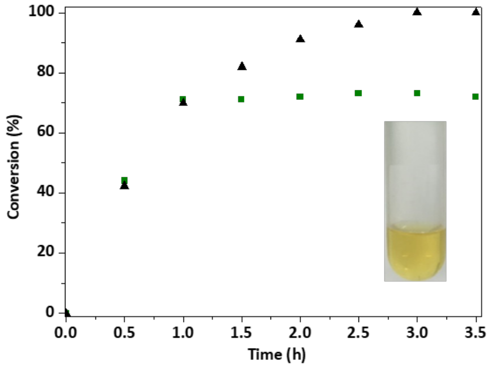


Fig. S13. Yield of oxidative coupling reaction of benzylamines based on a filtration test after 1 hour (green squares) and no filtration (black triangle).

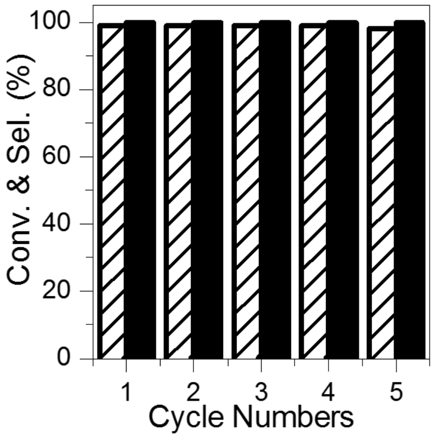
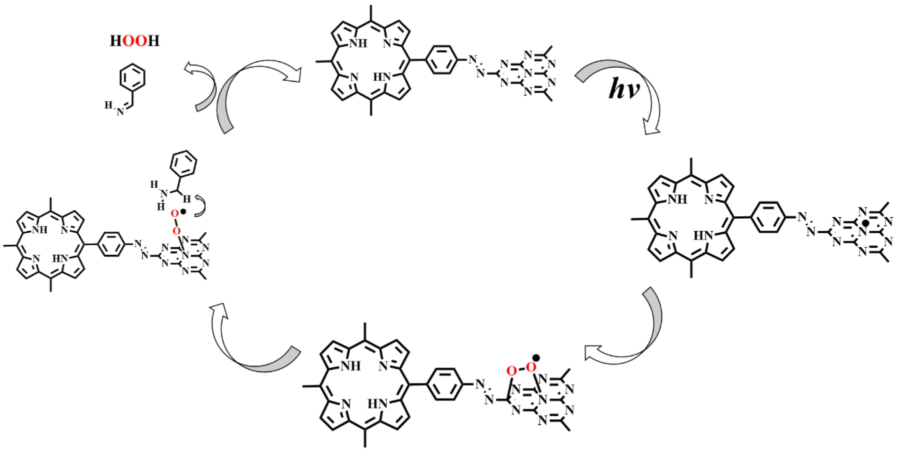


Fig. S14. Recyclability of PHP in photocatalytic oxidative conversion of amines into imines. Reaction conditions: amine (1.0 mmol), O_2 (1 atm), cat. PHP (20 mg), CH_3CN (30.0 mL), λ > 420 nm, 3 h, 25 °C.



Scheme S2. Proposed mechanism for H_2O_2 formation on the photo activated from and O_2 via electron transfer pathway.

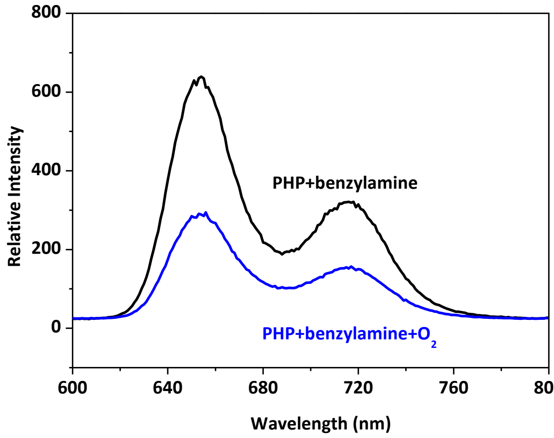


Fig. S15. Photo-luminescence (PL) response of PHP to benzylamine after bubbling O_2.

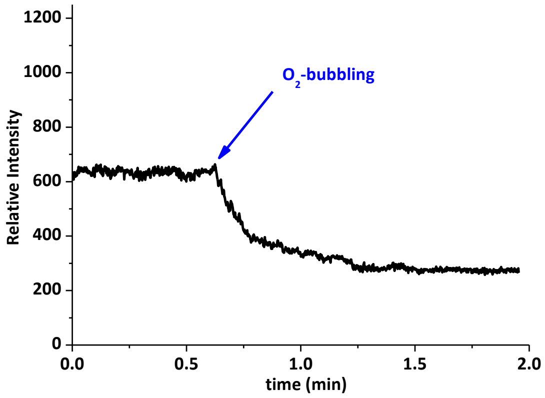


Fig. S16. Photo-luminescence (PL) of PHP to benzylamine after bubbling O_2.

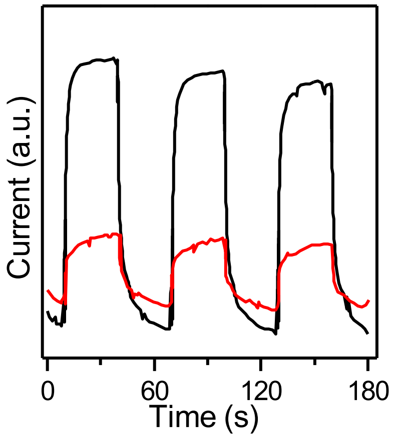


Fig. S17. Photocurrent response of the photo anodes of PHP (black line) and g-C_3N_4 (red line).

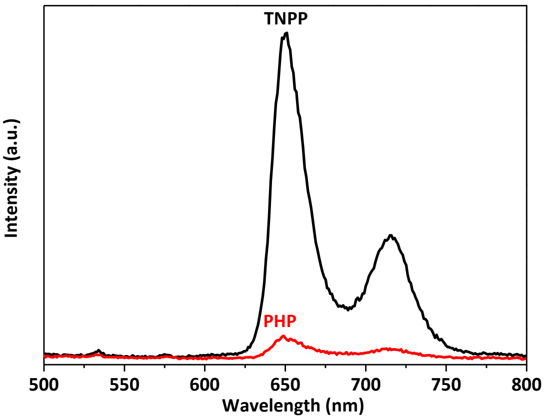


Fig. S18. The photo-luminescence (PL) response of the PHP (red) and TNPP (black) excited at 420 nm.

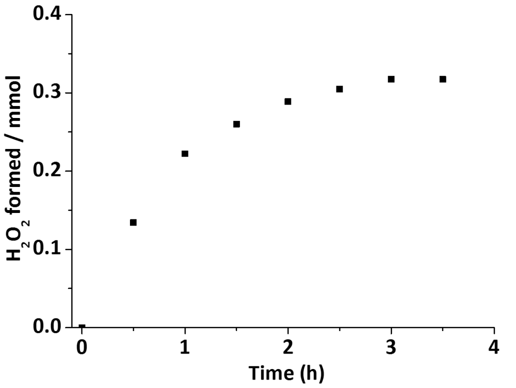


Fig. S19. Time-dependent change in the amounts of H_2O_2.

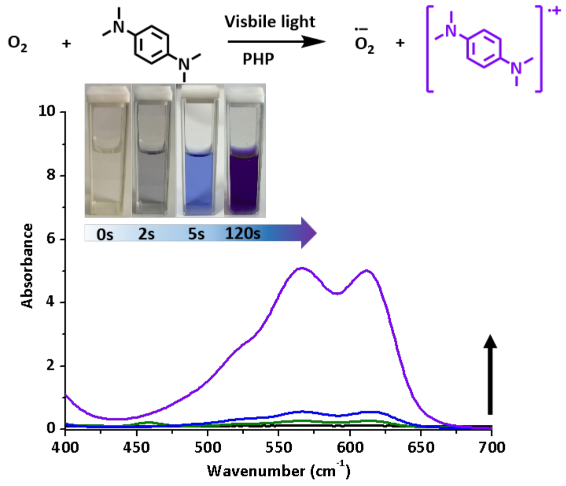


Fig. S20. (a) Time-dependent UV-vis absorption spectra and photograph of the cationic radical species of 1,4-bis(dimethylamino)benzene generated by PHP (b) Time-dependent UV-vis absorption spectra of DPBF (in DMF) upon irradiation.

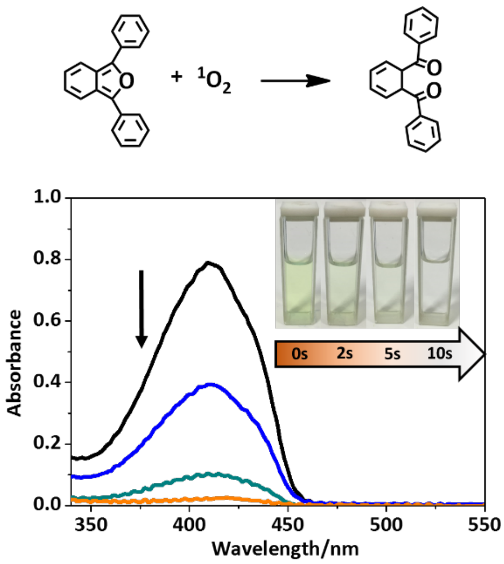


Fig. S21. Time-dependent UV-vis absorption spectra of DPBF (in DMF) upon irradiation.

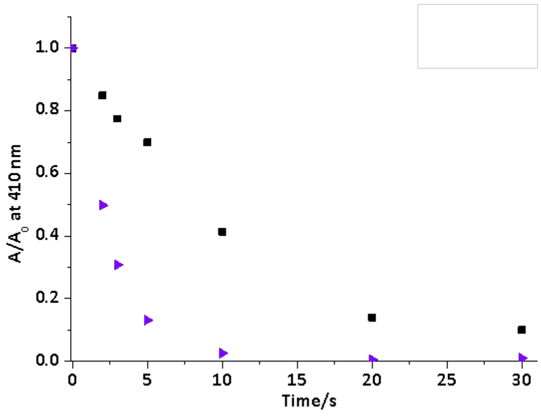


Fig. S22. Decay rate comparison of DPBF in the presence of TNPP (black squares) and PHP (purple triangles).

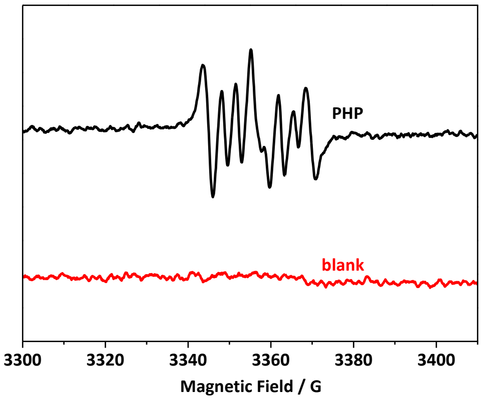


Fig. S23. ESR spectra of DMPO-$O_2^{\cdot-}$ adducts for PHP

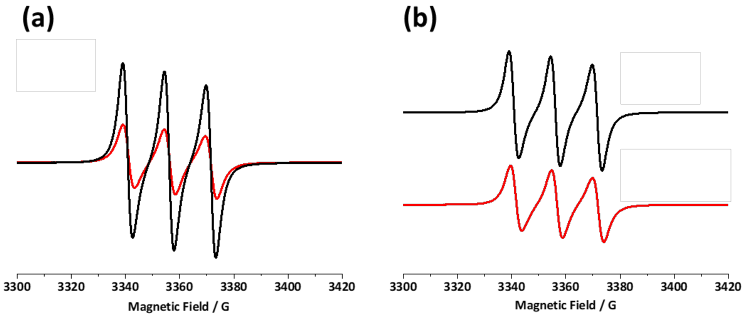


Fig. S24. ESR spectra of TEMPO-$^1O_2$ adducts for TNPP (red line) and PHP (black line) (left); PHP+benzylamine (red line) and PHP (black line) (right).

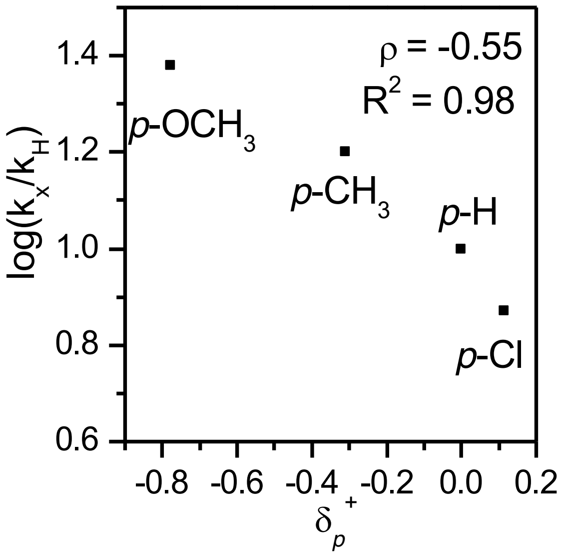


Fig. S25. Hammett plot for the oxidation of benzylamine and its para-substituted derivatives photocatalyzed by PHP.

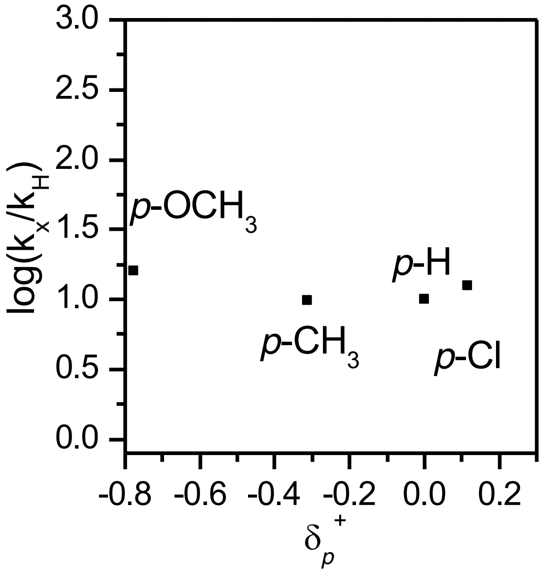


Fig. S26. Hammett plot for the oxidation of benzylamine and its para-substituted derivatives photocatalyzed by TNPP.

Table S3. Photocatalytic oxidative coupling reaction of benzylamine by PHP[a]

Entry	1	2	3	4	5[c]	6[d]	7[e]

PHP	+	+	-	+	+	+	+
hv	+	-	+	+	+	+	+
O_2	+	+	+	N_2	+	+	+
Yield (%)[b]	>99	trace	trace	-	29	64	23

[a] Reaction conditions: amine (1.0 mmol), O_2 (1 atm), cat. PHP (20 mg), CH_3CN (30.0 mL), λ > 420 nm, 3 h, 25 °C. [b] Determined by ^{1}H-NMR spectroscopic analysis. [c] KI as hole scavenger. [d] NaN_3 as single oxygen scavenger. [e] Benzoquinone (BQ) as superoxide scavenger.

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