Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Electronic Supplementary Information for

Construction of aggregation-induced emission photosensitizers based on supramolecular polymers for enhanced photocatalytic oxidative coupling of amines

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List of supplementary results.

Fig. S1 ^{1}H NMR spectra of TPE-DBr in $CDCl_3$.

Fig. S2 ^{1}H NMR spectra of TPE-Epy in DMSO-d_6.

Fig. S3 ^{13}C NMR spectra of TPE-Epy in DMSO-d_6.

Fig. S4 CIE chromaticity coordinates of TPE-Epy-CB[8] (from 0 to 1:1) ([TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M).

Fig. S5 (a) ^{1}H NMR spectra of TPE-Epy in DMSO-d_6; ^{1}H NMR spectra of (b) TPE-Epy, (c) TPE-Epy-CB[8], and (d) CB[8] in D_2O.

Fig. S6 The Job's plot of TPE-Epy-CB[8] (λ_{ex} = 410 nm) with the total concentration of TPE-Epy and CB[8] fixed at 2.0×10^{-5} M. Experimental conditions: [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

Fig. S7 Zeta potentials of (a) TPE-Epy and (b) TPE-Epy-CB[8].

Fig. S8 (a) UV-vis absorption spectra of ABDA in the absence of PSs under white light irradiation in aqueous solution. The absorption spectra of ABDA (1.6×10^{-4} M) after irradiation (white light) for different time in the presence of (b) TPE-Epy (2.0×10^{-5} M) and (c) TPE-Epy-CB[8] (2.0×10^{-5} M). [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

Fig. S9 The fluorescence emission spectra of DHE (1.6×10^{-4} M) after irradiation (white light) for different time in the presence of (a) TPE-Epy (2.0×10^{-5} M) and (b) TPE-Epy-CB[8] (2.0×10^{-5} M). [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

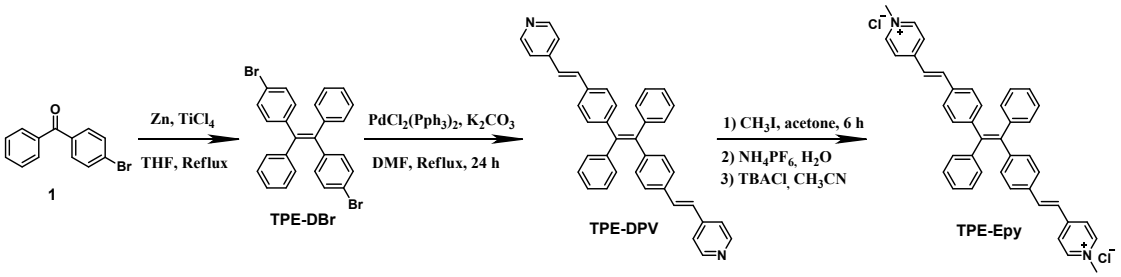
Fig. S10 ^{1}H NMR spectra of **2a** in $CDCl_3$.

Fig. S11 Control experiments of the photooxidation reaction in the presence of different scavengers of NaN_3, BQ, KI, and TEA.

1. Materials and instruments

Unless otherwise stated, the chemicals used are all purchased from reagent companies. ^{1}H NMR was characterized on Bruker Avance 400 NMR instrument. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. DLS and Zeta potential tests were constructed on Malvern Zeta sizer Nano ZS90. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 operating at 120 kV. Samples for TEM measurements were prepared by dropping the mixed aqueous solution on the carbon-coated copper grid (300 mesh) and drying by slow evaporation.

2. Synthesis of TPE-Epy



Scheme S1 The synthetic route of the TPE-Epy.

Synthesis of compound TPE-DBr: To a mixture of (4-bromophenyl)(phenyl)methanone (1.30 g, 5 mmol) and Zn (1.95 g, 30.0 mmol) in 100 mL dry THF was added dropwise $TiCl_4$ (1.65 mL, 15.0 mmol) under N_2 at 0 °C. The mixture was stirred at 0 °C for 30 min and another 2 h at room temperature Then the reaction mixture was refluxed overnight. After cooling down to room temperature, 10% K_2CO_3 (aq) was added and the mixture was filtered. The filtrates were extracted with dichloromethane and the extracts were washed with brine. After solvent removal under reduced pressure, the crude product was purified by column chromatography to afford TPE-DBr as white solid (0.93 g, 76 %).

Synthesis of compound TPE-DPV Tris-tolyl phosphine (150 mg, 0.57 mmol) and Dichlorobis(triphenyl-phosphine)palladium (50 mg, 0.07 mmol) and were introduced into a dry and degassed triethylamine/N,N-dimethylformamide (15 mL, v/v= 10:5) mixture, which was stirred for 15 min. The mixture was degassed again by gentle bubbling of nitrogen, and TPE-DBr (735 mg, 1.5 mmol) and 4-vinylpyridine (500 μL, 4.8 mmol) were added. The system was stirred at 90 ℃ under nitrogen for 8 h. The resulting mixture was allowed to cool to room temperature, and triethylamine was removed in vacuo. The crude mixture was diluted with dichloromethane and washed with water and saturated sodium bicarbonate, after concentration, the residue was purified by column chromatography. And then we can get the product TPE-DPV (461mg, 57 %).

3. General procedure for photooxidation reactions of benzylamine and its derivatives

The benzylamine (11 μL, 0.1 mmol) was dissolved in freshly prepared (2.0 mL, [TPE-Epy]=2.5 × 10^{-4} M, [CB[8]]=2.5 × 10^{-4} M). The mixture was subsequently irradiated with a white light (6000-6500 K) for 24 h at room temperature. Afterward, the organic product was extracted with ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4, the solvent removed by reduced pressure distillation. The fractions of the resulting oil were analyzed by ^1H NMR.

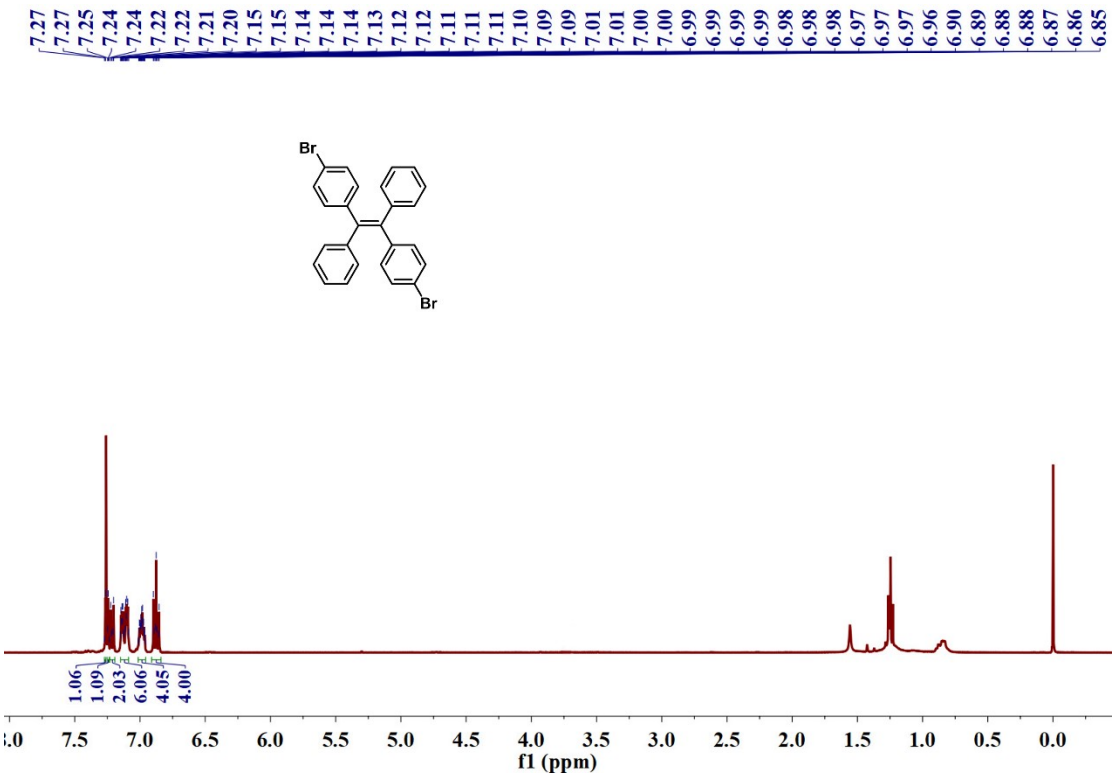


Fig. S1 ^{1}H NMR spectra of TPE-DBr in $CDCl_3$.

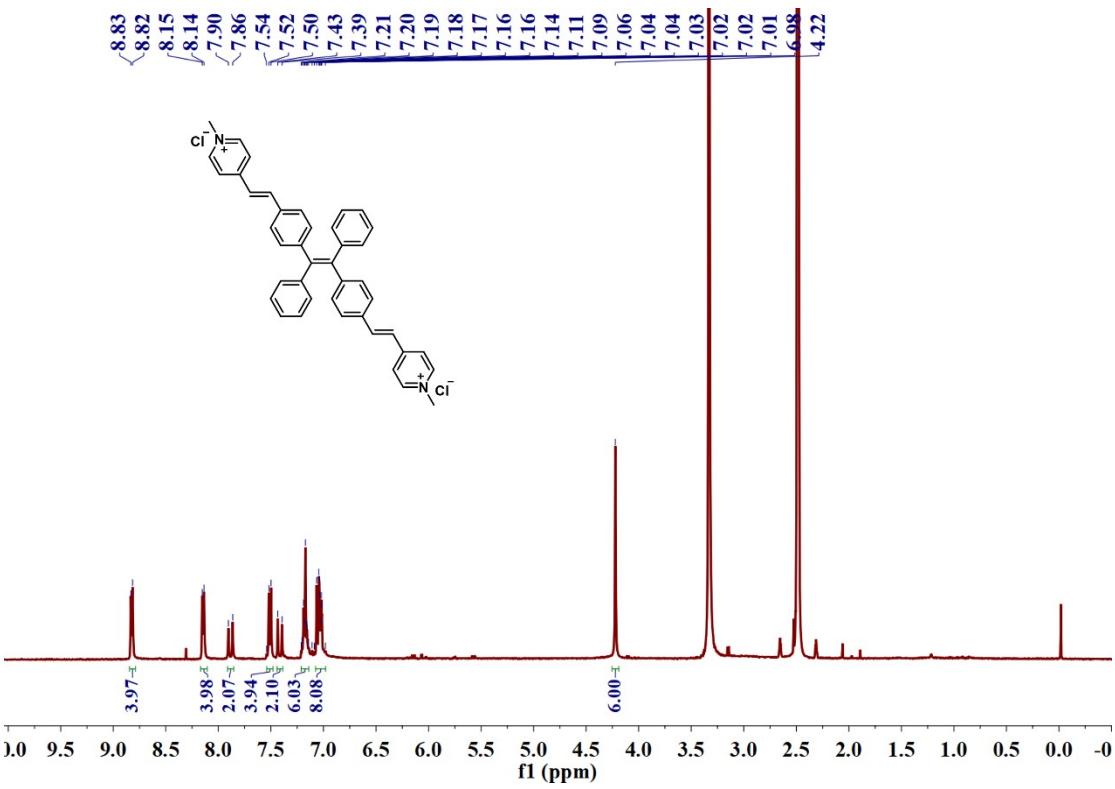


Fig. S2 ^{1}H NMR spectra of TPE-Epy in DMSO-d_6.

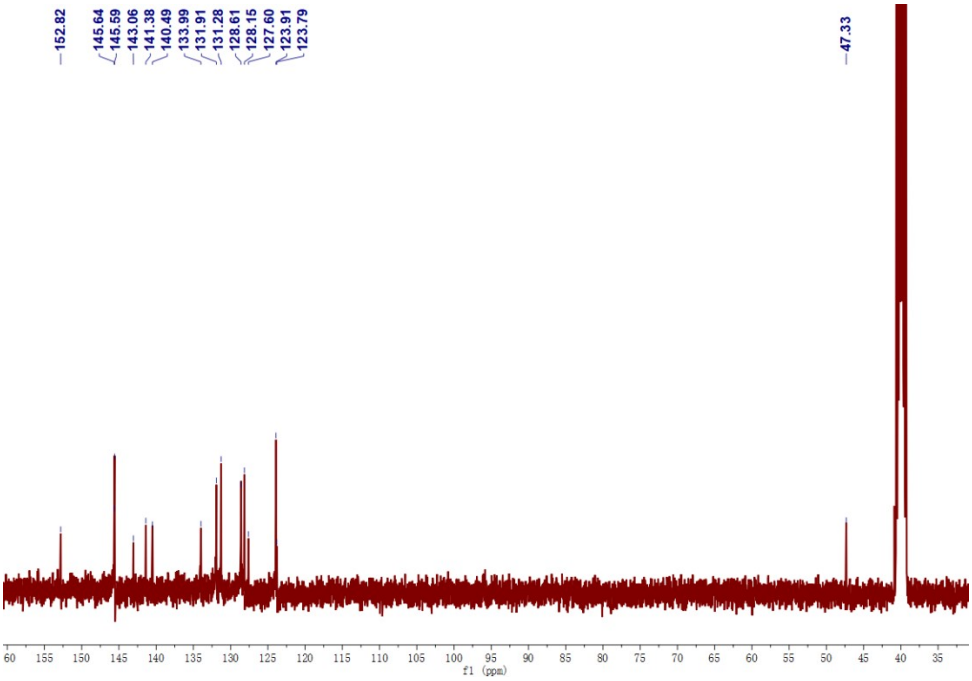


Fig. S3 ^{13}C NMR spectra of TPE-Epy in DMSO-d_6.

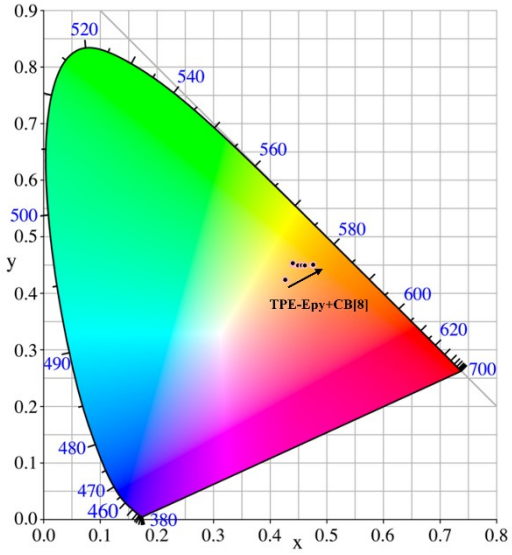


Fig. S4 CIE chromaticity coordinates of TPE-Epy-CB[8] (from 0 to 1:1) ([TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M).

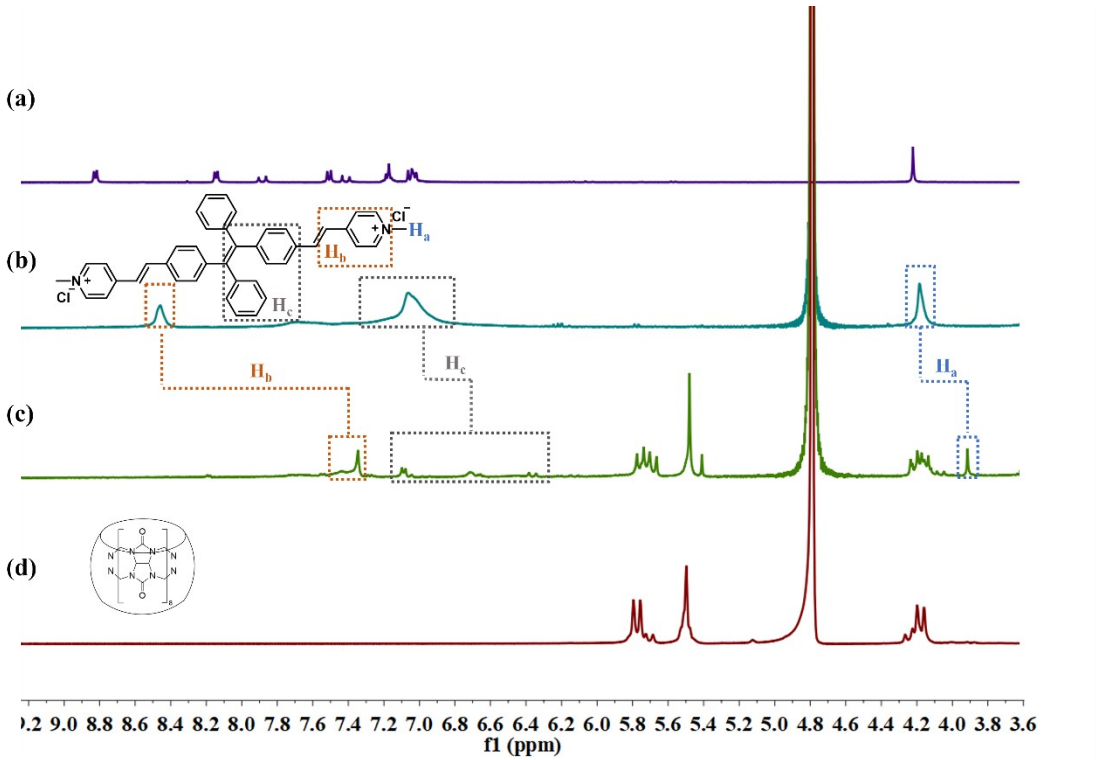


Fig. S5 (a) ^{1}H NMR spectra of TPE-Epy in DMSO-d_6; ^{1}H NMR spectra of (b) TPE-Epy, (c) TPE-Epy-CB[8], and (d) CB[8] in D_2O.

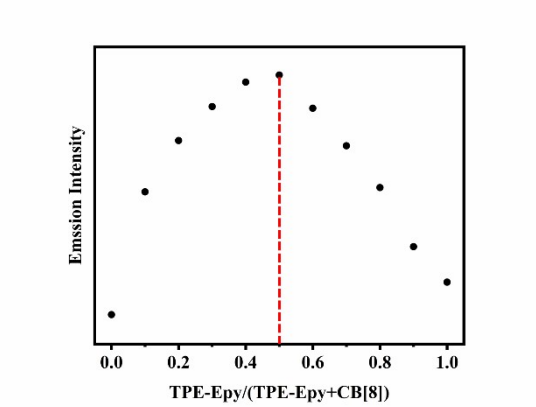


Fig. S6 The job's plots of TPE-Epy-CB[8] (λ_{ex} = 410 nm) with the total concentration of TPE-Epy and CB[8] fixed at 2.0×10^{-5} M. Experimental conditions: [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

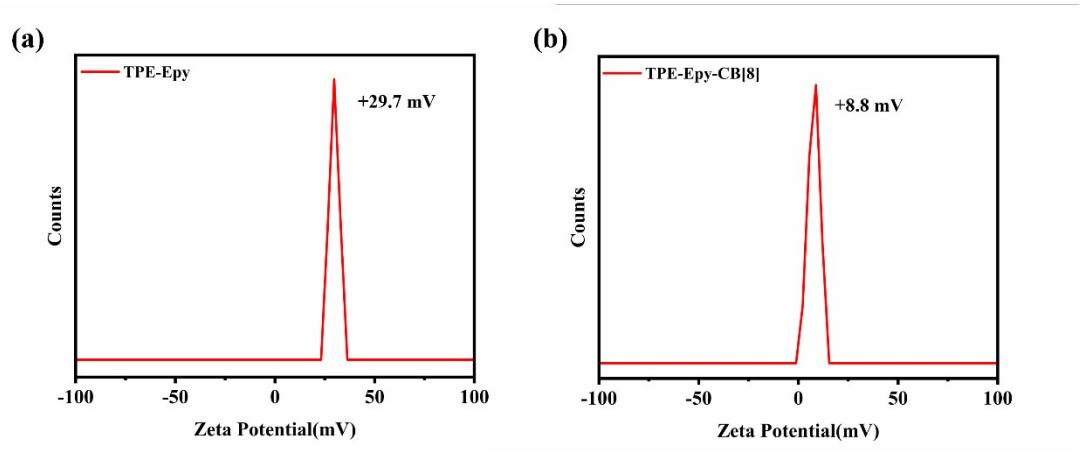


Fig. S7 Zeta potentials of (a) TPE-Epy and (b) TPE-Epy-CB[8].

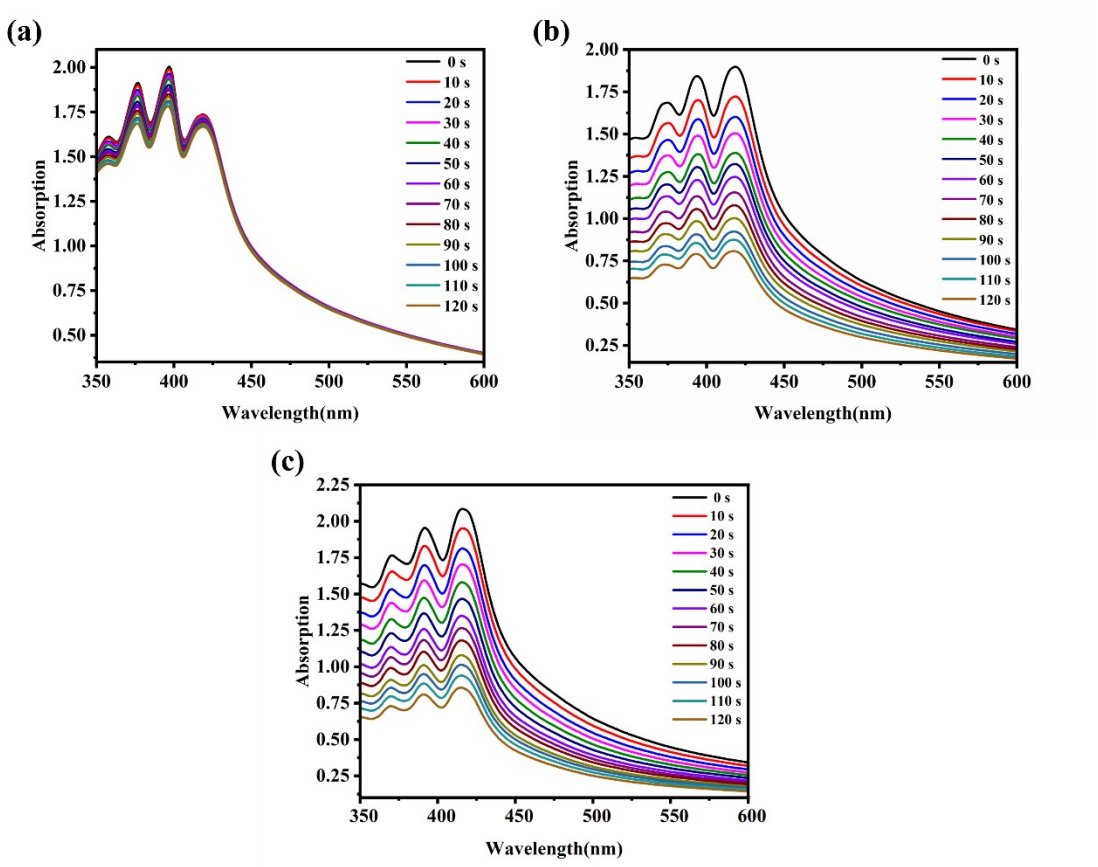


Fig. S8 (a) UV-vis absorption spectra of ABDA in the absence of PSs under white light irradiation in aqueous solution. The absorption spectra of ABDA (1.6×10^{-4} M) after irradiation (white light) for different time in the presence of (b) TPE-Epy (2.0×10^{-5} M) and (c) TPE-Epy-CB[8] (2.0×10^{-5} M). [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

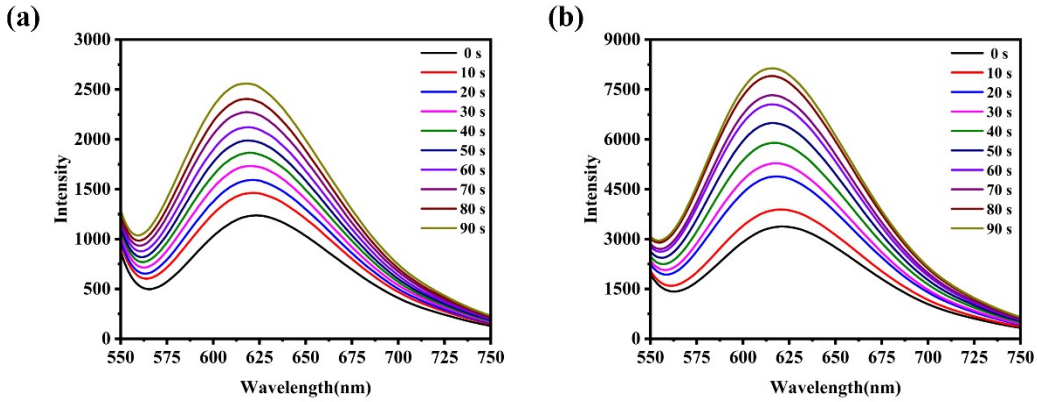


Fig. S9 Fluorescence emission spectra of DHE (1.6×10^{-4} M) after irradiation (white light) for different time in the presence of (a) TPE-Epy (2.0×10^{-5} M) and (v) TPE-Epy-CB[8] (2.0×10^{-5} M). [TPE-Epy] = 2.0×10^{-5} M, [CB[8]] = 1.5×10^{-3} M.

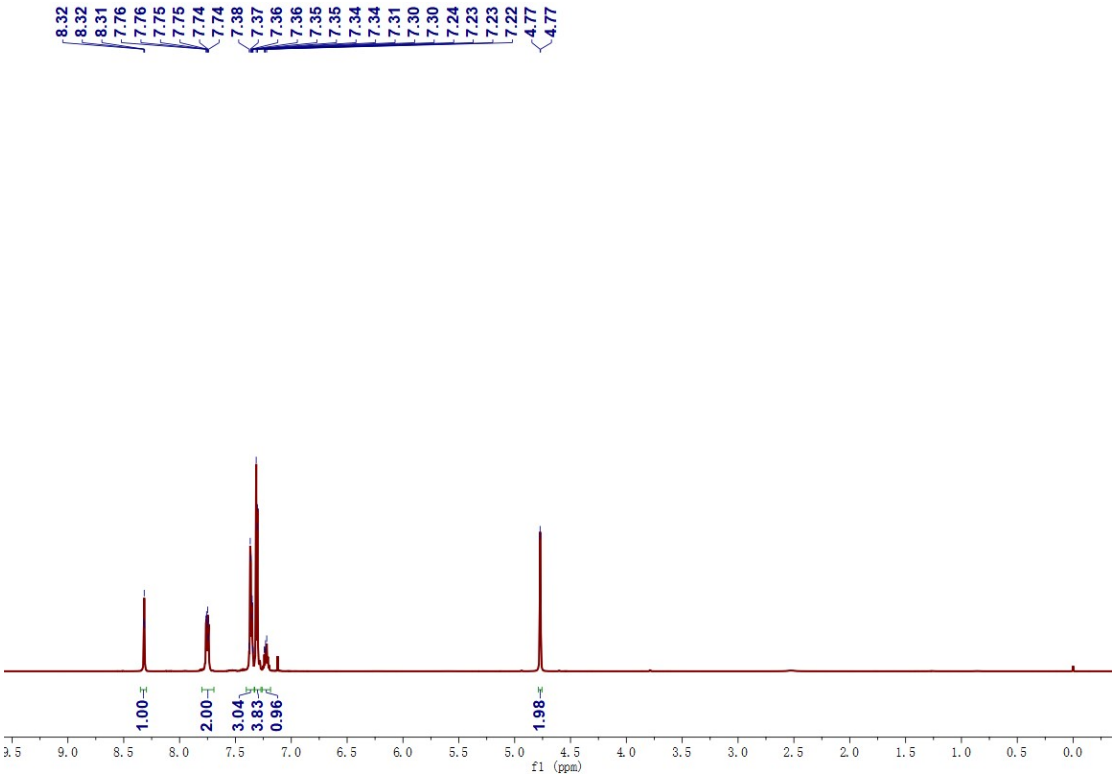


Fig. S10 ^{1}H NMR spectra of **2a** in $CDCl_3$.

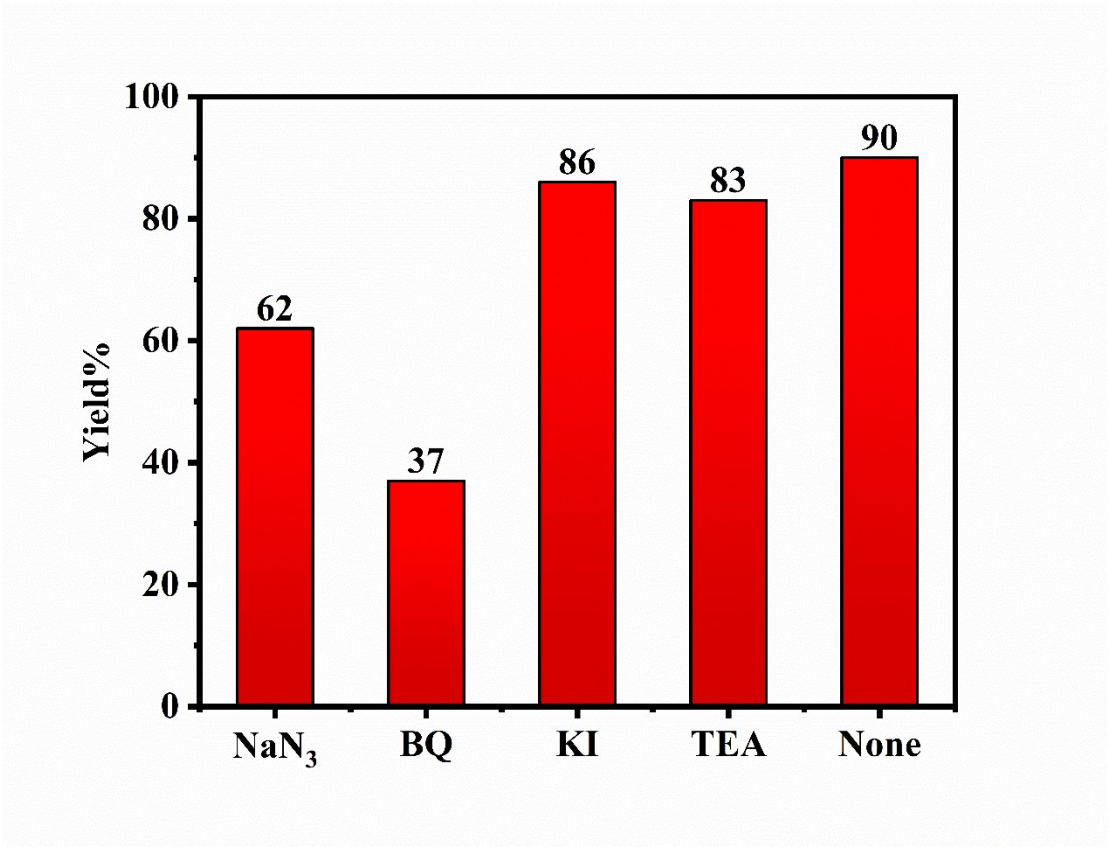
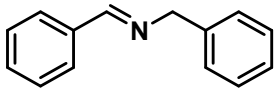


Fig. S11 Control experiments of the photooxidation reactions in the presence of different scavengers of NaN_3, BQ, KI, and TEA.

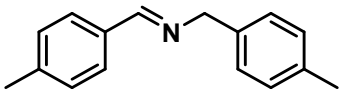
^{1}H NMR data of 2a-2l

2a. benzyl-1-phenylmethanimine



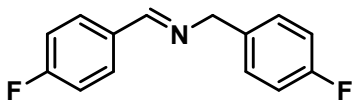
90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.5 Hz, 1H), 7.80 – 7.69 (m, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.27 (m, 4H), 7.26 – 7.19 (m, 1H), 4.77 (d, *J* = 1.5 Hz, 2H).

2b. 4-methylbenzyl-1-(p-tolyl)methanimine



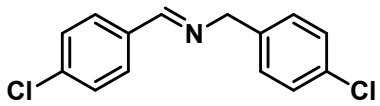
80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.15 (s, 2H), 7.09 (s, 2H), 4.69 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H).

2c. 4-fluorobenzyl-1-(4-fluorophenyl)methanimine



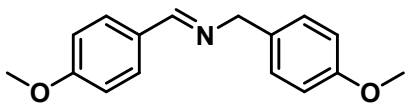
84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.67 (d, *J* = 19.0 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.10 – 7.06 (m, 4H), 4.78 (s, 2H).

2d. 4-chlorobenzyl-1-(4-chlorophenyl)methanimine



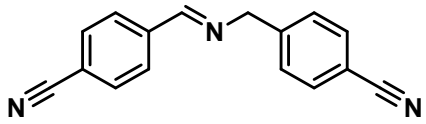
58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.30 (d, *J* = 5.7 Hz, 4H), 4.77 (s, 2H).

2e. 4-methoxybenzyl-1-(4-methoxyphenyl)methanimine



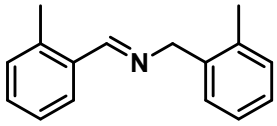
86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 4H), 4.73 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H).

2f. 4-(((4-cyanobenzyl)imino)methyl)benzonitrile



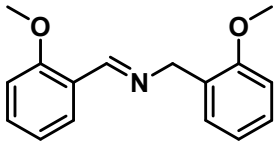
79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.72 – 7.69 (m, 2H), 7.35 (d, *J* = 2.0 Hz, 4H), 7.27 (d, *J* = 1.0 Hz, 2H), 4.75 (s, 2H).

2g. 2-methylbenzyl-1-(o-tolyl)methanimine



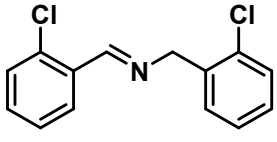
69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.19 (d, *J* = 2.8 Hz, 7H), 4.80 (m, 2H), 2.51 (s, 3H), 2.39 (s, 3H).

2h. 2-methoxybenzyl-1-(2-methoxyphenyl)methanimine



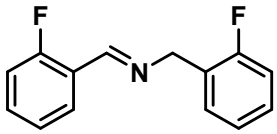
63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.82 (m, 2H), 7.74 – 7.61 (m, 2H), 7.16 (m, 2H), 6.85 (m, 2H), 4.80 (m, 2H), 3.82 (s, 3H), 3.72 (s, 3H).

2i. 2-chlorobenzyl-1-(2-chlorophenyl)methanimine



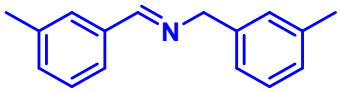
87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.75 (m, 2H), 7.60 (m, 2H), 7.10 - 7.18 (m, 4H),4.80 (m, 2H).

2j. 2-fluorobenzyl-1-(2-fluorophenyl)methanimine



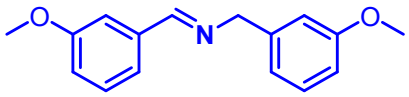
81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.05 – 8.01 (m, 1H), 7.43 – 7.35 (m, 4H), 7.21 – 7.13 (m, 3H), 4.88 (s, 2H).

2k. 3-methylbenzyl-1-(m-tolyl)methanimine



90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.90 – 7.44 (m, 4H), 7.14 (d, *J* = 5.5 Hz, 4H), 4.78 (s, 2H), 2.40 (m, 3H), 2.34 (s, 3H).

2l. 3-methoxybenzyl-1-(3-methoxyphenyl)methanimine



63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (m, 1H), 7.41 – 7.35 (m, 2H), 7.30 (s, 2H), 7.23 (s, 2H), 7.00 – 6.96 (m, 2H), 4.80 (s, 2H), 3.76 (s, 3H). 3.70 (s, 3H).