

Electronic Supporting Information

A hydrophilic covalent organic framework for photocatalytic oxidation of benzylamine in water

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Section 1. Materials

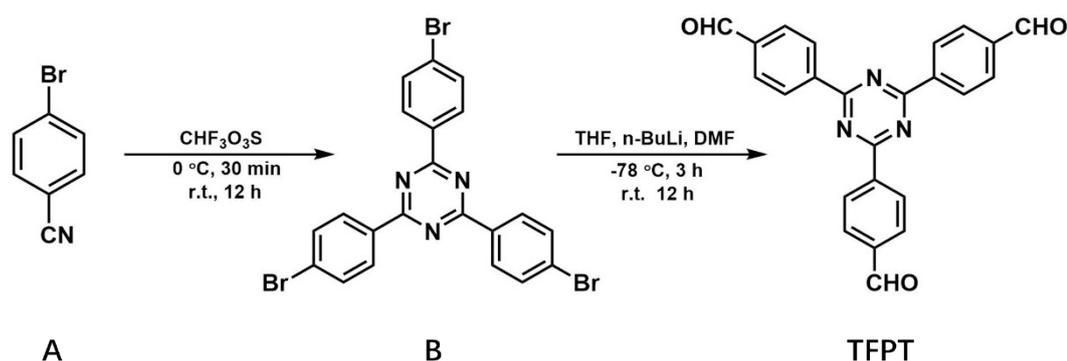
All chemicals were obtained from commercial sources without further purification. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 98%) were purchased from Aladdin Industrial Inc. Ethylenediaminetetraacetic acid disodium salt (EDTA-Na⁺, 99%), benzoquinone (AR), sodium azide (NaN₃, AR) were purchased from Macklin Inc. *N*-Butyllithium (99%) was purchased from J&K Ltd.

Section 2. Instruments

¹H and ¹³C spectra were obtained by using Bruker AVANCE-400 NMR spectrometer. Powder X-ray diffraction (PXRD) data were collected using a PANalytical B. V. Empyrean by depositing powder on a glass substrate. The nitrogen adsorption and desorption isotherms were performed at 77 K with a Micromeritics ASAP 2020M system. Surface areas were calculated using Langmuir and Brunauer–Emmett–Teller (BET) methods, respectively. The pore-size-distribution curves were calculated from nitrogen adsorption isotherms using nonlocal density functional theory (NLDFT). Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8000 microscope. Transmission electron microscopy (TEM) images were obtained with a Tecnai G2 S–Twin F20 field-emission transmission electron microscope. ¹³C CP-MAS NMR measurements were carried out using a Bruker Avance III 400WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. FT–IR spectra analyses were performed using a Bruker IFS66 V spectrometer from 400 to 4000 cm⁻¹ by using KBr pellets. Solid-state UV/Vis absorption spectroscopy was analyzed using a Shimadzu U–4100 UV–Vis–NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) and XPS valance band analyses were carried out on a Thermo ESCALAB 250 XPS spectrometer. Photoluminescence, fluorescence quantum yield and luminescence lifetime were performed with a FLS920 spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA–Q500 thermogravimeter by measuring the weight loss under nitrogen. Electron paramagnetic resonance (EPR) spectra were recorded on JEOL JES–FA200 EPR spectrometer.

Section 3. Synthesis

1. Synthesis of TFPT^[1]



a) Synthesis of B

3.54 mL (6 g, 40 mmol) trifluoromethanesulfonic acid was slowly added to 4 g (22 mmol) of **A** at $0\text{ }^\circ\text{C}$ and stirred for 30 min. It was further stirred at room temperature overnight. The resulting mixture was washed with 100 mL of deionized water and filtered under vacuum. Purification of the product afforded 3.95 g of white solid in a yield of 99%.

b) Synthesis of TFPT

1.46 g **B** (3 mmol) was dissolved in dry THF (250 mL) under a N_2 atmosphere. 12 mL n-BuLi (30 mmol) was added dropwise in the stirred solution at $-78\text{ }^\circ\text{C}$. After stirring for 3 h, DMF (5 mL) was added to the obtained red solution at $-78\text{ }^\circ\text{C}$ and the reaction mixture was further stirred for 12 h at room temperature. The mixture was acidified with 3 M HCl aqueous solution (50 mL). The organic volatiles were partially removed by evaporation under reduced pressure, and the product was extracted with CHCl_3 . The organic layer was washed with brine, dried over NaSO_4 , and concentrated in vacuo. Recrystallization of the mixture in the mixed petroleum ether and CH_2Cl_2 to afford TFPT as white solid with a yield of 56%.

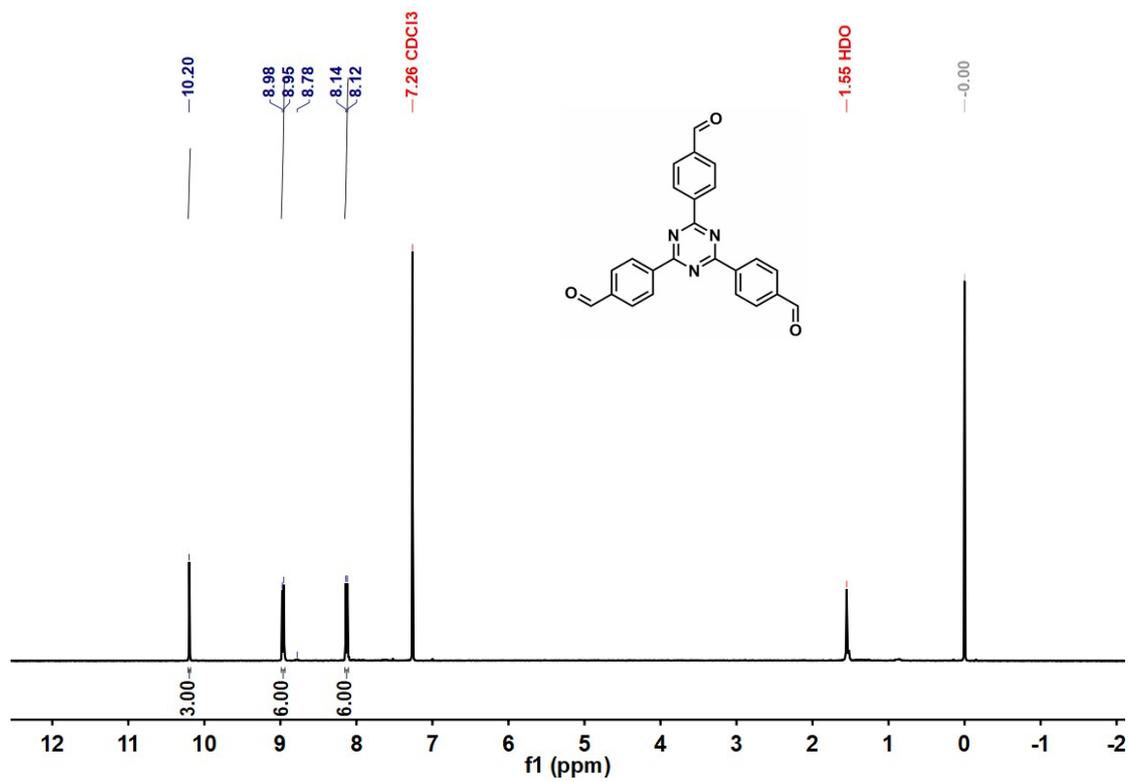
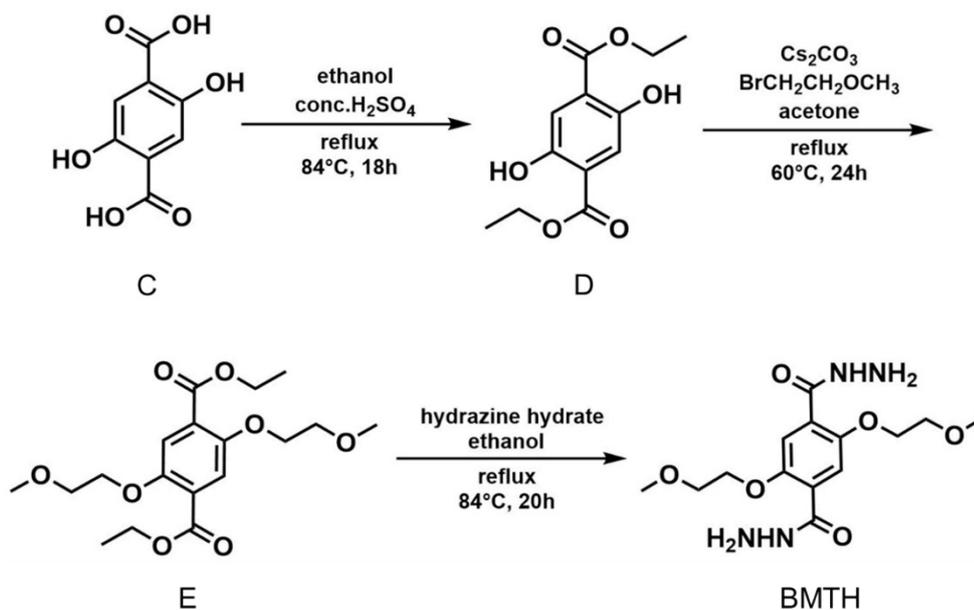


Figure S1. ^1H NMR spectrum of TFPT.

2. Synthesis of BMTH^[2]

a) Synthesis of D



A solution of **C** (3 g, 15.2 mmol) in ethanol (60 mL) was added carefully to conc. H₂SO₄ (12 mL) and reflux at 84 °C for 18 h. The mixture was filtered and washed with iced water. The product was dried, and collected with a yield of 97%.

b) Synthesis of E

D (1.20 g, 4.76 mmol), Cs₂CO₃ (10.41 g, 31.90 mmol) and 2-bromoethyl methyl ether (1.39 g, 10.00 mmol) were suspended in acetone (42 mL). The mixture was refluxed at 60 °C until starting material disappear (monitored by TLC). The mixture was filtered and the solvent evaporated. The residue was dissolved in CH₂Cl₂, washed with water and then dried over Na₂SO₄. The solvent was removed under reduced pressure, giving crude product. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, v/v=6:1) to obtain target product as a white solid with a yield of 54%.

c) Synthesis of BMTH

E (0.85 mg, 2.3 mmol), hydrazine hydrate (21.6 mL, 61.9 mmol) and ethanol (36 mL, 48.4 mmol) were added in a flask and reflux at 84 °C for 20 h. The mixture was cooled to -15 °C, and then the product was filtered and dried under reduced pressure to yield a white solid with a yield of 94%.

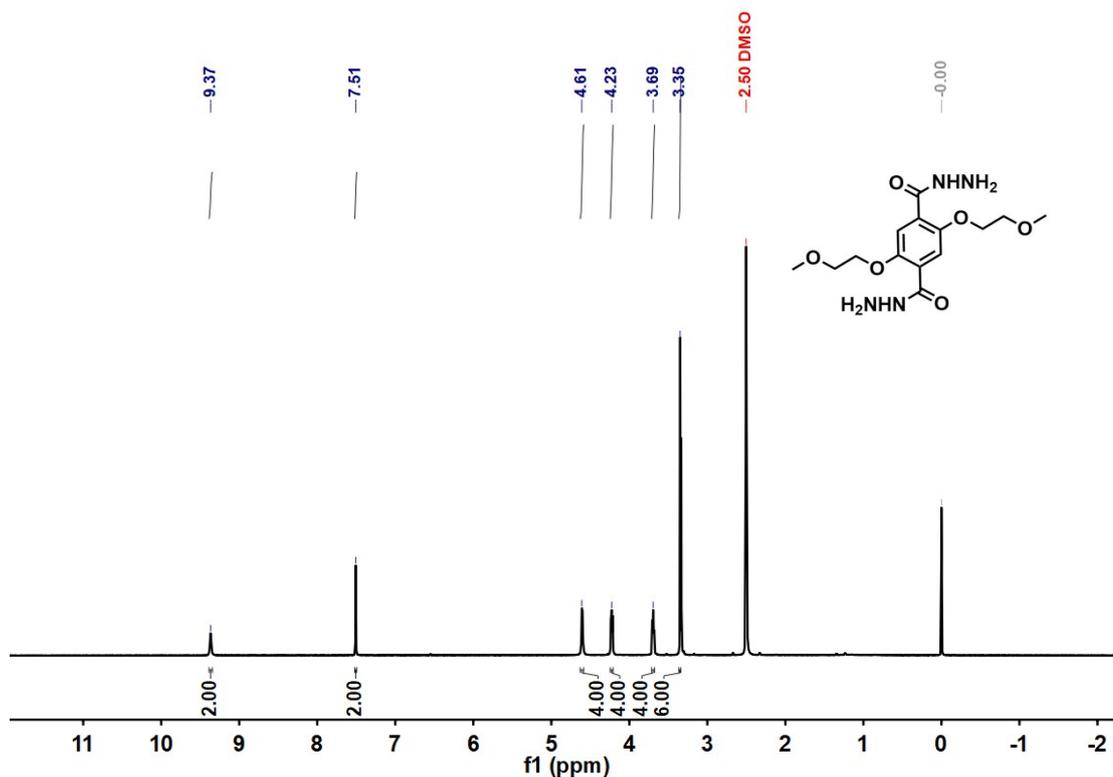
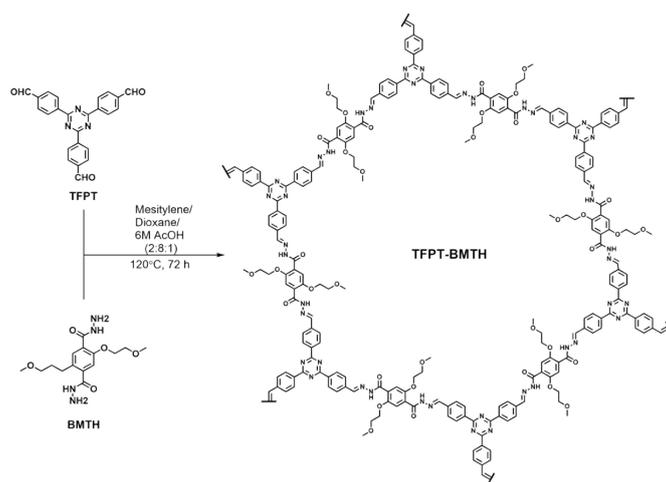


Figure S2. ¹H NMR spectrum of **BMTH**.

3. Synthesis of TFPT-BMTH

A tube was charged with **TFPT** (30.1 mg), **BMTH** (23.1 mg), mesitylene (0.8 mL) and 1,4-dioxane (0.2 mL), and then immersed in ultrasonic bath for 2 min. The solution of 0.1 mL 6 M acetic acid was added to the tube. The tube was flash frozen at 77 K in liquid nitrogen and evacuated to the internal pressure of ~ 100 mTorr, and then the tube was sealed. The reaction mixture was then placed to static oven and heated to 120 °C and kept for 3 days. After cooling down to room temperature, the resulting mixture was washed with THF (30 mL) and acetone (30 mL). After filtration, the product was dried at 60 °C under vacuum to give **TFPT-BMTH** as a fluffy yellow powder.



Scheme S1 Synthesis of TFPT-BMTH

Section 4. Photocatalytic Experiments

General Procedure for the Photo-oxidative Coupling of Benzylamine and Derivatives

TFPT-BMTH (5 mmol%, 5.6 mg) was added to a glass vial with 0.2 mmol substrate dissolved in 5 mL H₂O. Then the suspension was irradiated for 24 h at room temperature under a irradiation of blue LED lamp (30 W, $\lambda=454$ nm). After removing the catalyst, the resulting mixture was analyzed by ¹H NMR spectroscopy using CDCl₃ as solvent.

Section 5. Characterization and analysis

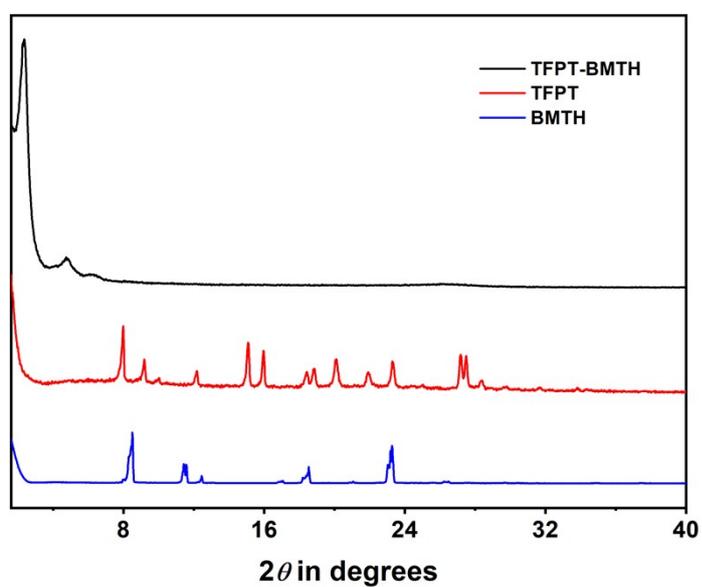
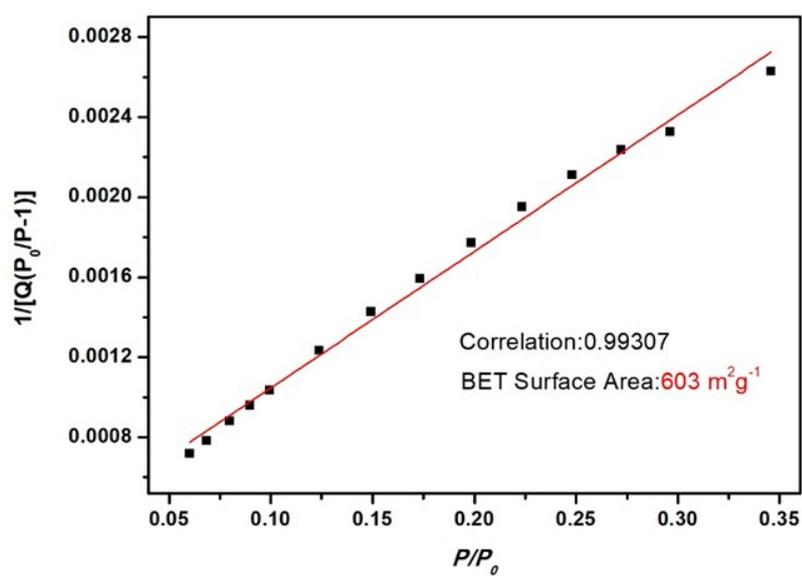


Figure S3. PXRD patterns of **TFPT-BMTH**, **TFPT** and **BMTH**.

Figure S4. BET surface area plot for **TFPT-BMTH**.



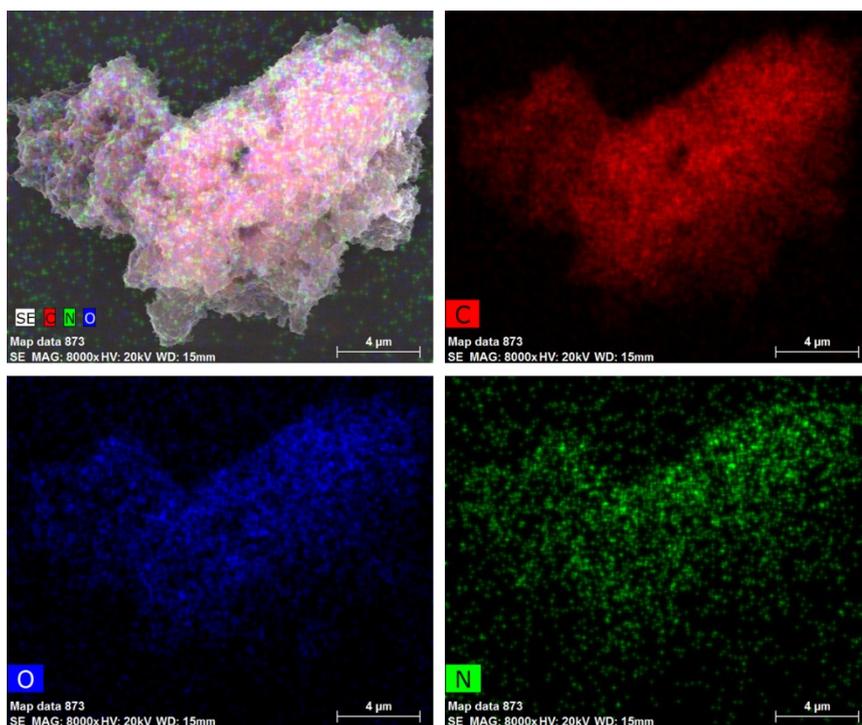


Figure S5. EDS images of TFPT-BMTH.

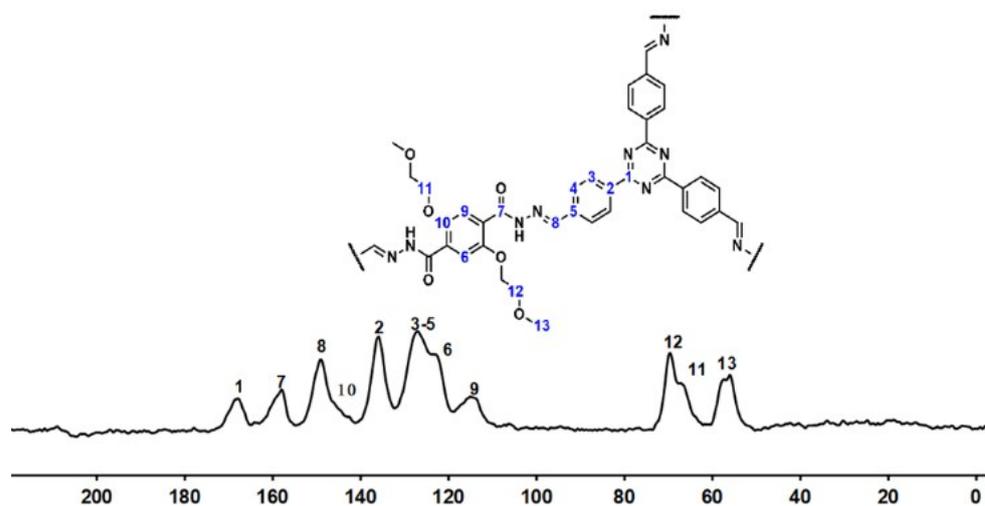
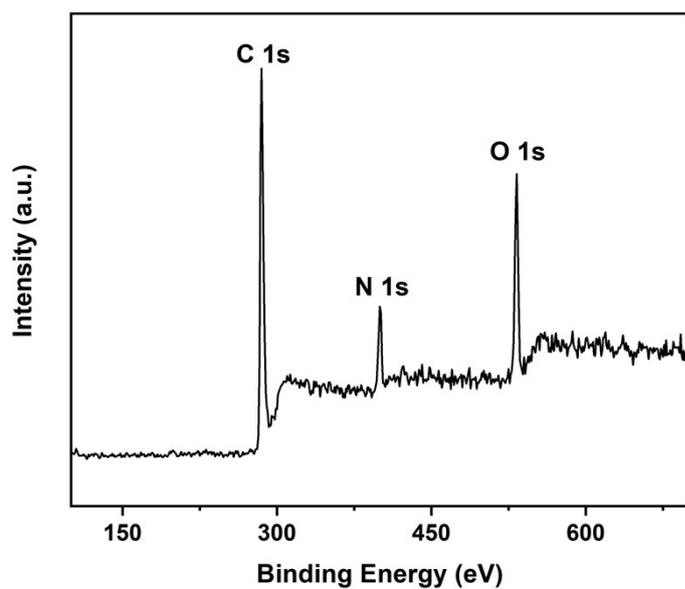


Figure S6. ^{13}C CP-MAS NMR spectrum of TFPT-BMTH. The assignments of the signals are indicated in the chemical structure of TFPT-BMTH.



1s

Figure S7. Survey XPS spectrum of TFPT-BMTH.

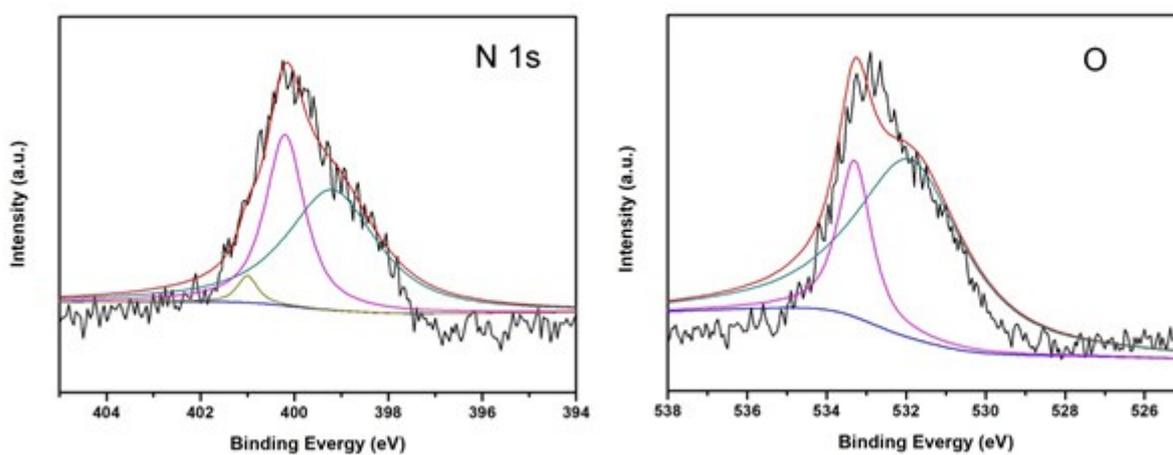


Figure S8. XPS spectra in the N 1s (left) region and O 1s (right) region of TFPT-BMTH.

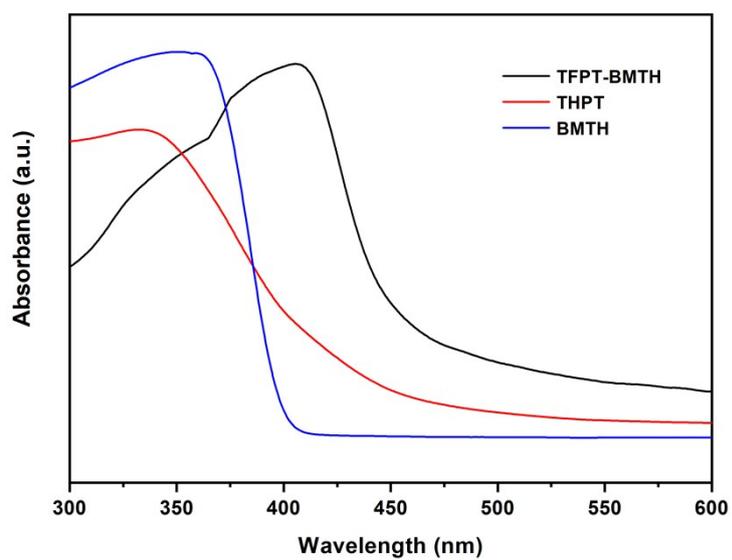


Figure S9. UV/Vis absorption spectra of **TFPT-BMTH**, **TFPT** and **BMTH**.

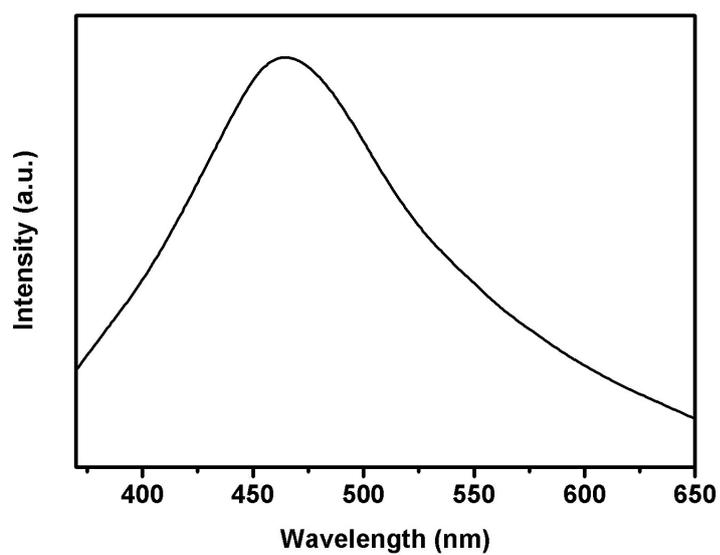


Figure S10. Fluorescence spectrum of **TFPT-BMTH**.

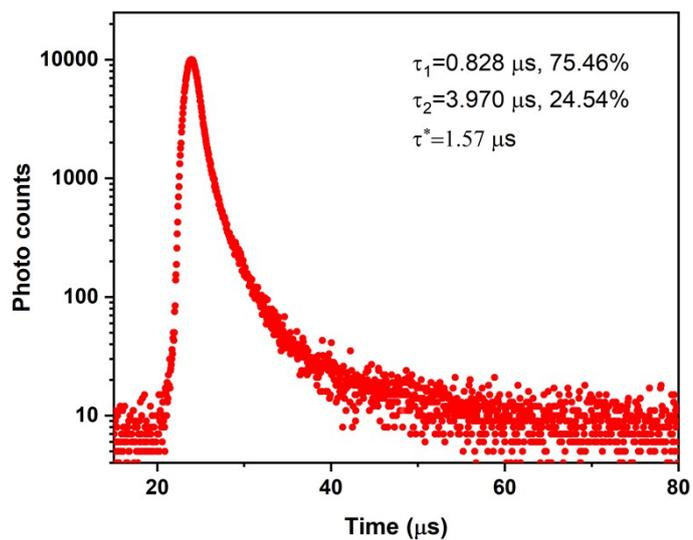


Figure S11. Luminescence lifetime for **TFPT-BMTH** dispersed in H_2O under air atmosphere. The luminescence lifetimes τ_1 and τ_2 are $0.828 \mu\text{s}$ (75.46%) and $3.970 \mu\text{s}$ (24.54%), the pre-exponential factors B1 and B2 are 9519.101 and 644.902, the average lifetime (τ^*) is $1.57 \mu\text{s}$. ($\tau^* = 75.46\% \tau_1 + 24.54\% \tau_2$)

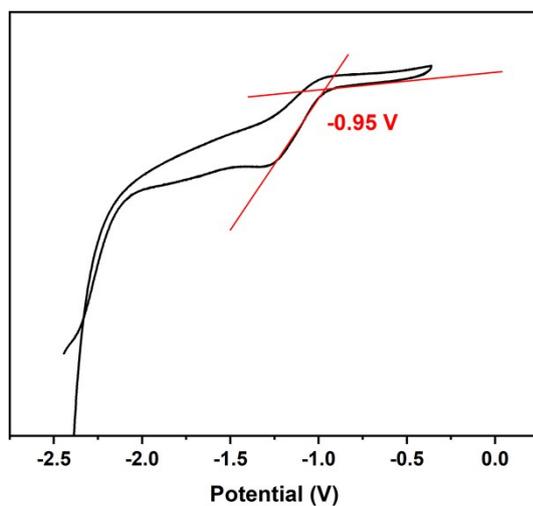
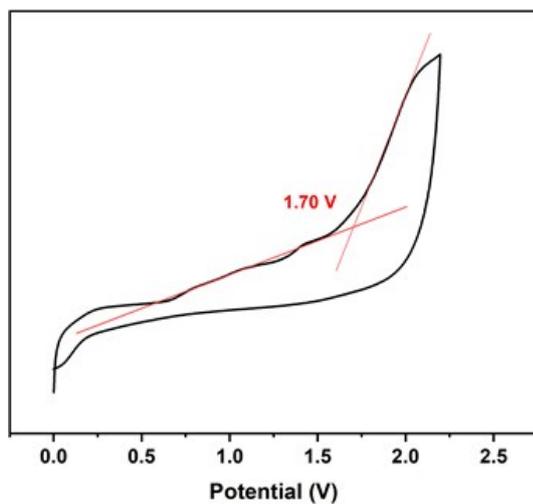


Figure S12. Cyclic voltammograms of TFPT-BMTH.

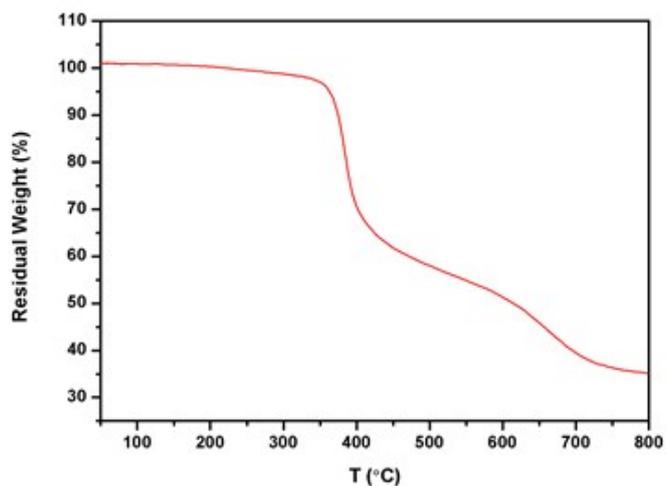


Figure S13. TGA curve of TFPT-BMTH.

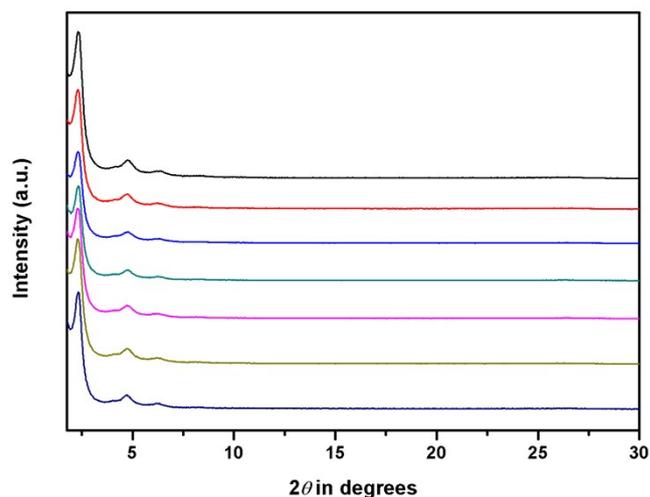


Figure S14. PXRD of **TFPT-BMTH** treated in different solvents. The same amount of **TFPT-BMTH** is immersed in different solvents for 12 hours at room temperature. Subsequently, the **TFPT-BMTH** was filtered and washed with a large amount of water and tetrahydrofuran, and finally dried for at 60 °C under vacuum for 3 hours. From top to bottom, THF, hexane, CHCl_3 , toluene, H_2O (pH=1), H_2O (pH=7), H_2O (pH=13).

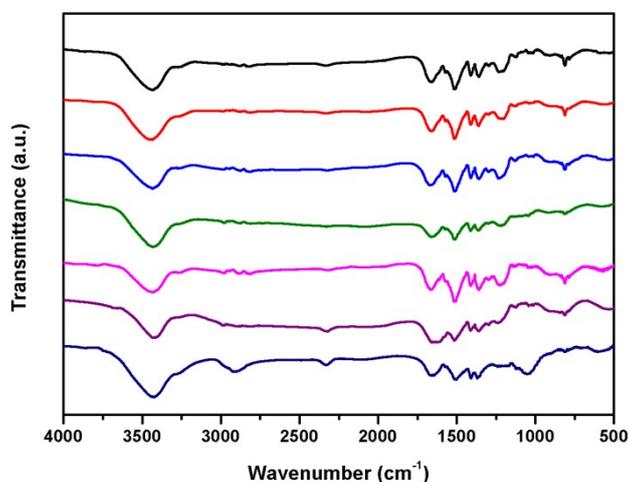


Figure S15. FT-IR spectra of **TFPT-BMTH** treated in different solvents. The same amount of **TFPT-BMTH** is immersed in different solvents for 12 hours at room temperature. Subsequently, the **TFPT-BMTH** was filtered and washed with a large amount of water and tetrahydrofuran, and finally dried for at 60 °C under vacuum for 3 hours. From top to bottom, THF, hexane, CHCl_3 , toluene, H_2O (pH=1), H_2O (pH=7), H_2O (pH=13).

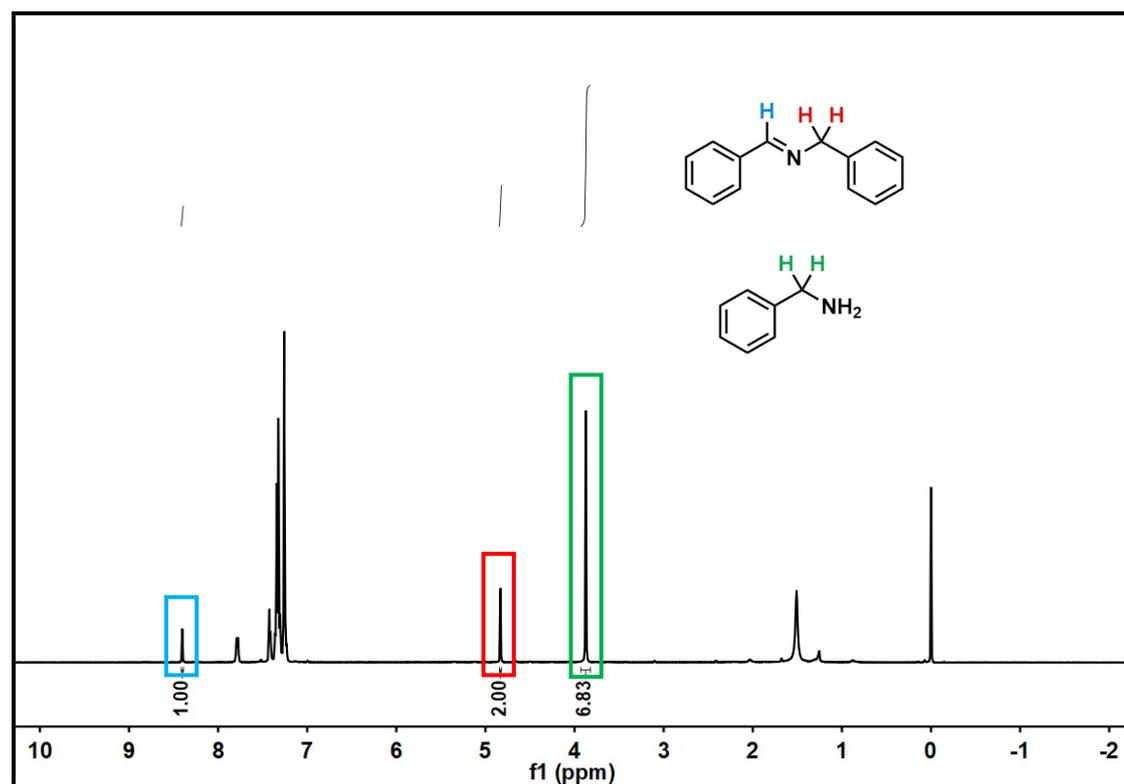
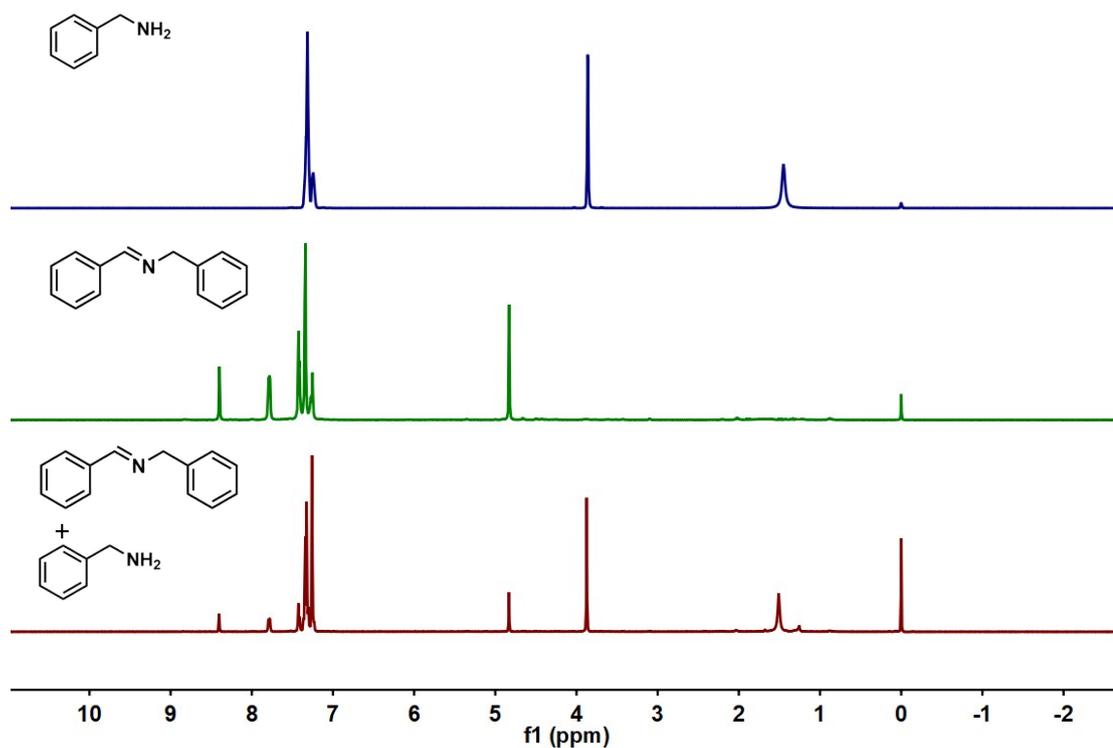


Figure S16. ^1H NMR spectra of benzylamine, benzylimine and the mixture of the photo-oxidation of benzylamine (Table S10, entry 10). The conversion is 37%.

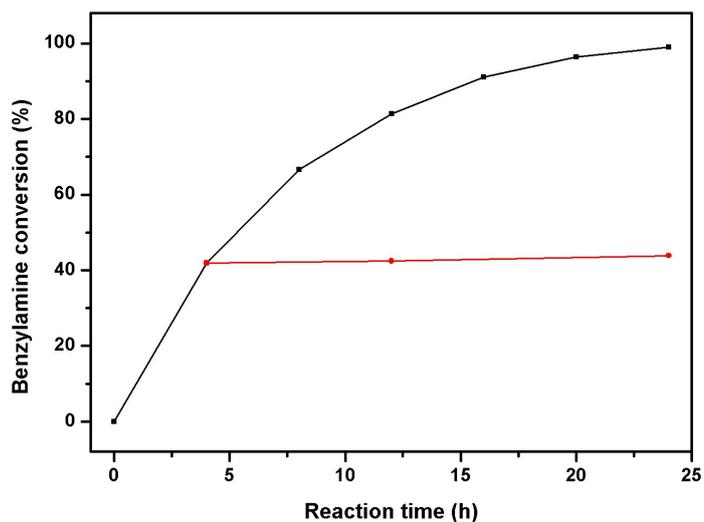


Figure S17. Kinetic profile for the photocatalytic oxidation of benzylamine (black line). After 4 hours, the **TFPT-BMTH** was filtered, and the filtrate was monitored for further reaction (red line).

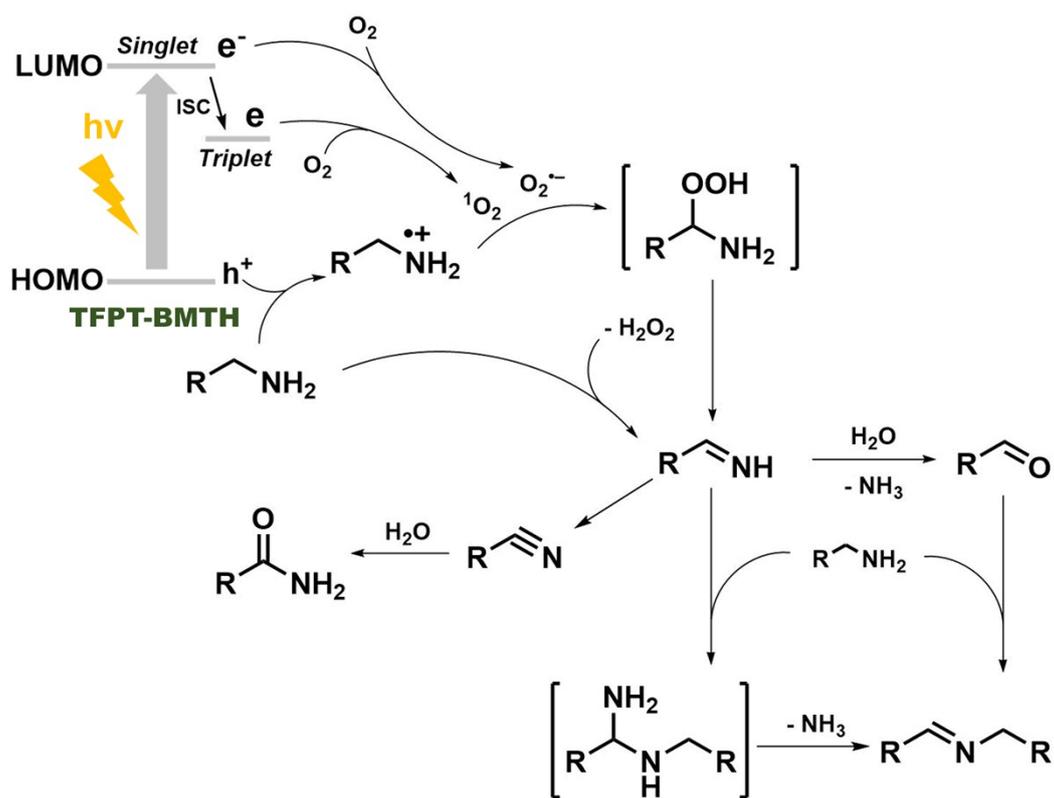


Figure S18. Proposed reaction mechanism of the photocatalytic oxidative coupling of benzylamine.

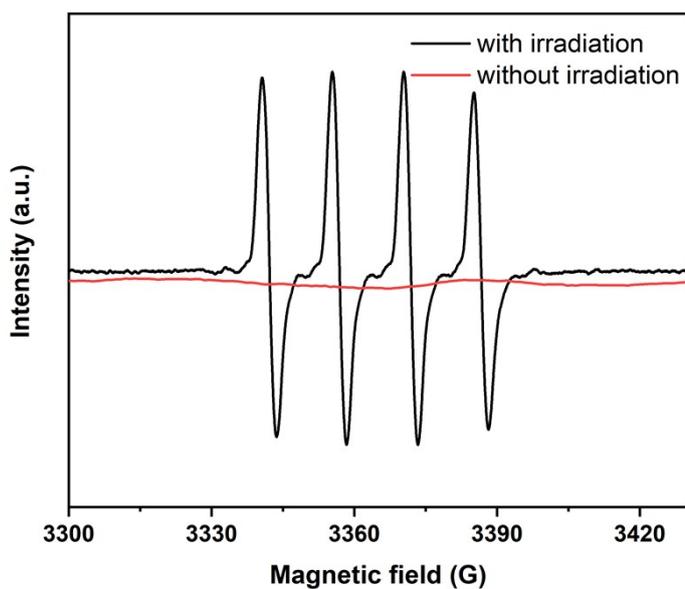


Figure S19. EPR spectra of $\text{DMPO-O}_2^{\bullet-}$. Room temperature EPR spectra of a solution of **TFPT-BMTH** in air-saturated H_2O (1.12 mg mL^{-1}) in the presence of DMPO (0.02 M) with irradiation for 10 min (black line) and without irradiation (red line).

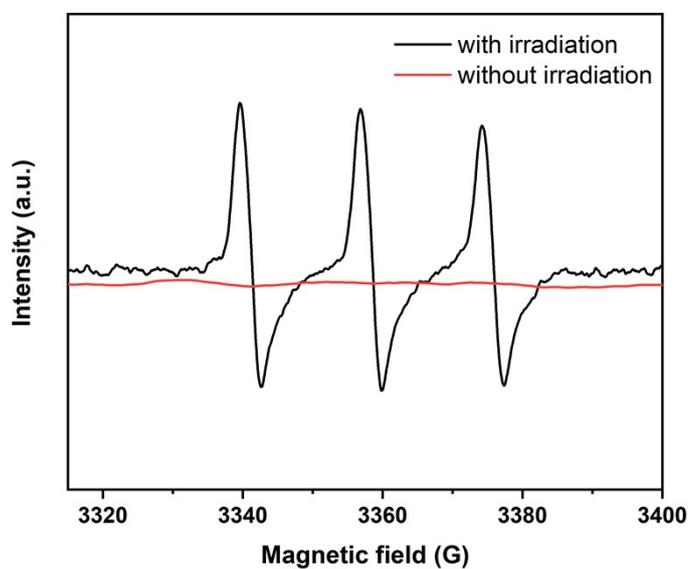


Figure S20. EPR spectra of $\text{TEMPO-}^1\text{O}_2$. Room temperature EPR spectra of a solution of **TFPT-BMTH** in air-saturated H_2O (1.12 mg mL^{-1}) in the presence of TEMPO (0.02 M) with irradiation for 10 min (black line) and without irradiation (red line).

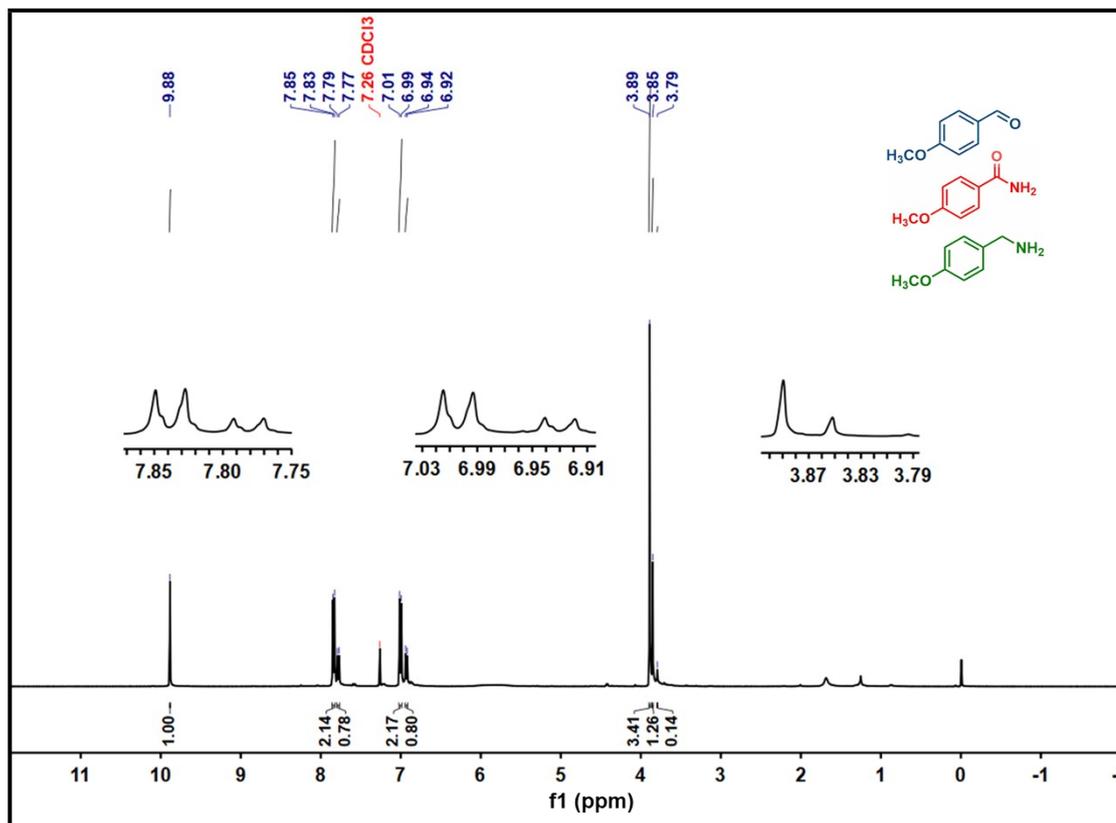


Figure S21. ¹H NMR spectrum of the product obtained by photocatalytic oxidation of *p*-methoxybenzylamine. NOTE: blue peaks are assigned to *p*-methoxybenzaldehyde, red peaks are assigned to *p*-methoxybenzamide, green peak is associated to residual *p*-methoxybenzylamine.

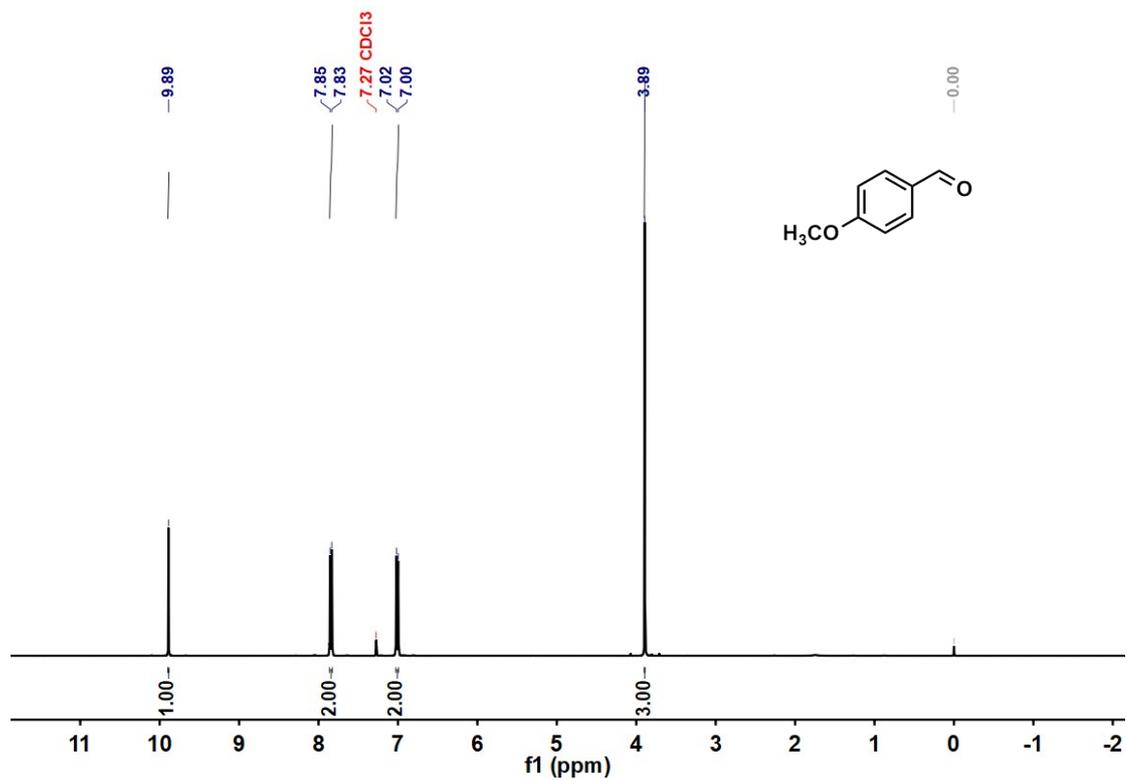


Figure S22. ^1H NMR spectrum of *p*-methoxybenzaldehyde obtained by column chromatography separation of the resulting mixture.

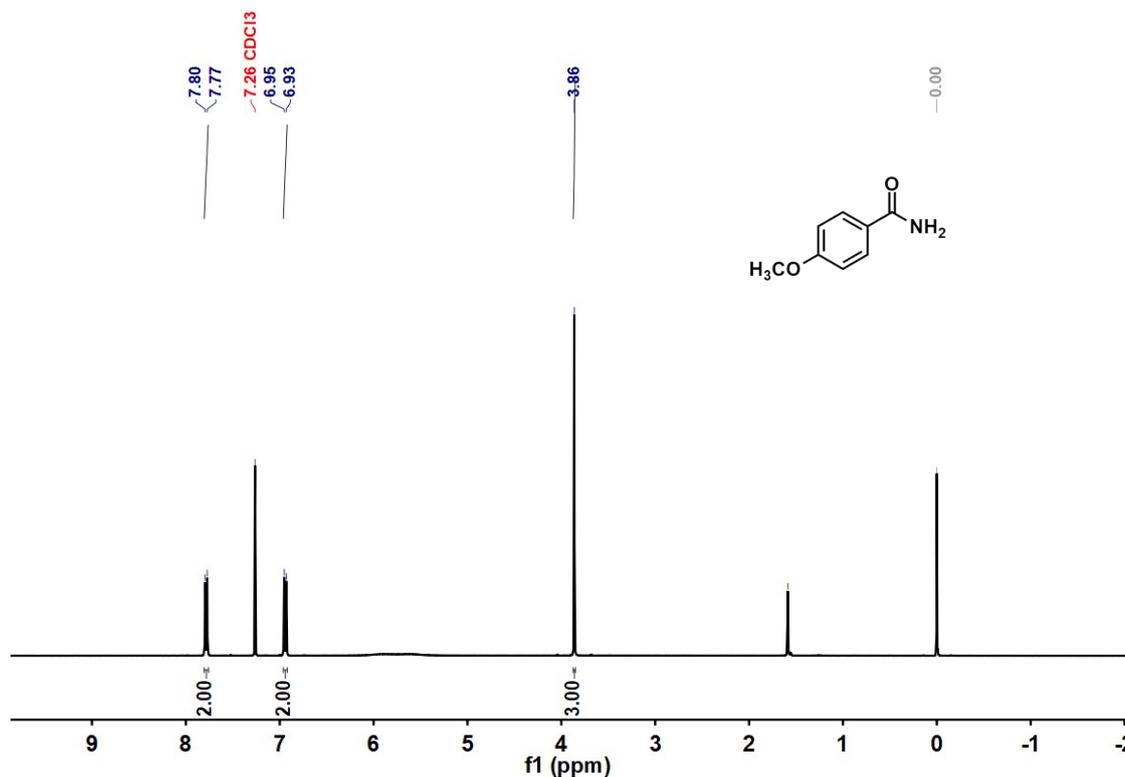


Figure S23. ¹H NMR spectrum of *p*-methoxybenzamide obtained by column chromatography separation of the resulting mixture.

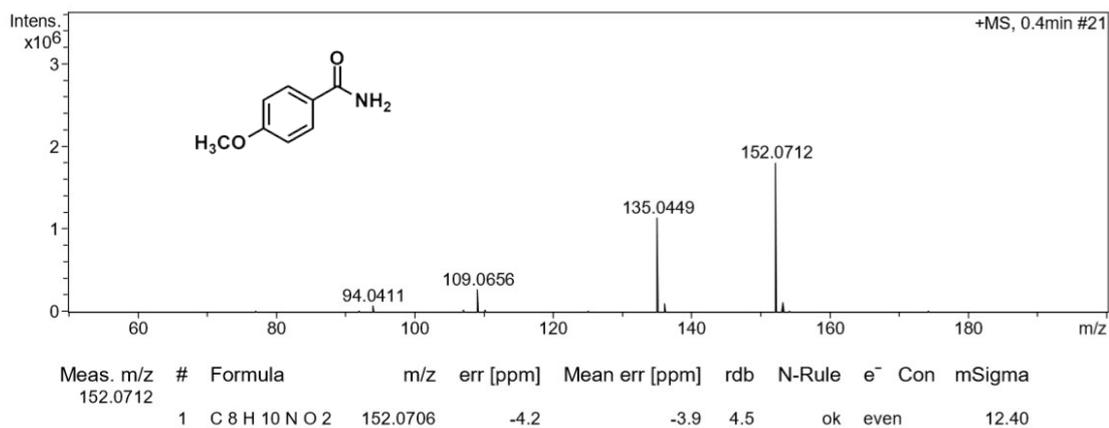


Figure S24. GC-MS spectrum of *p*-methoxybenzamide.

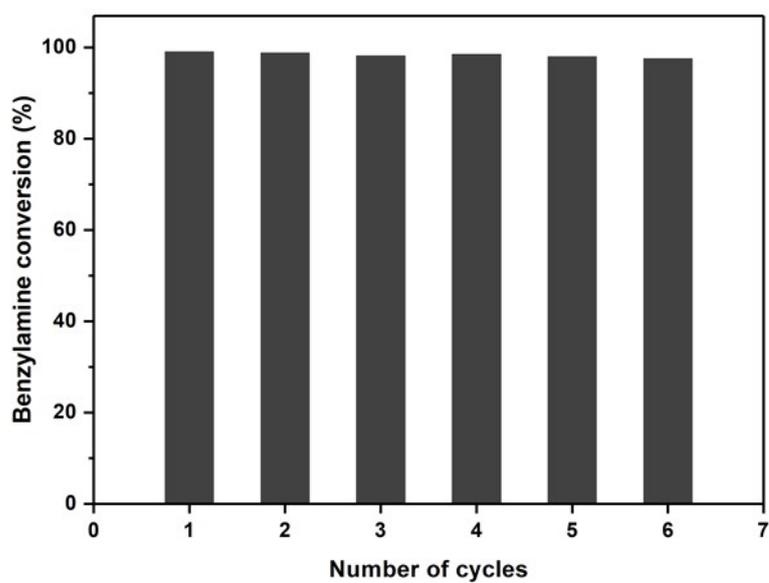


Figure S25. Reusability test for **TFPT-BMTH**. In each cycle, the **TFPT-BMTH** was recovered by filtration, washed, dried and reused in the next run of the reaction.

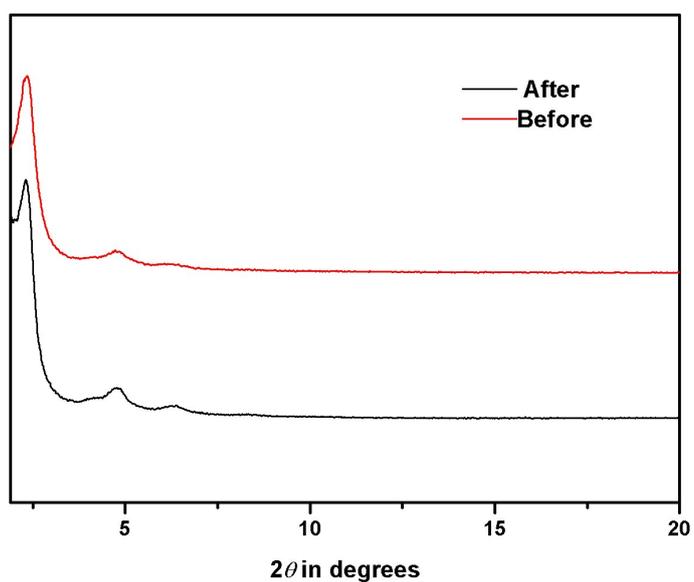


Figure S26. PXRD patterns of **TFPT-BMTH** before and after six cycles.

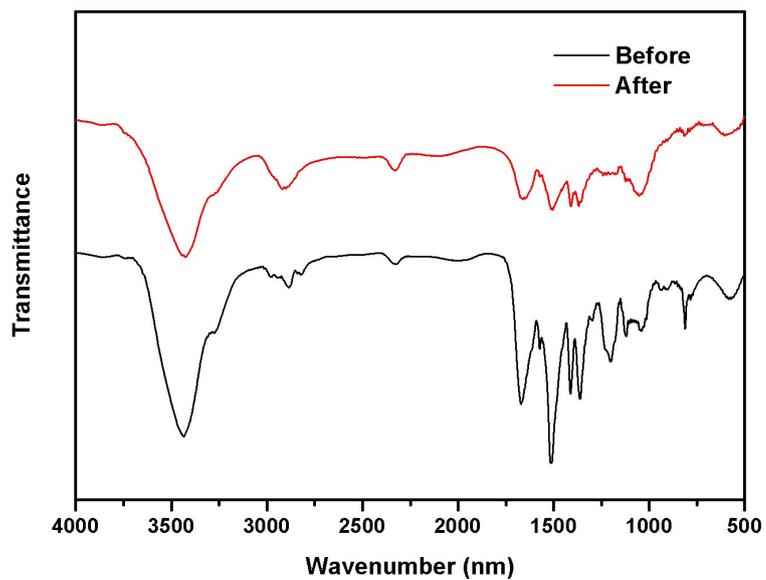


Figure S27. FT-IR spectra of **TFPT-BMTH** before and after six cycles.

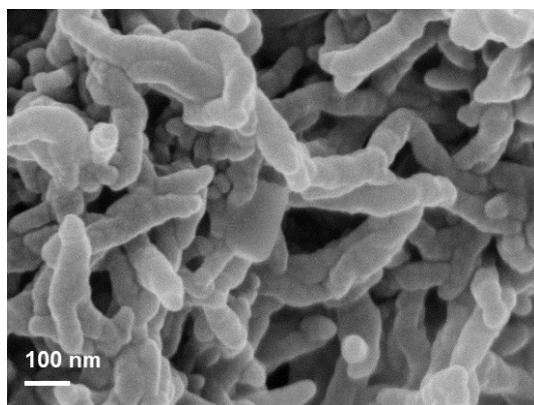


Figure S28. SEM image of **TFPT-BMTH** after six cycles.

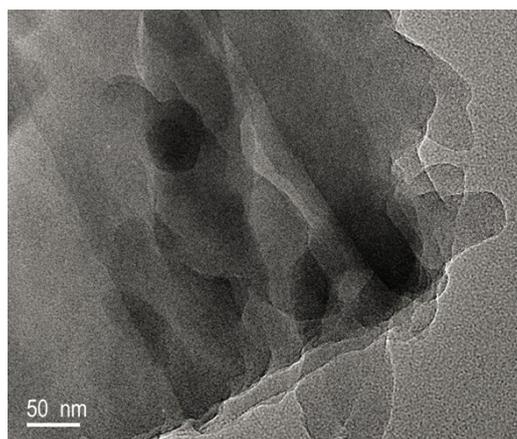
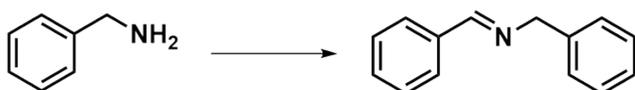


Figure S29. TEM image of **TFPT-BMTH** after six cycles.

Table S1. Oxidation of benzylamine catalyzed by **TFPT-BMTH**^a

Entry	Cat. (mmol%)	H ₂ O (mL)	Time (h)	Light	Additive	Conv. ^b (%)
1	10	5	24	+	-	99
2	5	5	24	+	-	99
3	2	5	24	+	-	63
4	5	5	12	+	-	84
5	5	2	24	+	-	81
6	0	5	24	+	-	7.5
7	5	5	24	-	-	trace
8 ^c	5	5	24	+	NaN ₃	86
9 ^d	5	5	24	+	Benzoquinone	54
10 ^e	5	5	24	+	EDTA(Na ⁺)	37
11 ^f	5	5	24	+	2-propanol	99

^aReaction conditions: benzylamine (0.2mmol), RT, air atmosphere, blue LED lamp (30 W, $\lambda=454$ nm). ^b

Determined by ¹H NMR spectroscopy. ^c NaN₃ as singlet oxygen scavenger. ^d Benzoquinone as superoxide radical scavenger. ^e EDTA(Na⁺) as hole scavenger. ^f 2-propanol as HO• scavenger.

Table S2. Representative heterogeneous catalysts for the oxidative coupling of benzylamines.

Catalyst	Solvent	Light source	Gas atmosphere	Time /h	Conv. ^a	Reference
B-BO-1,3,5	CH ₃ CN	23W blue LED	O ₂	24	99%	<i>Adv. Mater.</i> 2015, 27 , 6265-6270
CF-HCP	CH ₃ CN	30W green LED	O ₂	6	91%	<i>J. Mater. Chem. A</i> , 2017, 5 , 8697-8704
Tx-CMP	CH ₃ CN	Sunlight	O ₂	4	99%	<i>ACS Catal.</i> 2012, 2 , 2630–2640
SC-HM	CH ₃ CN	50W Xe lamp	O ₂	4	99%	<i>J. Am. Chem. Soc.</i> 2017, 139 , 2468–2473
mpg-C ₃ N ₄	CH ₃ CN	300W Xe lamp	O ₂	3.5	99%	<i>Angew. Chem. Int. Ed.</i> 2011, 50 , 657–660
R-WO ₃	CH ₃ CN	Sunlight	O ₂	2	38%*	<i>J. Am. Chem. Soc.</i> 2016, 138 , 8928-8935
MOF 6 (Ru(bpy) ₃ ²⁺)	CH ₃ CN	300W Xe lamp	O ₂	1	83%	<i>J. Am. Chem. Soc.</i> 2011, 133 , 13445-13454
NH ₂ -MIL125(Ti)	CH ₃ CN	300W Xe lamp	O ₂	12	73%**	<i>Appl. Catal. B</i> 2015, 164 , 428-432
PCN-222 (Zr)	CH ₃ CN	300W Xe lamp	Air	1	100%*	<i>Chem. Sci.</i> 2018, 9 , 3152-3158
BiOBr-OV	CH ₃ CN	420 nm Xe lamp	Air	12	96%	<i>J. Am. Chem. Soc.</i> 2018, 140 , 1760-1766
pTCP-2P	CH ₃ CN	26W white CFL	Air	6	98%	<i>J. Mater. Chem. A</i> 2018, 6 , 15154-15161
UNLPF-12 (Zr) (Sn ^{IV} porphyrin)	CH ₃ CN	14 W CFL	Air	2	99%	<i>ACS Catal.</i> 2015, 5 , 5283-5291
Zn-PDI	CH ₃ CN	500W Xe lamp	Air	4	74%	<i>J. Am. Chem. Soc.</i> 2016, 138 , 3958-3961
TFPT-BMTH	H ₂ O	30W blue LED	Air	24	99%	This work

^aThe conversion rates were determined by ¹H NMR analysis.

*The conversion rates were determined by gas chromatography-mass spectrometry (GC-MS).

**The conversion rate was determined by gas chromatography-flame Ionization detector (GC-FID).

References

- [1] H. Tanaka, K. Shizu, H. Nakanotani, C. Adachi, *Chem. Mat.* **2013**, *25*, 3766–3771.
- [2] S. Bartoli, G. De Nicola, S. Roelens, *J. Org. Chem.* **2003**, *68*, 8149–8156.