Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Boranil-based conjugated microporous polymer for the efficient visible-light-driven heterogeneous photocatalysis

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Contents

Section 1. Experiments

Characterization

All solvents and reagents were purchased from Aladdin Chemical Reagent or Energy Chemical, unless otherwise noted, and used without further purification. ^{1}H NMR spectra were recorded using a Bruker Avance II 400 instrument with $CDCl_3$ as solvents, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform infrared spectra (FTIR) analysis was measured by using JASCO IR-4100 spectrometer from 400 to 4000 cm^{-1}. Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) spectra were carried out on an Agilent DD2-500MHz nuclear magnetic resonance spectrometer. UV-Vis studies were recorded on a Hitachi UV-4100 spectrometer at room temperature. X-ray diffractions (XRD) measurements were analyzed on a Rigku D/max-2400 diffractometer by depositing powder on a glass substrate, from $2\theta = 2°$ to 40° with a scanning rate of 2° min^{-1} at 25 °C. Field emission scanning electron microscopy (FE-SEM) studies were conducted by using an FEI Nova Nano SEM 450 scanning electron microscopy with 20 kV. Nitrogen sorption isotherms were measured at 77 K with a Quantachrome Autosorb iQ analyzer. Before measurement, the samples were degassed in vacuum at 120 °C overnight. Thermogravimetric analysis (TGA) was performed by using a Mettler Toledo TGA/DSC 3+ thermal analyzer under an atmosphere of flowing N_2. All samples were heated at room temperature to 800 °C at a heating rate of 10 ℃ min^{-1}. The EPR spectra were recorded on a Bruker A200－9.5/12 EPR spectrometer. Samples were quantitatively injected into 0.5 mm quartz capillaries for ESR analysis. The date of TEMP solution with a concentration of 0.1 M was collected.

Photoelectrochemical measurement

The photoelectrochemical properties of **TDFB-TEB** and **TCT-TEB** were studied on a CHI 660E electrochemical workstation using a standard three-electrode system. A glassy carbon electrode is used as the working electrode，platinum wire and saturated silver chloride electrode was served as the counter electrode and the reference electrode, respectively. Sample preparation: **TDFB-TEB** or **TCT-TEB** powder (2 mg) and 5% Nafion were mixed in 0.49 mL of ethanol, sonicated for 1 h, and the mixture was dripped onto a glassy carbon working mold (2.5 μl×4), and the solvent was evaporated in a vacuum chamber for 1 h. Anhydrous sodium sulfate solution (0.2 M) was used as the electrolyte. The scan rate is 0.1 V/s in the range -1.0 V to 1.0 V.

UV-Vis measurements of N, N, N', N'-tetramethyl-p-phenylenediamine (NTPD):

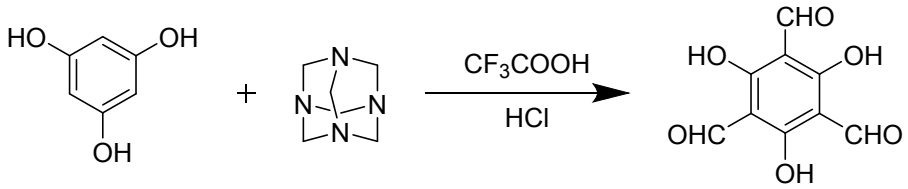
In a typical experimental procedure, three standard solutions of N, N, N', N'-tetramethyl-p-phenylenediamine (NTPD) were prepared separately in acetonitrile. **TDFB-TEB** (2.45 mg) and **TCT-TEB** (2.38 mg) were added to two of the solutions separately, and the solutions were stirred for 1h under constant irradiation by visible light (26 W LED). Observe the absorption band in the 450-650 nm range.

EPR measurements of TEMP-$^{1}O2$:

TDFB-TEB (2.45 mg) and **TCT-TEB** (2.38 mg) were dispersed in 0.1 M TEMP (3 ml in CH3CN) separately, and the solutions were both continuously irradiated for 30 min with a blue lamp (λ=460 nm) before measurement.

Section 1. Syntheses

Synthesis of 1,3,5-triformylphloroglucinol (S1)



Under N_2 atmosphere, 90 mL CF_3COOH was added to hexamethylenetetramine (14.019 g, 100 mmol) and phloroglucinol (6.306 g, 50 mmol). The mixture was heated at 100℃ for 4 h. Then about 150 mL of 3 M HCl was subsequently added and the solution was heated for another 3 h at 100℃. After cooling to room temperature, the solution was filtered, extracted with dichloromethane (3×150ml). The organic phase was dried over anhydrous magnesium sulfate, and filtered. Rotary evaporation of the solution afforded an orange-pink powder. Yield: 12% (1.26 g). ^{1}H NMR (400 MHz, Chloroform-d): δ 14.12 (s, 3H), 10.16 (s, 3H).[1]

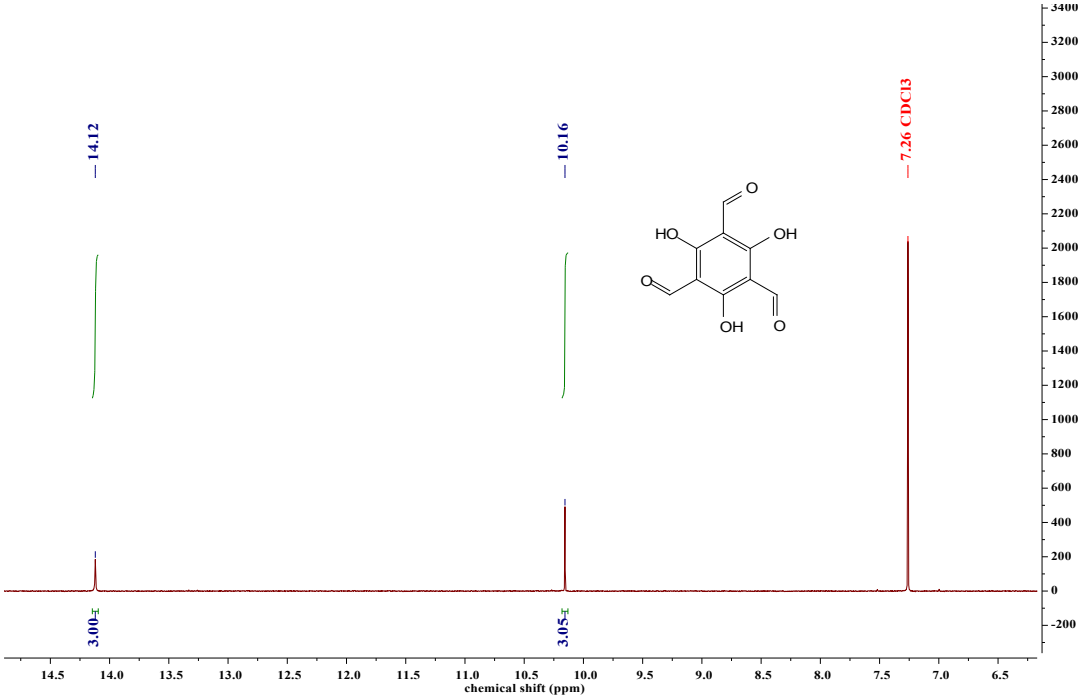
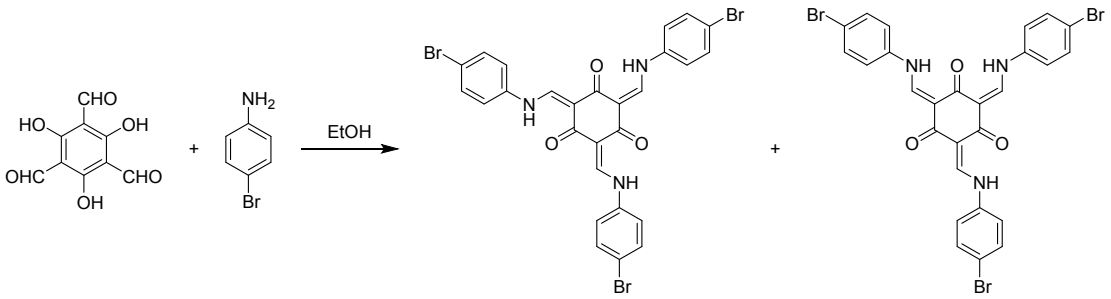


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, rt) of 1,3,5-triformylphloroglucinol.

Synthesis of 2,4,6-tris((4-bromophenylamino)methylene)cyclohexane-1,3,5-trione (TCT)



Under N_2 atmosphere, S1 (210 mg, 1 mmol), 4-Bromoaniline (860.15 mg, 5 mmol), and 10 mL anhydrous EtOH was added to a dried round bottom flask and heated at reflux under nitrogen for 2 days. The resulting heterogeneous mixture was filtered hot to isolate a yellow solid, which was washed with boiling EtOH (10 mL × 3) and dried in vacuo. Yield: 96% (645 mg). ^{1}H NMR (400 MHz, Chloroform-d): δ13.42-12.96 (m, 3H), 8.78-8.66 (m, 3H), 7.57-7.55 (m, 6H), 7.22-7.17 (m, 6H).[2, 3]

In Figure S2, the part in the insert shows that TCT-1 occupies most of the product. Therefore, the structure of TCT-1 is used to refer to TCT-1 and TCT-2 in the following text and in the manuscript, collectively referred to as TCT.

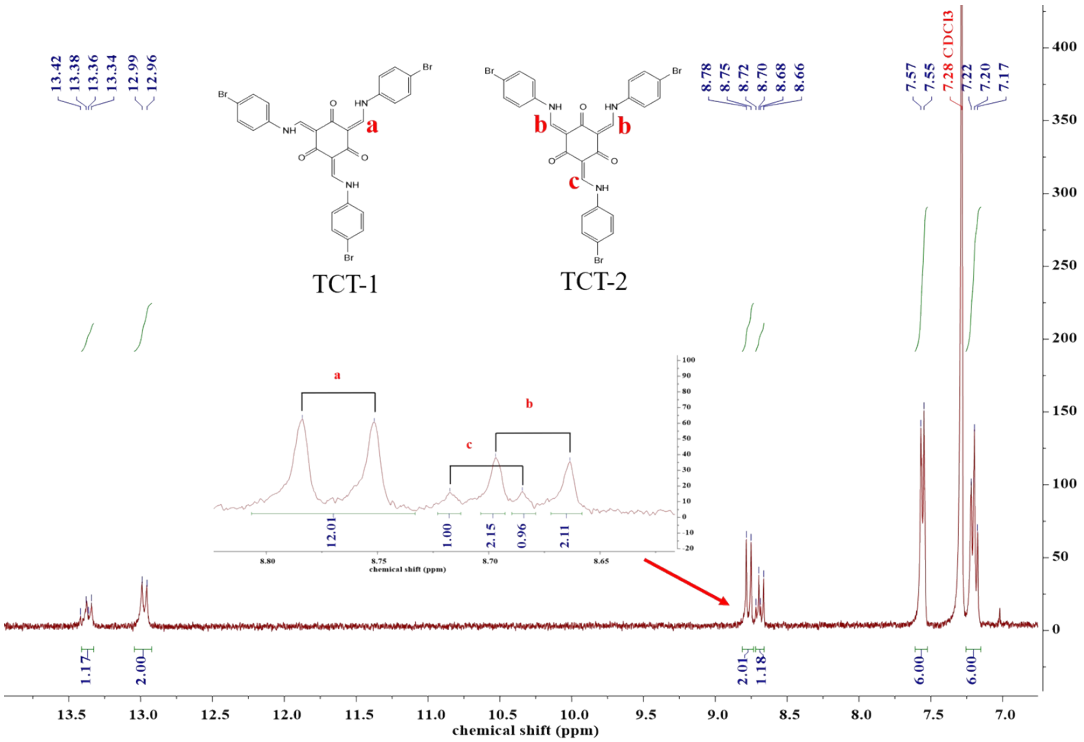
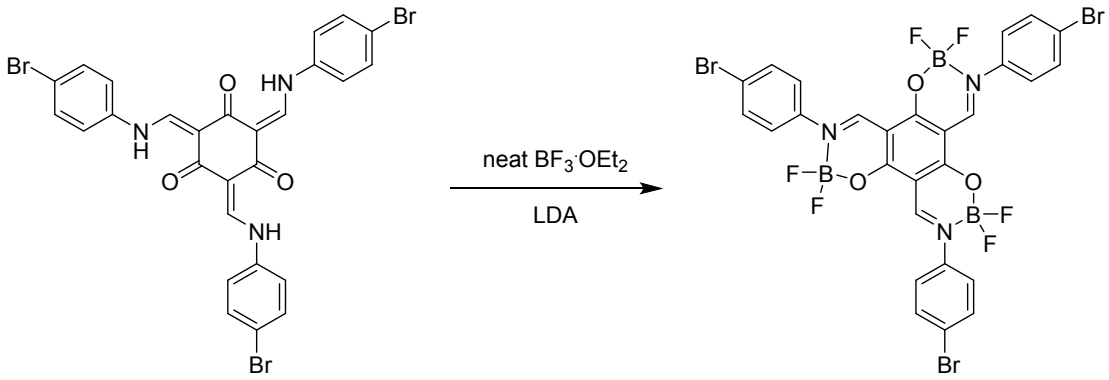


Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, rt) of **TCT** (inset: The partial ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, rt) of TCT.).

Synthesis of 1,3,5-Tris(difluoroboronyloxy)-2,4,6-tris((4-bromophenylamino)methyl)-benzene(TDFB)



Under N_2 atmosphere, **TCT** (672.17 mg, 1 mmol) and neat $BF_3 \cdot Et_2O$ (13 ml) was added to a dried round flask via syringe. The reaction mixture was stirred for 5 min and cooled to 0 ˚C. Lithium diisopropylamide (10 mmol, in 2M THF solution) was added over a period of 0.5 h and stirred for 12 h. The reaction was cooled to 0 ˚C and quenched by adding water (15 mL). The yellow solid product was isolated by filtration, washed with water and methanol, and dried in vacuo. (yield: 92%,750 mg).[1]H NMR (400 MHz, Chloroform-d): δ 8.91 (s, 3H), 7.69-7.65 (m, 3H), 7.47-7.42 (m, 6H).[2] [13]C NMR (125 MHz, DMSO-d_6): δ 167.60, 159.73, 140.92, 132.34, 125.85, 122.12, 100.89.

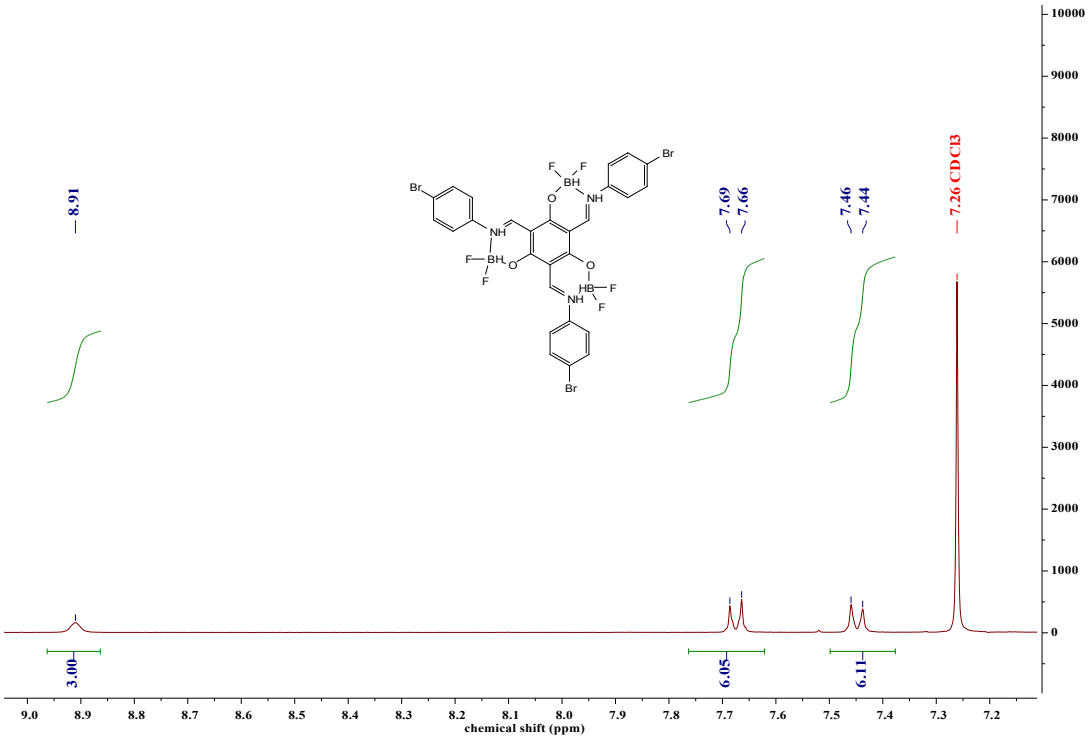


Figure S3. [1]H NMR spectrum ($CDCl_3$, 400 MHz, rt) of **TDFB**.

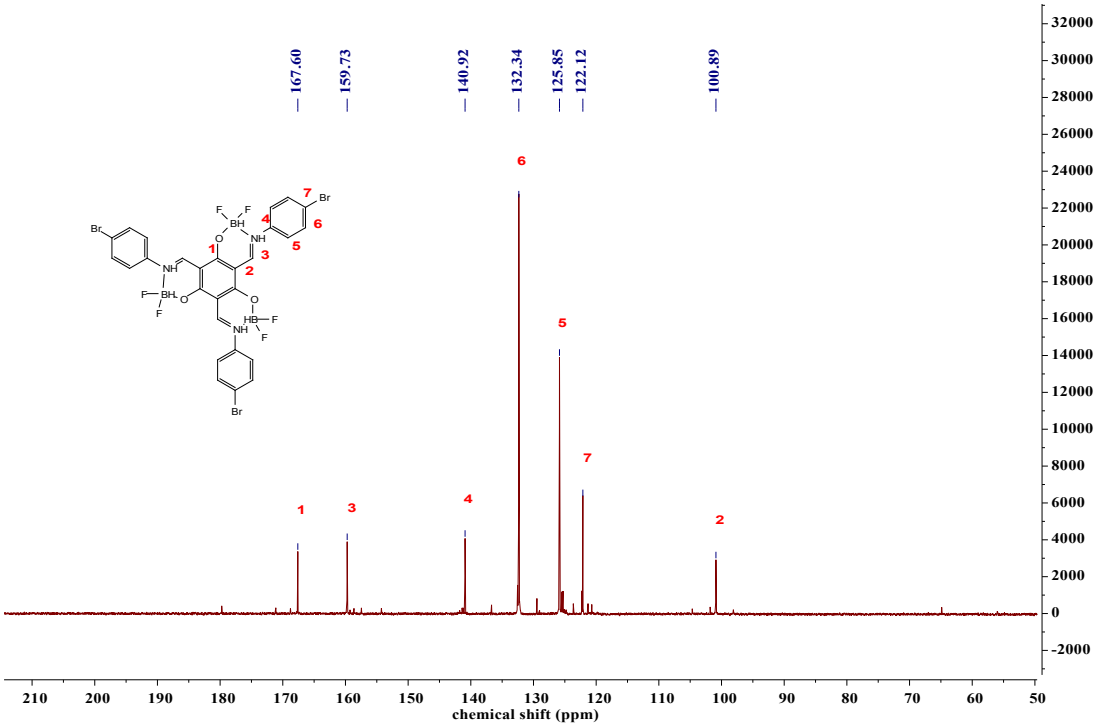
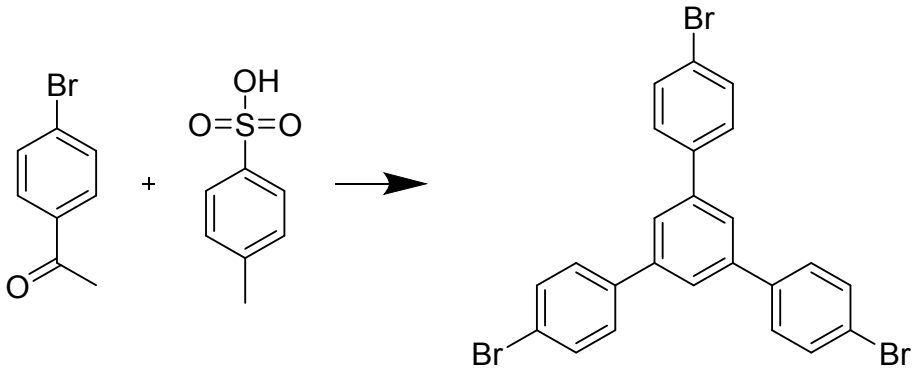


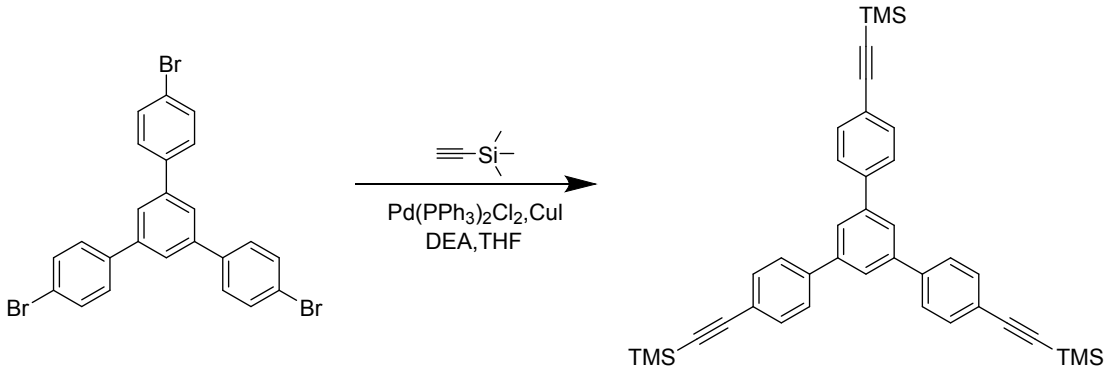
Figure S4. ^{13}C NMR spectrum (DMSO-d_6, 125 MHz, rt) of **TDFB**.

Synthesis 1,3,5-Tris(4-bromophenyl)benzene (S2)



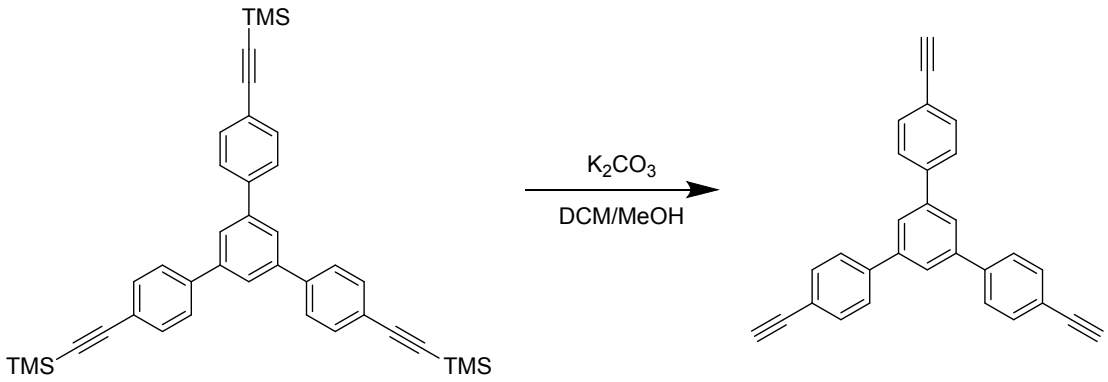
4-Bromoacetophenone (1g, 5 mmol) and p-toluenesulfonic acid (0.1 g, 0.58 mmol) were taken into a mortar and ground well. Then transferred to a 100 mL round bottom flask and the mixture was heated at 140℃ such that it becomes semi-liquid. After 24 h, the brown compound was washed with a saturated solution of sodium carbonate and extracted with dichloromethane. The solvent was removed under vacuum and crude was washed with diethyl ether to get a pure product as brown solid. (Yield: 80%, 0.727 g).[4]

Synthesis of 1,3,5-tris-(4-trimethylsilylethynylphenyl)benzene (S3)



Under N_2 atmosphere, S2 (1.086 g, 2 mmol), CuI (11.4 mg, 0.06 mmol), triphenyl phosphine (52.65 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (71.77 mg, 0.1 mmol) were added to a 250 mL two-neck round bottom flask. Then dry and degassed triethylamine (100 mL) was added to this mixture and heated for 30 min at 50℃. Trimethylsilylacetylene (1.23 mL, 9 mmol) was added dropwise to the mixture under high nitrogen flow and the reaction mixture was refluxed for 36 h. The solvent was removed under vacuum and the crude was purified by column chromatography using 1% ethyl acetate (EA) in hexane mixture to afford the product as white solid. (Yield: 1.01 g, 85%).[4]

Synthesis of 1,3,5-tris-(4-ethynylphenyl)benzene (TEB)



A mixture of S3 (1.2 g, 2.02 mmol) and K_2CO_3 (1.26 g, 9.09 mmol) in dichloromethane (25 mL) and methanol (25 mL) was stirred at room temperature for 24 hours. The mixed reaction was added water (50 ml) and then extracted with dichloromethane (3×50ml) and. The organic phase was dried over anhydrous magnesium sulfate and then concentrated in vacuum and the crude was purified by column chromatography using hexane as eluent to afford the product as a white solid. (Yield: 80%, 612 mg). ^{1}H NMR (400 MHz, Chloroform-d): δ 7.69 (s, 3H), 7.59 (d, J=8.0 Hz, 6H), 7.54 (d, J=8.0 Hz, 6H), 3.09 (s, 3H).[4]

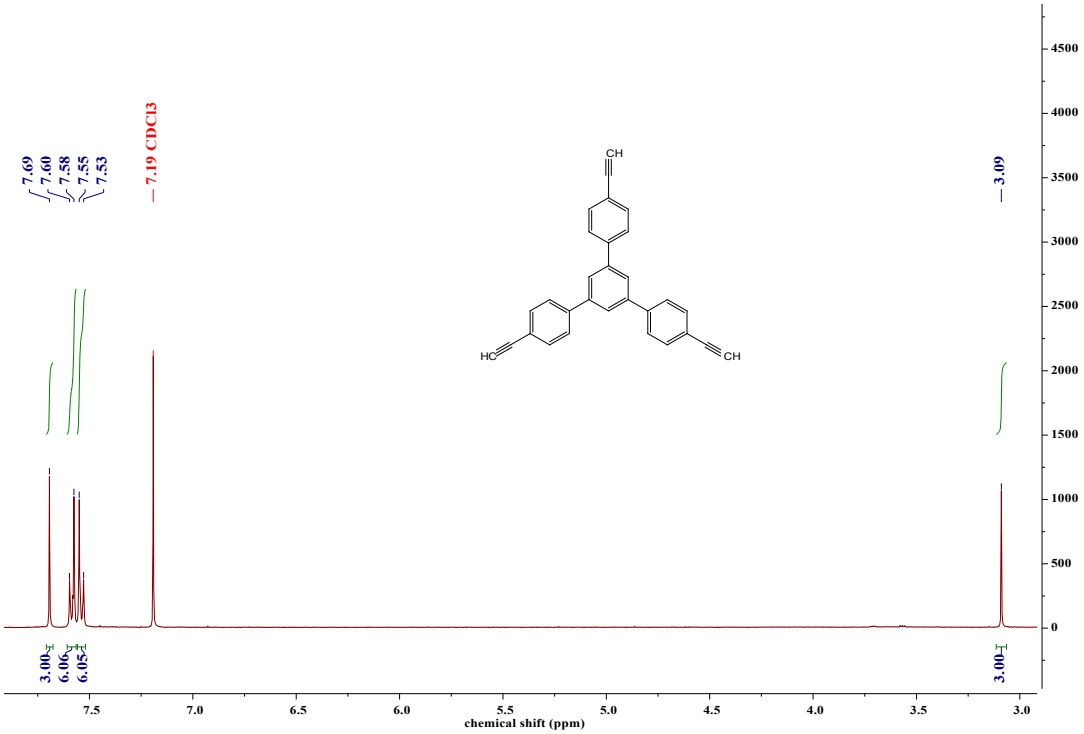
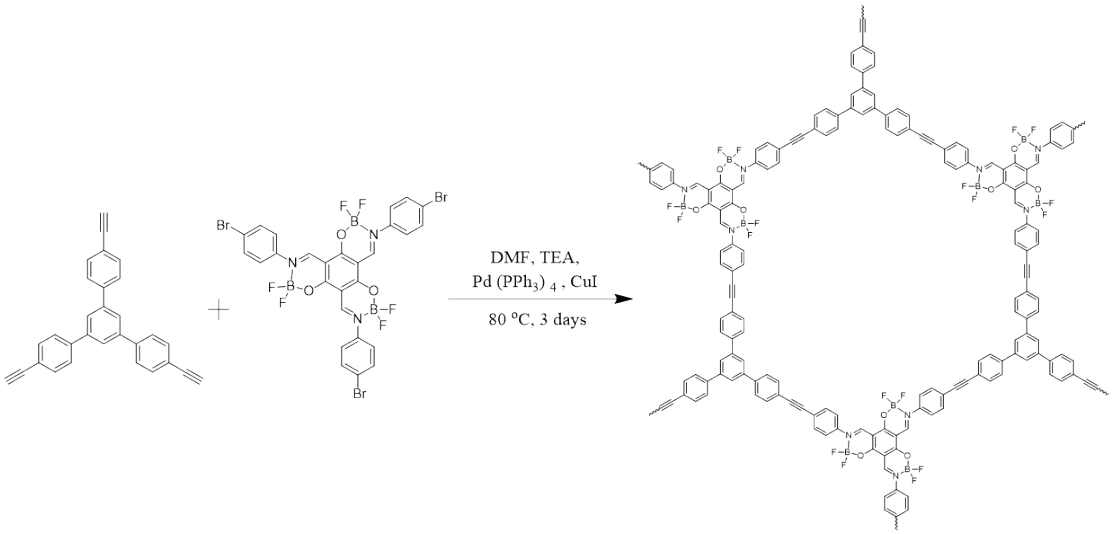


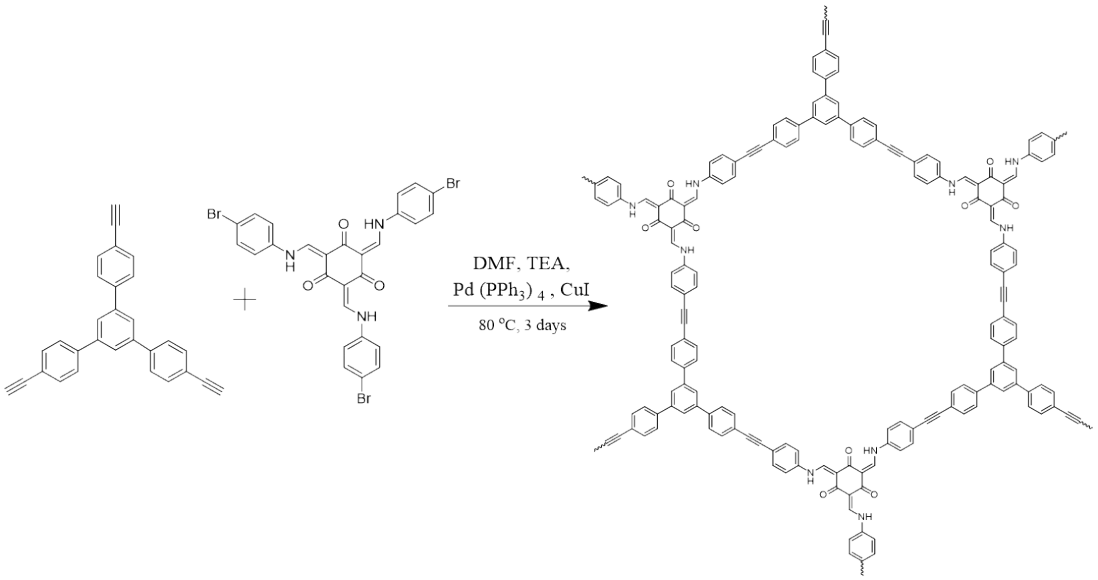
Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, rt) of **TEB**.

Synthesis of TDFB-TEB



TDFB (0.5mmol, 408 mg), **TEB** (0.5mmol, 189 mg), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), and CuI (15 mg, 0.08 mmol) were added into a 50 mL dried Schlenk tube with the mixed dry N,N-dimethyl formamide(DMF) (15 mL) and triethylamine (15 mL). The reaction suspension was degassed and then stirred at 80 °C for 3 days under an inert nitrogen atmosphere. After cooling to room temperature, the solid was obtained by filtration and washed with DMF, water, trichloromethane, methanol and acetone. Further purification was carried out by Soxhlet extraction with methanol and, trichloromethane successively for 24 h each. The product was then dried under vacuum for 24 h at 60 °C to give 450 mg (yield:95%) as a brown solid.[5, 6]

Synthesis of TCT-TEB



TCT (0.5mmol, 336 mg), **TEB** (0.5mmol, 189 mg), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), and CuI (15 mg, 0.08 mmol) were added into a 50 mL dried Schlenk tube with the mixed dry N,N-dimethyl formamide(DMF) (15 mL) and triethylamine (15 mL). The reaction suspension was degassed and then stirred at 80 °C for 3 days under an inert nitrogen atmosphere. After cooling to room temperature, the solid was obtained by filtration and washed with DMF, water, trichloromethane, methanol and acetone. Further purification was carried out by Soxhlet extraction with methanol and, trichloromethane successively for 24 h each. The product was then dried under vacuum for 24 h at 60 °C to give 384 mg (yield:95%) as a yellow solid.[5, 6]

Section 3. XPS pattern.

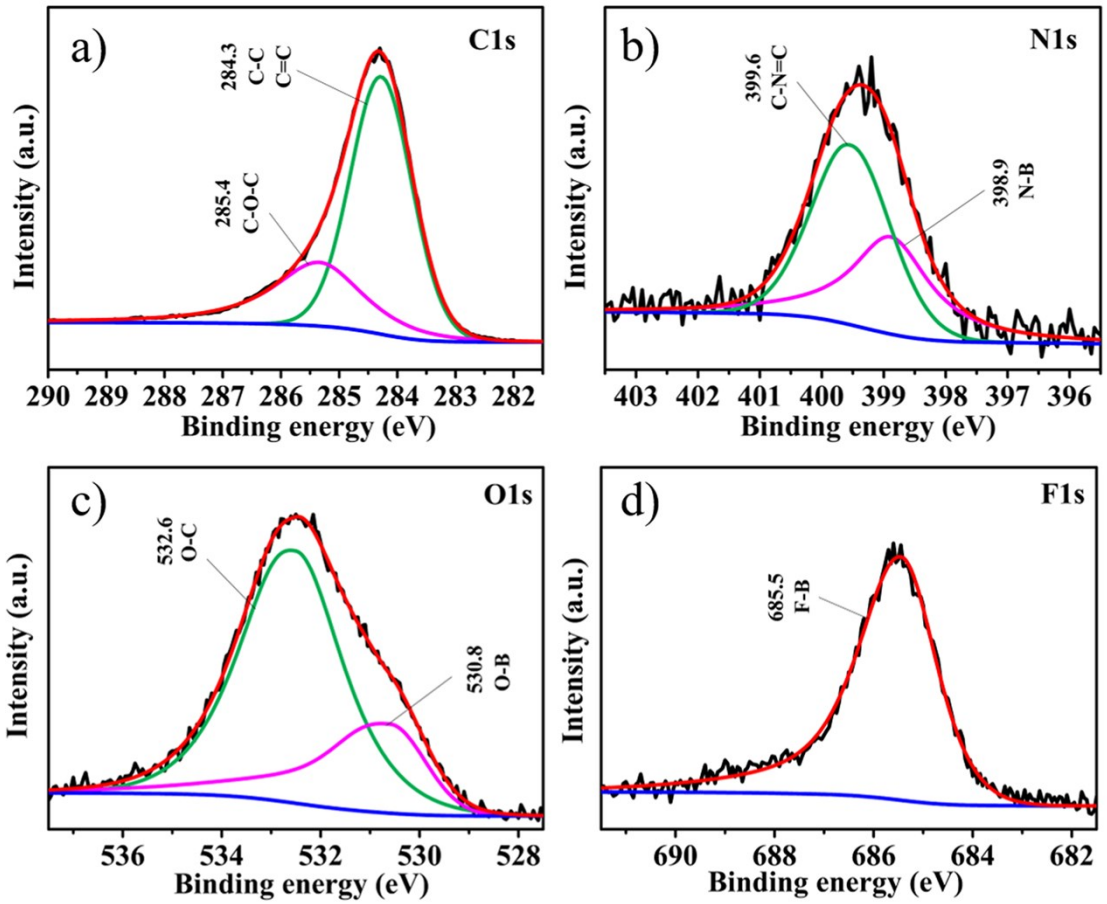


Figure S6. a) C 1s region XPS spectrum, b) N 1s region XPS spectrum, c) O 1s region XPS spectrum, and d) F 1s region XPS spectrum of **TDFB-TEB** before photocatalysis.

Name	Peak BE	Height CPS	FWHM eV	Area (P)CPS.eV	Atomic %
C1s	284.32	30886.46	1.44	54738.65	78.42
N1s	399.36	2074.59	1.77	5081.66	4.47
O1s	532.45	5163.02	3.16	18034.57	9.59
F1s	685.54	4058.8	1.85	10392.14	4.09
B1s	192.69	305.02	1.24	919.94	3.43

Table S1. The XPS peak table of **TDFB-TEB**.

Section 4. Pore size distributions

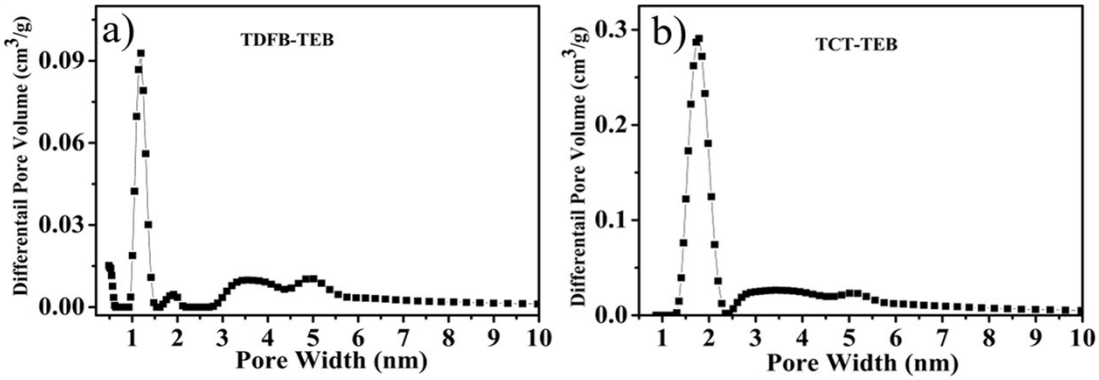


Figure S7. Pore size distribution of a) **TDFB-TEB** and b) **TCT-TEB.**

Section 5. TGA Curve

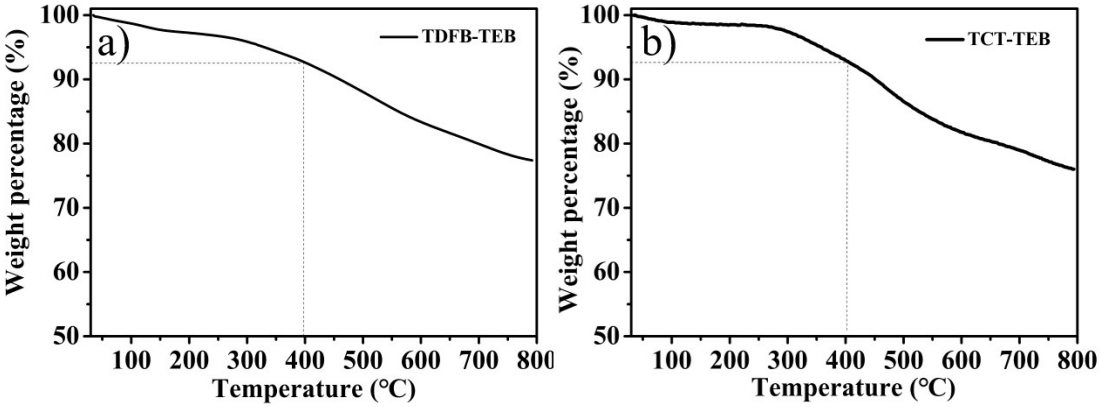


Figure S8. Thermogravimetric analysis of a) **TDFB-TEB** and b) **TCT-TEB**.

Section 6. SEM Image

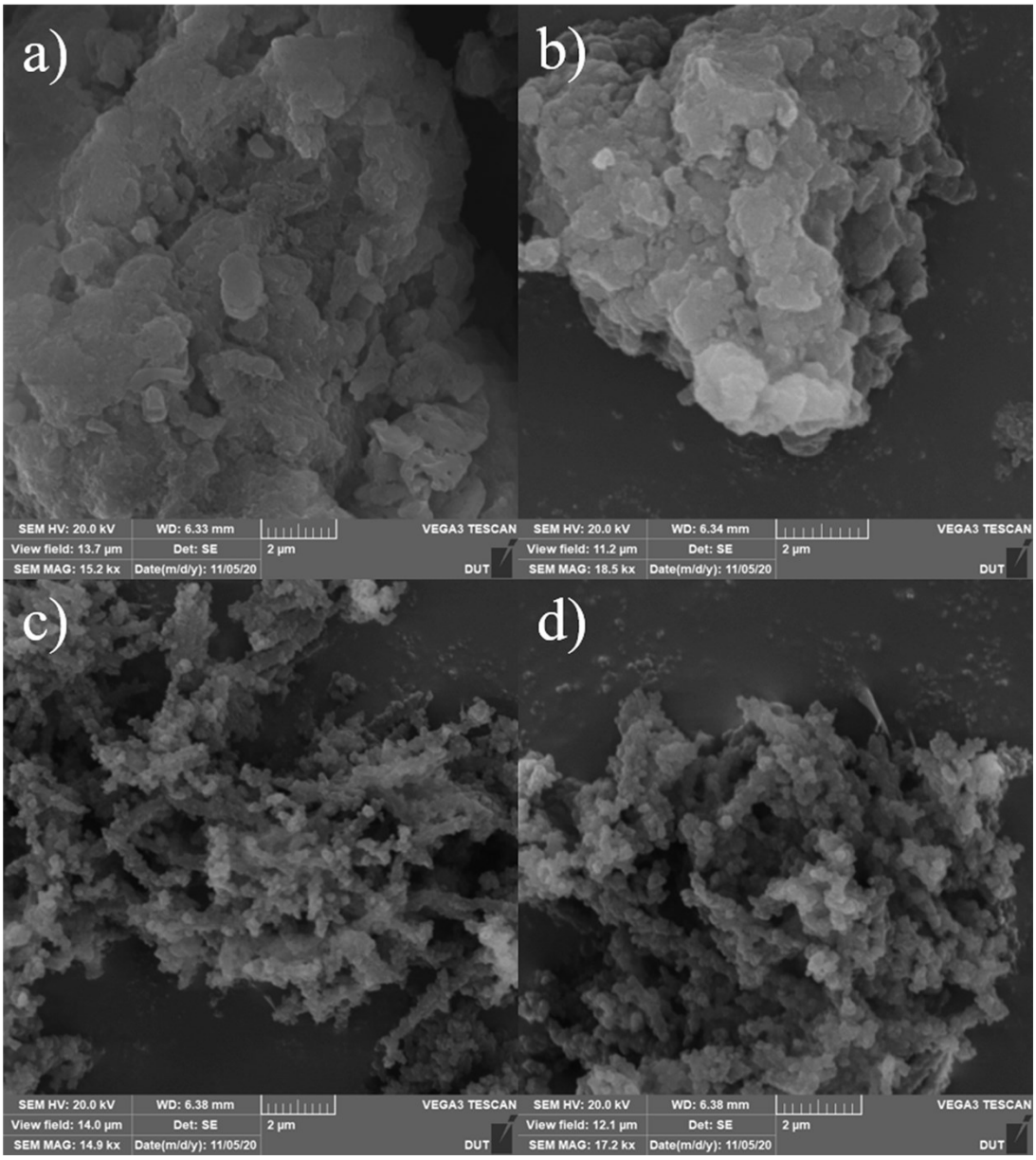


Figure S9. SEM images of a), b) **TDFB-TEB** and c), d) **TCT-TEB**.

Section 7. XRD Pattern

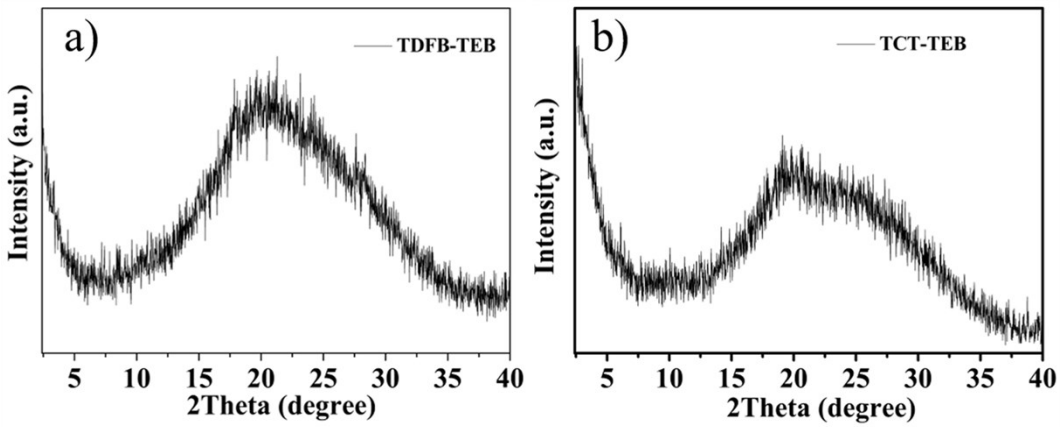


Figure S10. Powder X-ray diffraction pattern of a) **TDFB-TEB** and b) **TCT-TEB**.

Section 8. Mott-Schottky plots

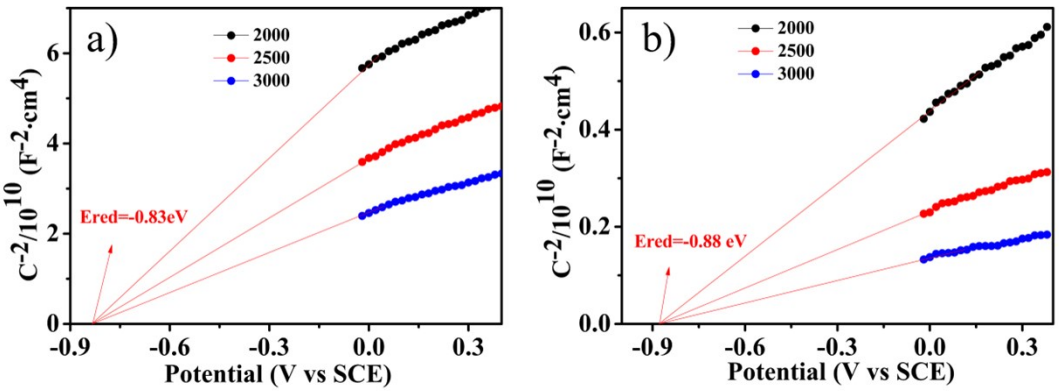
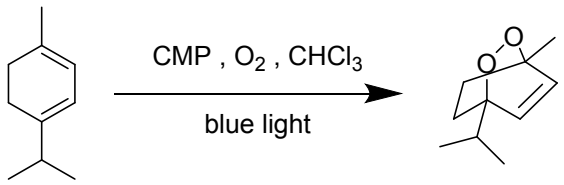


Figure S11. Mott-Schottky plots of a) **TDFB-TEB** and b) **TCT-TEB**.

Section 9. Characterization Data of Catalytic Products



Reaction conditions: α-terpinene (0.5mmol), photocatalyst (2.45mg, 0.5% mmol), $CHCl_3$(5mL), air, 24W blue LED lamp, room temperature (RT), 3h; Conversion was determined by ^1H NMR.

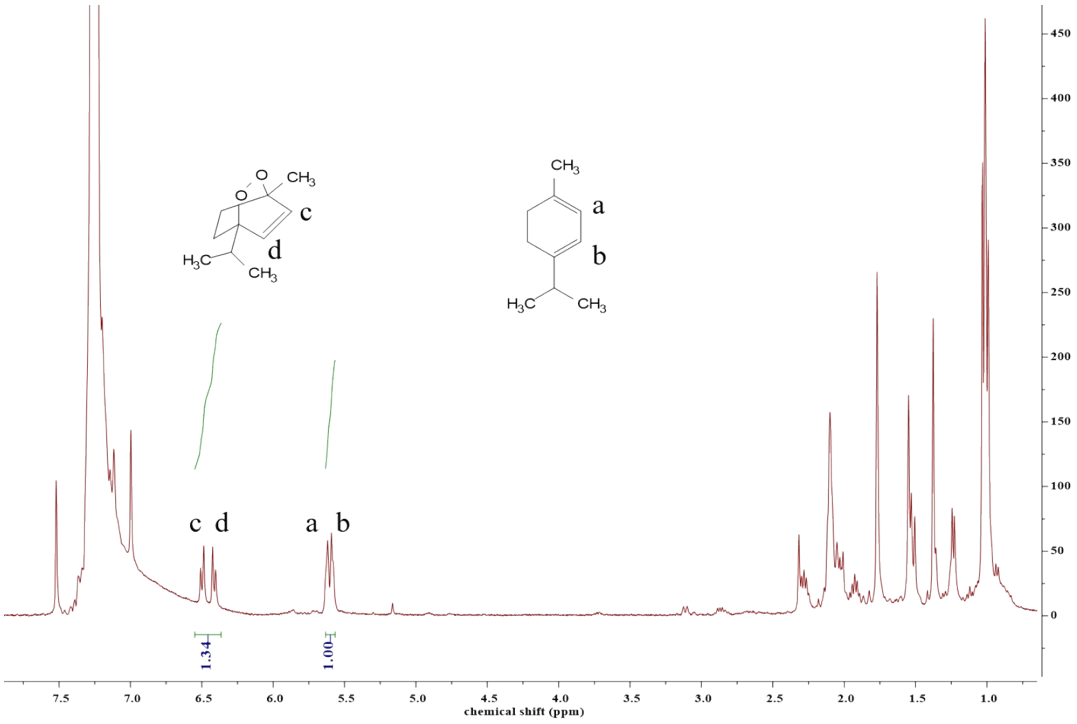


Figure S12. ^1H NMR spectra ($CDCl_3$, 400 MHz, rt) of photocatalytically oxidation α-terpinene to α-pinworm ether.

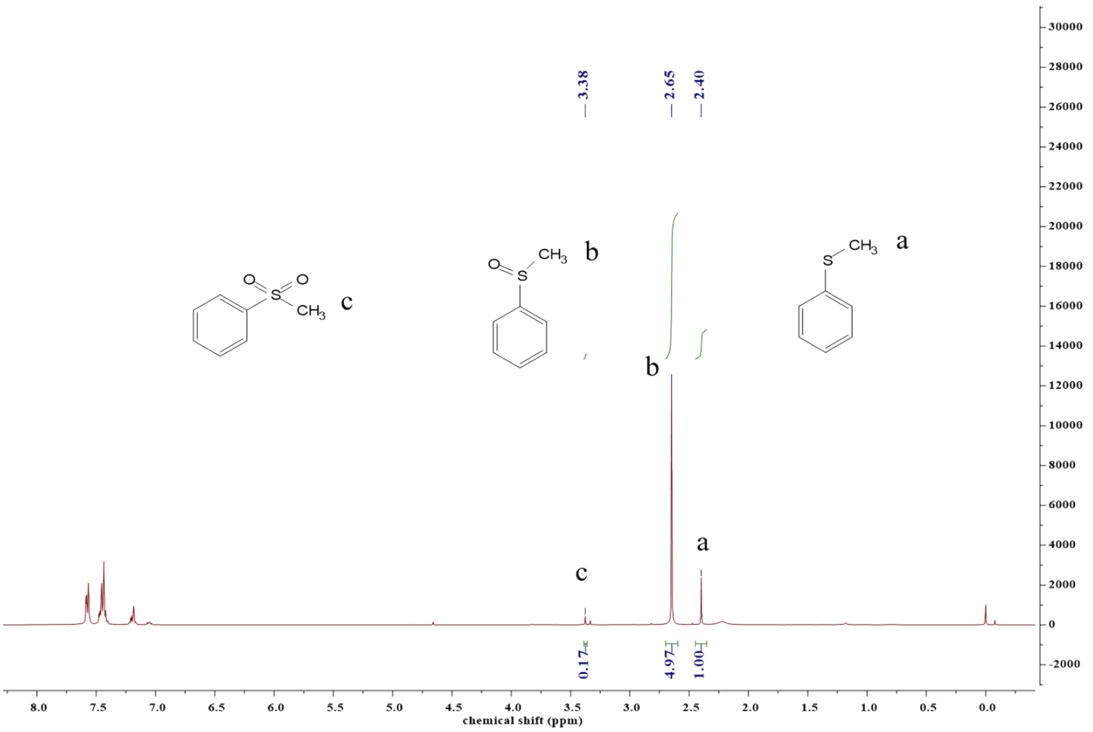


Figure S13. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, rt) of sulfide oxidation mixture.

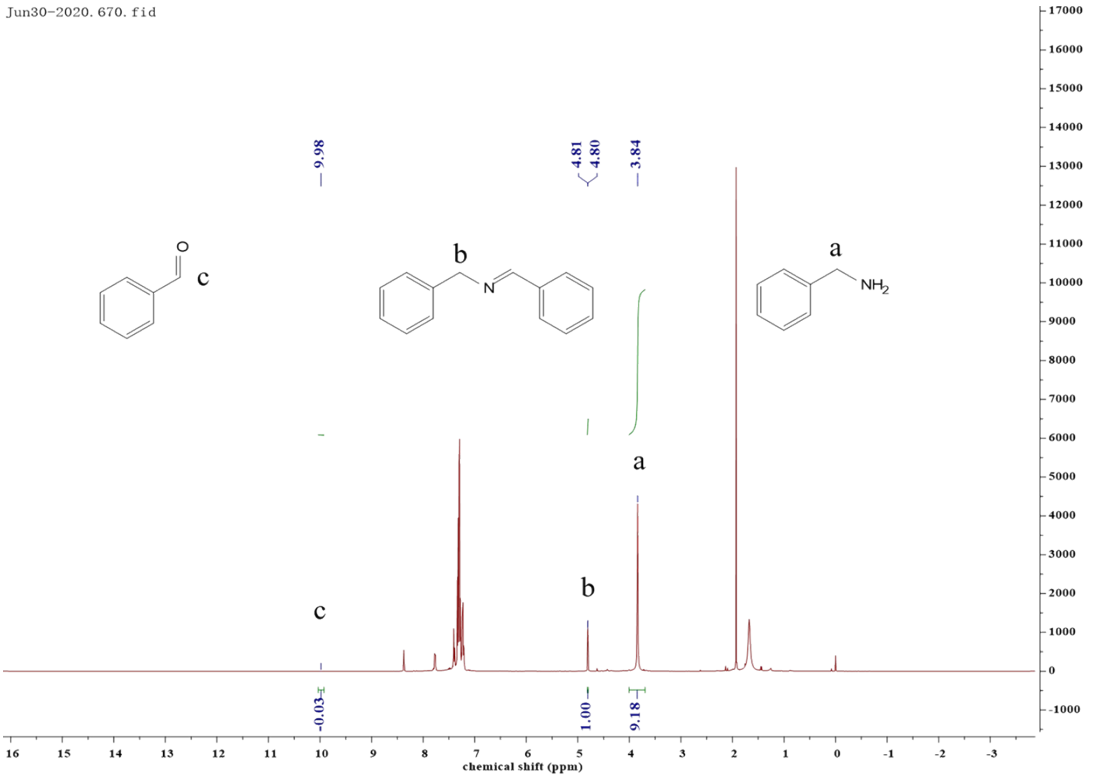


Figure S14 ^{1}H NMR spectra ($CDCl_3$, 400 MHz, rt) of phenylmethanamine oxidation.

Section 10. Stability and cycling

Recycle experiments of aerobic oxidation of sulfide to sulfoxide

TDFB-TEB (2.6mg, 2.5 μmol, 0.5 mol% based on monomer) and sulfide (0.5 mmol) in methanol (5 mL) were stirred at room temperature under the irradiation of a 26 W blue LED in the presence of air. After the first run reaction was finished, the photocatalyst **TDFB-TEB** was recovered by centrifugation, and thoroughly washed with ethyl acetate and dichloromethane several times to remove any residual products or unreacted substrates. The recovered **TDFB-TEB** was dried under vacuum at 100°C overnight. The used photocatalyst was re-employed in the next cycle under identical conditions.

Recycle experiments of benzylamine photocatalytic oxidative coupling

TDFB-TEB (2.6mg, 2.5 μmol, 0.5 mol% based on monomer) and amine (0.5 mmol) in acetonitrile (5 mL) were mixed and stirred at room temperature under the irradiation of a 26 W blue LED in the presence of air. After the first run reaction was finished, the photocatalyst **TDFB-TEB** was recovered by centrifugation, and thoroughly washed with acetonitrile and dichloromethane several times to remove any residual products or unreacted substrates. The recovered **TDFB-TEB** was dried under vacuum at 100°C for overnight. The used photocatalyst was re-employed in the next cycle under identical conditions.

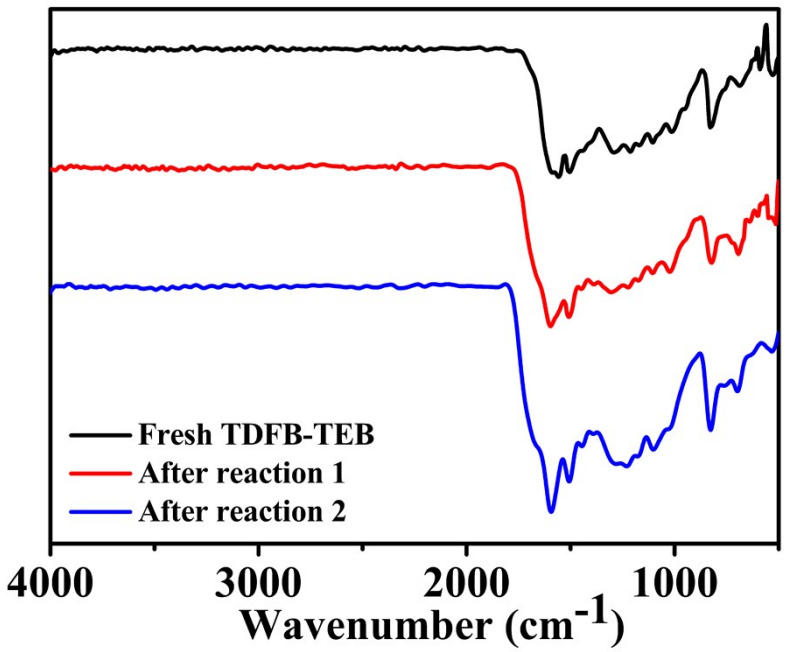
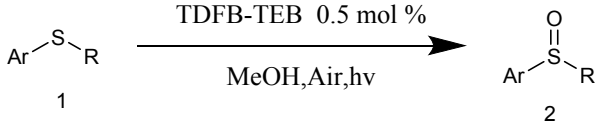


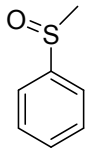
Figure S15. The FT-IR spectra of the fresh and recovered **TDFB-TEB**. (Reaction 1 is the oxidative amine coupling, reaction 2 is the sulfides oxidation.)

Section 11. General procedure for Photocatalytic

General procedure of aerobic oxidation of sulfide to sulfoxide:



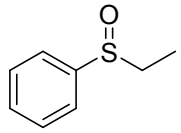
A mixture of **TDFB-TEB** (2.45 mg, 2.5 μmol, 0.5 mol% based on the monomer) and sulfide (0.5 mmol) in MeOH (5 mL) was stirred under air at room temperature over 26 W blue LED irradiation. Reaction progress was monitored by TLC (hexane: CH_2Cl_2 v/v 1:1) and ^{1}H NMR. The catalyst was removed by filtration, and the filtrate was dried under vacuum. ^{1}H NMR was taken for the crude product, and the ratio between the integrated peaks of the starting material and product was used to calculate the conversions. The integrated peaks of the sulfoxide and sulfone were used to calculate selectivity. The ^{1}H NMR spectra of the sulfoxides are consistent with the previous literature values.[7,8]



(Methylsulfinyl)benzene (2A)

The title compound was made following the general procedure using thioanisole (62 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

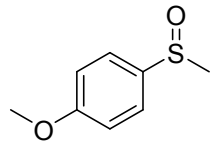
^{1}H NMR (400 MHz, Chloroform-d): δ 2.65 (s, 3H), 7.45 (m, 3H), 7.57 (m, 2H).



(Ethylsulfinyl)benzene (2B)

The title compound was made following the general procedure using ethyl(phenyl)sulfane (69 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

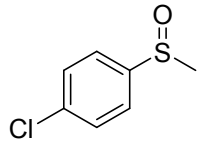
^{1}H NMR (400 MHz, Chloroform-d): δ 1.2 (t, J1 = 4.0 Hz, J2 = 8.0 Hz, 3H), 2.88 (m, 1H), 2.92 (m, 1H), 7.51 (m, 3H), 7.61 (m, 2H).



1-Methoxy-4-(methylsulfinyl)benzene (2C)

The title compound was made following the general procedure using thioanisole (77 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

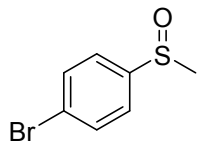
^{1}H NMR (400 MHz, Chloroform-d): δ 2.62 (s, 3H), 3.76 (s, 3H), 6.94 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H).



1-Chloro-4-(methylsulfinyl)benzene (2D)

The title compound was made following the general procedure using (4-chlorophenyl)-(methyl)sulfane (79 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

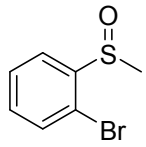
^{1}H NMR (400 MHz, Chloroform-d): δ 2.77 (s, 3H), 7.55 (d, J = 8.0 Hz, 2H), 7.62 (d, J =8.0 Hz, 2H).



1-bromo-4-(methylsulfinyl)benzene (2E)

The title compound was made following the general procedure using (4-bromophenyl)-(methyl)sulfane (102 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (97% yield).

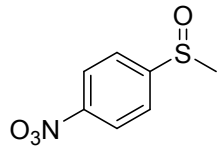
^{1}H NMR (400 MHz, Chloroform-d): δ 2.75 (s, 3H), 7.26 (m, 2H), 7.88 (m, 2H).



1-bromo-2-(methylsulfinyl)benzene (2F)

The title compound was made following the general procedure using (2-bromophenyl)-(methyl)sulfane (102 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (94% yield).

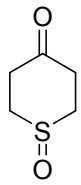
^{1}H NMR (400 MHz, Chloroform-d): δ 2.74 (s, 3H), 7.28~7.31 (m, 1H), 7.47~7.52 (m, 2H), 7.855 (d, J=4.0 Hz, 1H).



1-bromo-4-(methylsulfinyl)benzene (2G)

The title compound was made following the general procedure using (4-bromophenyl)-(methyl)sulfane (93 mg, 0.5 mmol) as the starting material. The product was obtained as a pale yellow solid (71% yield).

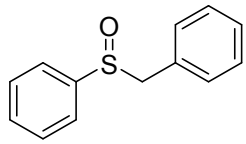
^{1}H NMR (400 MHz, Chloroform-d): δ 2.74 (s, 3H), 7.78 (d, J = 8.0 Hz, 2H), 8.31 (d, J =8.0 Hz, 2H).



tetrahydro-4H-thiopyran-4-one 1-oxide (2H)

The title compound was made following the general procedure using tetrahydro-4H-thiopyran4-one (58 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

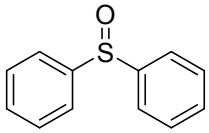
^{1}H NMR (400 MHz, Chloroform-d): δ 1.97 (dd, J1 = 20.0 Hz, J2 = 20.0 Hz, 1H), 2.36 (m, 1H), 2.77 (t, J1 = 12.0 Hz, J2 = 16.0 Hz,1H), 2.99 (d, J =16.0 Hz, 1H), 3.23 (s, 2H), 3.26 (s, 2H).



(benzylsulfinyl)benzene (2I)

The title compound was made following the general procedure using benzyl(phenyl)sulfane (100 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (99% yield).

^{1}H NMR (400 MHz, Chloroform-d): δ 4.03 (dd, J1= 4.0 Hz, J2 = 4.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 7.21~7.27 (m,3H), 7.35~7.44 (m, 5H).

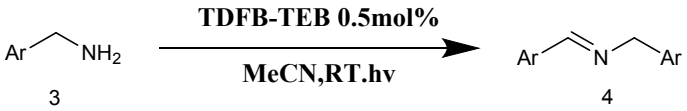


(Phenylsulfinyl)benzene (2J)

The title compound was made following the general procedure using diphenylsulfide (93 mg, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (30% yield).

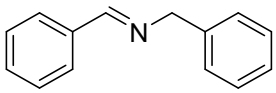
^{1}H NMR (400 MHz, Chloroform-d): δ 7.28-7.35 (m, 6H), 7.53-7.55 (m, 4H).

General procedure for aerobic oxidation coupling of amine:



3 4

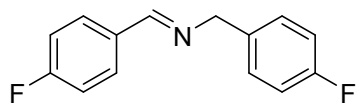
The mixture of **TDFB-TEB** (2.45 mg, 2.5 μmol, 0.5 mol% based on the monomer) and respective amine (0.5 mmol) in MeCN (5 mL) was stirred under air at room temperature over 26 W blue LED. Reaction progress was monitored by TLC (hexane: CH_2Cl_2 v/v 2:1) and ^{1}H NMR. The catalyst was removed by filtration, and the filtrate was dried under vacuum. ^{1}H NMR was taken for the crude product, and the ratio between the integrated peak of the starting material and product was used to calculate the conversion, integrated peak of the product and byproduct was used to calculate selectivity. The ^{1}H NMR spectra of the products are consistent with the previous literature values.[8,9]



(E)-N-benzyl-1-phenylmethanimine (4A)

The titled compound was made following the general procedure using phenylmethanamine (54 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

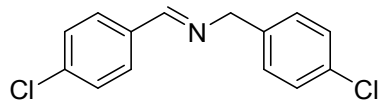
^{1}H NMR (400 MHz, Chloroform-d): δ 4.75 (s, 2H), 7.00~7.04 (m, 1H), 7.07~7.11 (m, 4H), 7.25~7.30 (m, 3H), 7.74~7.78 (m, 2H), 8.33 (s, 1H).



(E)-N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (4B)

The titled compound was made following the general procedure using (4-fluorophenyl)-methanamine (63 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

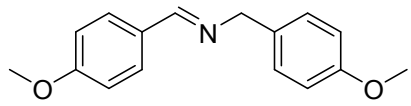
^{1}H NMR (400 MHz, Chloroform-d): δ 4.67 (s, 2H), 7.16-7.18 (m, 2H), 7.21-7.23 (m, 2H), 7.29-7.31 (m, 2H), 7.60-7.62 (m, 2H), 8.24 (s, 1H).



(E)-N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (4C)

The titled compound was made following the general procedure using (4-chlorophenyl)-methanamine (71 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

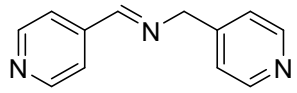
^{1}H NMR (400 MHz, Chloroform-d): δ 4.62 (s, 2H), 6.77-6.79 (m, 2H), 6.80-6.82 (m, 2H), 7.13-7.15 (m, 2H), 7.60-7.62 (m, 2H), 8.19 (s, 1H).



(E)-N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (4D)

The titled compound was made following the general procedure using (4-methoxyphenyl)-methanamine (69 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

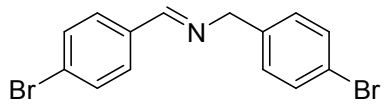
^{1}H NMR (400 MHz, Chloroform-d): δ 3.91 (s, 6H), 4.86 (s, 2H), 7.25-7.27 (m, 4H), 7.29-7.30 (m, 2H), 7.65-7.67 (m, 2H), 8.42 (s, 1H).



(E)-1-(pyridin-4-yl)-N-(pyridin-4-ylmethyl)methanimine (4E)

The titled compound was made following the general procedure using pyridin-4-ylmethanamine (54 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

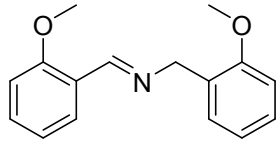
^{1}H NMR (400 MHz, Chloroform-d): δ 4.91 (s, 2H), 7.08-7.15 (m, 2H), 7.56-7.57 (m, 2H), 8.50 (s, 1H), 8.65 (m, 2H), 8.79 (s, 2H).



(E)-N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (4F)

The titled compound was made following the general procedure using (4-bromophenyl)-methanamine (93 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

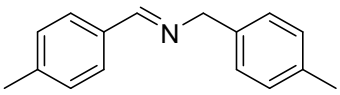
^{1}H NMR (400 MHz, Chloroform-d): δ 4.94 (s, 2H), 6.97-7.08 (m, 4H), 7.22-7.24 (m, 2H), 7.32-7.42 (m, 2H), 8.41 (s, 1H).



(E)-N-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (4G)

The titled compound was made following the general procedure using (2-methoxyphenyl)-methanamine (69 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

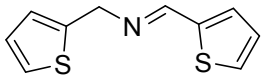
^{1}H NMR (400 MHz, Chloroform-d): δ 3.77 (s, 6H), 4.74 (s, 2H), 6.78-6.84 (m, 4H), 7.12-7.14 (m, 2H), 7.21-7.28 (m, 2H), 8.32 (s, 1H).



(E)-N-(4-methylbenzyl)-1-(p-tolyl)methanimine (4H)

The titled compound was made following the general procedure using p-tolylmethanamine (61 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

^{1}H NMR (400 MHz, Chloroform-d): δ 2.32 (s, 3H), 2.36 (s, 3H), 4.75 (s, 2H), 7.12-7.14 (m, 2H), 7.19-7.22 (m, 4H), 7.65 (d, J = 8.0 Hz, 2H), 8.32 (s, 1H).



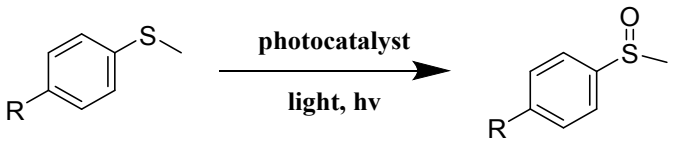
(E)-1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine (4I)

The titled compound was made following the general procedure using thiophen-2-ylmethanamine (61 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% yield).

^{1}H NMR (400 MHz, Chloroform-d): δ 4.91 (s, 2H), 7.27-7.30 (m, 2H), 7.415 (dd, J1= 2.0 Hz, J2 = 2.0 Hz, 1H), 7.57 (dd, J1= 2.0 Hz, J2 = 2.0 Hz, 2H), 8.095 (dd, J1= 4.0 Hz, J2 = 2.0 Hz, 1H), 8.80 (s, 1H).

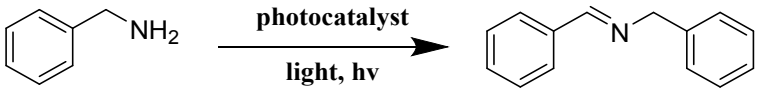
Section 12. Comparison of photocatalysts

Table S2. Physicochemical properties and photocatalytic activity of different photocatalysts for selective oxidation of sulfides.



entry	catalysts	-R	Substrate (mmol)	Inputs (cat.)	light	gas	time (h)	conv. (%)	sel. (%)	co-catalyst
1[10]	Ry-Td	H	1	5mg	Xe lamp ($\lambda > 420$ nm)	O_2		100	96	none
2[11]	spherical-COF 1a						48	100		
	laminar-COF 1b	CH_3	0.3	2.4mg	blue light ($\lambda = 450$ nm)	O_2	48	80		none
	3D-COF 1c						48	77		
3[12]	4 wt % C_{60}/g-C_3N_4	H	0.2	30mg	Xe lamp ($\lambda > 400$ nm)	O_2	10	94.35	100	none
4[13]	B-$(NPh_2)_3$						48	33	99	
	B-CB_3	H	2	10mg	LED lamp ($\lambda = 460$ nm)	air	48	93	99	none
	B-CB_2-BT						24	98	99	
5[14]	C-CMP	H	1	20mg	300W Xe lamp ($\lambda > 400$ nm)	O_2	8	99	93	none
6[15]	CPOP-28	H	0.5	1mol%	23 W white LED lamp	air	10	79	98	none
	CPOP-29						10	99	99	
7[16]	CMP-BDD	H	1	20mg	14 W blue LED lamp	O_2	24	99	99	HCl
	CMP-B							21	99	HCl
8	This work	H	0.5	2.45mg (0.5mol%)	LED lamp ($\lambda = 460$ nm)	air	48	99	99	none

Table S3. Physicochemical properties and photocatalytic activity of different photocatalysts for selective oxidation of amines to imines.



entry	catalysts	Substrate (mmol)	Inputs (cat.)	light	gas	time (h)	conv. (%)	sel. (%)	temperature (℃)
11[7]	mpg-C_3N_4	1	50mg	Xe lamp ($\lambda > 420$ nm)	O_2	3.5	99	99	80
2[18]	K-PHI	0.05	5mg	blue LED ($\lambda = 461$ nm)	CO_2	24	100	90	35
3[19]	CNUIO-5	0.05	5mg	Xe lamp ($\lambda > 420$ nm)	air	5	58.9	99	RT
4[20]	2-ZSCN	0.5	50mg	visible light ($\lambda > 420$ nm)	O_2	5	92	97	RT
5[21]	B-BO-1,3,5	1	6mg	blue LED ($\lambda = 460$ nm)	O_2	24（3）	99（48）		RT
6[22]	TFPT-BMTH	0.2	5mmol%	30 W blue LED ($\lambda = 454$ nm)	air	24	99		RT
7[23]	Py-BSZ-COF	0.2	5mg	15 W LED bulb ($\lambda = 520$ nm)	air	12	99		RT
8	This work	0.5	2.45mg（0.5mol%）	LED lamp ($\lambda = 460$ nm)	air	24	99	99	RT

Section 13. Reference

References:

1. X. Zhu, S. An, Y. Liu, J. Hu, H. Liu, C. Tian, S. Dai, X. Yang, H. Wang, C. W. Abney and S. Dai, *AIChE J.*, 2017, **63**, 3470-3478.
2. J. A. Riddle, S. P. Lathrop, J. C. Bollinger and D. Lee, *J. Am. Chem. Soc.*, 2006, **128**, 10986-10987.
3. C. R. DeBlase, K. E. Silberstein, T. T. Truong, H. D. Abruna and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 16821-16824.
4. P. Das, A. Kumar, A. Chowdhury and P. S. Mukherjee, *ACS Omega*, 2018, **3**, 13757-13771.
5. S. Bandyopadhyay, A. G. Anil, A. James and A. Patra, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27669-27678.
6. M. Liras, M. Iglesias and F. Sánchez, Macromolecules, 2016, 49, 1666-1673.
7. J. A. Johnson, X. Zhang, T. C. Reeson, Y.-S. Chen, and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 15881−15884.
8. J. Luo, J.-Z. Lu and J. Zhang, *J. Mater. Chem. A*, 2018, **6**, 15154–15161.
9. J. A. Johnson, J. Luo, X. Zhang, Y.-S. Chen, M. D. Morton, E. Echeverría, F. E. Torres, and J. Zhang, *ACS Catal.*, 2015, **5**, 5283–5291.
10. S. Wang, Q. Sun, W. Chen, Y. Tang, B. Aguila, Y. Pan, A. Zheng, Z. Yang, L. Wojtas, S. Ma and F.-S. Xiao, *Matter*, 2020, **2**, 416-427.
11. A. Jiménez-Almarza, A. López-Magano, L. Marzo, S. Cabrera, R. Mas-Ballesté and J. Alemán, *ChemCatChem*, 2019, **11**, 4916-4922.
12. X. Chen, K. Deng, P. Zhou and Z. Zhang, *ChemSusChem*, 2018, **11**, 2444-2452.
13. Z. J. Wang, S. Ghasimi, K. Landfester and K. A. Zhang, *Chem. Commun.*, 2014, **50**, 8177-8180.
14. C. Su, R. Tandiana, B. Tian, A. Sengupta, W. Tang, J. Su and K. P. Loh, *ACS Catal.*, 2016, **6**, 3594-3599.
15. H.-P. Liang, Q. Chen and B.-H. Han, *ACS Catal.*, 2018, **8**, 5313-5322.
16. H. Zhang, Q. Huang, W. Zhang, C. Pan, J. Wang, C. Ai, J. Tang and G. Yu, *ChemPhotoChem*, 2019, **3**, 645-651.
17. F. Su, S. C. Mathew, L. Mohlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem. Int. Ed.,* 2011, **50**, 657-660.
18. Y. Markushyna, P. Lamagni, J. Catalano, N. Lock, G. Zhang, M. Antonietti and A. Savateev, *ACS Catal.*, 2020, **10**, 7336-7342.
19. S. Zhang, K. Chen, W. Peng and J. Huang, *New J. Chem.*, 2020, **44**, 3052-3061.
20. P. Chen, L.-H. Meng, L. Chen, J.-K. Guo, S. Shen, C.-T. Au and S.-F. Yin, *ACS Sustainable Chem. Eng.*, 2019, **7**, 14203-14209.
21. Z. J. Wang, S. Ghasimi, K. Landfester and K. A. Zhang, *Adv. Mater.*, 2015, **27**, 6265-6270.
22. Z. Liu, Q. Su, P. Ju, X. Li, G. Li, Q. Wu and B. Yang, *Chem. Commun.,* 2020, **56**, 766-769.

23. S. Li, L. Li, Y. Li, L. Dai, C. Liu, Y. Liu, J. Li, J. Lv, P. Li and B. Wang, *ACS Catal.*, 2020, **10**, 8717-8726.