Supporting Information

Naphthalene-Based Donor–Acceptor Covalent Organic Frameworks as Electron Distribution Regulator for Boosting Photocatalysis Under Green Light Irradiation

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1. Experimental Section.

Materials and Methods

1,3,5-tri(4-formylphenyl)triazine (TfpTz, 97%) was purchased from Bidepharm. 1, 5diaminaphthalene (DaNap, 99.79%), 1,3,5-tribromobenzene (98%), 4-formylphenylboronic (98%) acid, and benzylamine (98%) were purchased from Energy Chemical. Commercially available reagents and solvents without special descriptions were purchased from Damao Chemical Reagent Factory. There was no additional purification to all the reagents and solvents.

Powder X-ray diffraction (PXRD) measurements: The PXRD was obtained on a D8 Advance XRD instrument, and the diffraction patterns were gathered from 2 to 30° at room temperature.

Fourier transform infrared spectroscopy (FT-IR) measurements: The FT-IR was recorded from 400 to 4000 cm⁻¹ on a ThermoFisher 6700 FTIR spectrometer by using KBr pellets. All the spectra were collected neatly in the ambient atmosphere. The signals are given in transmittance (%) against wavenumbers (cm⁻¹).

¹³C cross polarization magic angle spinning (CP-MAS) NMR measurements: The solid
 ¹³C CP-MAS NMR spectroscopy was performed on the Agilent DD2-500MHz spectrometer.

Thermogravimetric analysis (TGA) measurements: The TGA was recorded on a TA Q500 thermogravimeter from 20 to 800 °C at a rate of 10 °C /min under an air atmosphere.

Scanning electron microscopy (SEM) measurements: The SEM was performed on the JSM-7610F Plus field emission SEM under an accelerating voltage of 500 V. The samples were randomly dispersed on the surface of the flat aluminum sample holder for SEM

measurements.

Transmission electron microscopy (TEM) measurements: The morphology was determined by TEM. TEM experiments were performed on a JEM-F200 field emission transmission electron microscope at an acceleration voltage of 300 kV.

Sorption studies: N_2 adsorption/desorption was determined with autosorb iQ physical adsorption instrument at 77 K. The samples were degassed for 6 hours at 120 °C, under the pressure below 1 Torr.

UV-Vis spectra: Liquid UV-Vis spectra were collected on a PERSEE T9CS spectrometer. Solid UV-vis spectra were recorded on Hitachi UH5700 UV-vis-NIR spectrophotometer.

Time-resolved decay fluorescence spectra: The time-resolved decay fluorescence spectra were recorded on Edinburgh FLS 1000 stable/transient fluorescence spectrometer.

Electron paramagnetic resonance (EPR) measurements: The EPR spectrums were recorded on a Bruker E500 instrument.

Nuclear magnetic resonance (¹H NMR) measurements: The ¹H NMR spectra were recorded on the Bruker Avance NEO 600 M spectrometer, Bruker Avance II 400 spectrometer, or Vaian 400 M spectrometer.

Electrochemical Experiments

Photocurrent measurements were conducted with a ZAHNER ENNIUM electrochemical workstation in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, Pt plate as the counter electrode in an aqueous solution of KCl at a scan rate of 100 mV·s⁻¹, and an Ag/AgCl as a reference electrode. A 520 nm LED was used as the light

source. The 2 mg of catalyst was added into 250 μ L of CH₃CH₂OH and 20 μ L of Nafion mixed solution. Then a 100 μ L suspension was dropped on the surface of an FTO glass and dried at room temperature for photocurrent measurements, and the signals were recorded under 10 s chopped light. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky plots were performed with a 30 μ L suspension on the working electrode with a bias potential of -1 V.

Molecular Oxygen Activation Measurements

3,3',5,5'-tetramethylbenzidine (TMB) oxidation experiments: The TMB oxidation experiments were measured according to previous reports.¹ 2 mL of CH₃CN or CH₃OH suspension containing the catalyst (1 mg·mL⁻¹) and 6 mg of TMB (mg·mL⁻¹ CH₃CN or CH₃OH solution) were mixed in the cuvette. A 520 nm LED equipment was used as the light source. TMB oxidation experiments were evaluated by UV-Vis measurements (the absorbance around 420 nm) at different time intervals.

Reactive Oxygen Species Trapping Experiment.

The O_2 ⁻⁻ and 1O_2 generated by NapTz–COF have been detected by EPR in the presence of DMPO and TEMP, respectively. Typically, 30 µL DMPO or TEMP in 1 mL CH₃CN was mixed with 0.5 mL of NapTz–COF/CH₃CN suspension (1 mg·mL⁻¹). The formed mixed solution is drawn with a capillary tube and placed into an EPR tube. EPR measurements were carried out during the 520 nm LED light irradiation under the air conditions.

General Procedure for Recycle

After the photocatalytic reaction, the mixture was centrifuged at 9000 rpm for 5 min, and the precipitate was washed with CH_2Cl_2 until no product was detected in the eluent. The recovered solid was reused for the next runs directly.

Preparation



Scheme S1. Synthesis of ligand TfpBz.

Synthesis of 1,3,5-tris(4-formylphenyl)benzene (TfpBz).

According to the existing literature, the synthesis process is modified slightly.² A mixture of 4-formylphenylboronic acid (4.64 g, 31.00 mmol), 1,3,5-tribromobenzene (1.57 g, 5.00 mmol), tetrakis(triphenylphosphine)palladium (0.23 g, 0.20 mmol) and K₂CO₃ (7.46 g, 54.00 mmol) was dissolved in 88 mL of a mixed solvent of 1,4-dioxane (80 mL) and water (8 mL) in a 250 mL three-necked flask. Then, the solution was stirred at 90 °C under Ar atmosphere for 72 h. After cooled at room temperature, the precipitate was collected by filtration and the residue was purified by column chromatography (dichloromethane is the eluent) to give TfpBz as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 10.13 (s, 3H), 8.05 (d, *J* = 8 Hz, 6H), 7.94 (s, 3H), 7.90 (d, *J* = 8 Hz, 6H).



Fig. S1. Schematic illustration of the synthesis process of NapTz–COF and NapBz–COF. Preparation of NapTz–COF

TfpTz (35.40 mg, 0.09 mmol) and DaNap (20.60 mg, 0.13 mmol) were added into the Pyrex tube together with dioxane (0.30 mL) and mesitylene (1.70 mL). After 25 min ultrasonic treatment, acetic acid aqueous solution (0.20 mL, 8 M) was added and treated with ultrasound again for 3 min. Then the Pyrex tube was frozen in liquid nitrogen, degassed by three cycles of freeze-pump-thaw, and then sealed in a vacuum. The mixture was then heated at 120 °C for 72 h. The filtrated solid products were washed three times with methanol and dichloromethane. Soxhlet extraction with methanol and dichloromethane respectively was used for further treatment of 12 h. The final product NapTz–COF was dried in a vacuum oven at 60 °C for 5 h to obtain orange-red powder.

Preparation of NapBz-COF

TfpBz (27.90 mg, 0.09 mmol) and DaNap (20.60 mg, 0.13 mmol) were added into the

Pyrex tube together with dioxane (0.30 mL) and mesitylene (1.70 mL). After 25 min ultrasonic treatment, acetic acid aqueous solution (0.20 mL, 8 M) was added and treated with ultrasound again for 3 min. Then the Pyrex tube was frozen in liquid nitrogen, degassed by three cycles of freeze-pump-thaw, and then sealed in a vacuum. The mixture was then heated at 120 °C for 72 h. The filtrated solid products were washed three times with methanol and dichloromethane. Soxhlet extraction with methanol and dichloromethane respectively was used for further treatment of 12 h. The final product NapBz–COF was dried in a vacuum oven at 60 °C for 5 h to obtain chartreuse powder.

2. Characterizations of Covalent organic framework



Fig. S2. FT-IR spectra of NapTz–COF and corresponding building blocks.



Fig. S3. FT-IR spectra of NapBz–COF and corresponding building blocks.



Fig. S4. PXRD pattern of NapTz-COF.



Fig. S5. PXRD pattern of NapBz–COF.



Fig. S6. Structural simulation of the NapTz–COF. (a, b) The unit cell structure of the NapTz–COF using the AA stacking model along c axis and b axis. (c, d) The unit cell structure of the NapTz–COF using the AB stacking model along c axis and b axis.



Fig. S7. Structural simulation of the NapBz–COF. (a, b) The unit cell structure of the NapBz–COF using the AA stacking model along c axis and b axis. (c, d) The unit cell structure of the NapBz–COF using the AB stacking model along c axis and b axis.



Fig. S8. PXRD patterns of TfpTz 、 DaNap 、 NapTz-COF.



Fig. S9. PXRD patterns of TfpBz 、 DaNap 、 NapBz–COF.



Fig. S10. SEM image of NapTz–COF.



Fig. S11. SEM image of NapBz–COF.



Fig. S12. TEM image of NapTz-COF.



Fig. S13. SEM image of NapBz–COF.



Fig. S14. N_2 adsorption and desorption isotherm of NapTz–COF



Fig. S15. N_2 adsorption and desorption isotherm of NapBz–COF.



Fig. S16. TGA spectra of NapTz–COF.



Fig. S17. TGA spectra of NapBz–COF.



Fig. S18. TGA spectra of comparison of NapTz–COF and NapBz–COF.



Fig. S19. Time-resolved decay fluorescence spectra of NapTz–COF and NapBz–COF.



Fig. S20. Mott-Schottky plot of NapTz–COF at frequencies of 500, 1000, and 1500 Hz.



Fig. S21. Mott-Schottky plot of NapBz–COF at frequencies of 500, 1000, and 1500 Hz.



Fig. S22. Time-dependent corresponding absorption of TMB ($3 \text{ mg} \cdot \text{mL}^{-1}$) at 420 nm in CH₃OH solution containing NapTz–COF under 520 nm irradiation or dark and NapBz–COF under 520 nm irradiation in the air atmosphere.



Fig. S23. Time-dependent corresponding absorption of TMB ($3 \text{ mg} \cdot \text{mL}^{-1}$) at 420 nm in CH₃CN solution containing NapTz–COF under 520 nm irradiation or dark and NapBz–COF under 520 nm irradiation in the air atmosphere.



Fig. S24. EPR spectra of O_2^{-} were generated over NapTz–COF under green light irradiation.



Fig. S25. EPR spectra of ${}^{1}O_{2}$ were generated over NapTz–COF under green light irradiation.

3. Catalysis Details

General procedure for the selective oxidative coupling of benzylamines.

The photocatalyzed selective oxidative coupling of benzylamines was performed in a sealed quartz flask (10 mL) containing COFs (5 mg), benzylamines (0.1 mmol), and CH₃CN (2 mL) under standard conditions. The resulting mixture was stirred in an oxygen atmosphere and irradiated at room temperature with a 520 nm LED. After reaction for 3 h, 1,3, 5-trimethoxybenzene was added as the internal standard, the COFs were separated by filtration, and the excess solvent was separated by vacuum rotary evaporation. The yield was determined by the ¹H NMR spectrum.

General procedures for the selective oxidation of thioethers.

The photocatalyzed selective oxidation of thioethers was performed in a sealed quartz flask (10 mL) containing COFs (5 mg), thioethers (0.1 mmol), and CH₃OH (2 mL) under standard conditions. The resulting mixture was stirred in an oxygen atmosphere and irradiated at room temperature with a 520 nm LED. After the reaction for 10 h, 1,3, 5-trimethoxybenzene was added as the internal standard, the COFs were separated by filtration, and the excess solvent was separated by vacuum rotary evaporation. The yield was determined by the ¹H NMR spectrum.

Cycle Catalysis Experiment.

After the photocatalytic reaction, the mixture was centrifuged at 9000 rpm for 5 min, and the precipitate was washed with CH_2Cl_2 until no product was detected in the eluent. The recovered solid was reused for the next runs directly. The yield after running 5 times did not decrease obviously.



Fig. S26. Quenching experiments of oxidative coupling of benzylamines.



Fig. S27. Yield-time plots of photocatalytic oxidative coupling of benzylamines over NapTz–COF under the standard conditions.



Fig. S28. Recycling experiments of photocatalytic oxidative coupling of benzylamines over NapTz–COF under the standard conditions.



Fig. S29. PXRD spectra of pristine NapTz–COF and NapTz–COF after photocatalytic oxidative coupling of benzylamines.



Fig. S30. FT-IR spectra of the pristine NapTz–COF and NapTz–COF after photocatalytic oxidative coupling of benzylamines.



Fig. S31. TGA of the pristine NapTz–COF and NapTz–COF after photocatalytic oxidative coupling of benzylamines.

	$ \begin{array}{c} S \\ \hline RT, 520 \text{ nm LED, 10 h} \end{array} $	0 \$
Entry	3a4aVariation from the standard conditions	Yield (%)
1	None	95
2	NapBz–COF instead of NapTz–COF	23
3	No light	N.R.
4	No catalyst	20
5	Ar instead of O ₂	N.R.
6	Air instead of O_2	23
7	Addition of 1 equiv 1,4-benzoquinone	27
8	Addition of 1 equiv DABCO	48
9	Addition of 1 equiv AgNO ₃	39
10	Addition of 1 equiv KI	32
11	Addition of 1 equiv tert-butyl alcohol	95
12	DaNap instead of NapTz-COF	3
13	TfpTz instead of NapTz-COF	N.R.
14	Mixture of DaNap and TfpTz instead of NapTz–COF	2

Table S1 Photocatalytic Performances of NapTz–COF for selective oxidation of thioethers. $^{\alpha}$

^{α} Standard reaction condition: Thioethers (0.1 mmol), NapTz–COF (5 mg), and CH₃OH (2 mL). The mixture solution was irradiated with a 520 nm LED at room temperature in the presence of oxygen for 10 h. The yield was determined by ¹H NMR analysis. N.R. = No reaction.



Fig. S32. Yield-time plots of photocatalytic selective oxidation of thioethers over NapTz–COF under the standard conditions.



Fig. S33. Recycling experiments of photocatalytic selective oxidation of thioethers over NapTz–COF under the standard conditions.



Fig. S34. PXRD spectra of pristine NapTz–COF and NapTz–COF after photocatalytic selective oxidation of thioethers.



Fig. S35. FT-IR spectra of the pristine NapTz–COF and NapTz–COF after photocatalytic selective oxidation of thioethers.



Fig. S36. TGA of the pristine NapTz–COF and NapTz–COF after photocatalytic selective oxidation of thioethers.



Fig. S37. Mechanism of oxidative coupling of benzylamines and selective oxidation of thioethers photocatalyzed by NapTz–COF.

Detection of NH₃:

Benzylamine (0.10 mmol) and NapTz–COF (5.0 mg) was mixed in CH₃CN (2.0 mL), which was stirred and irradiated by green LED for 3 h at room temperature in O₂. Then, NapTz–COF was separated from the reaction mixture by centrifugation. After that, 2.0 mL distilled water was added into the above solution, which subsequently was extracted by 5.0 mL CH₂Cl₂ for twice. The aqueous layer was subject to pH test, showing its basic solution (pH = 9.23). However, in the absence of NapTz–COF or light irradiation, the water layer is neutral (PH=7), which also indicated that the NH₃ molecule was released from the coupling reaction.



Fig. S38. The pH test for the reaction solution after different conditions.

4. Copies of Crude ¹H NMR Spectrum

It has been reported that the characteristic peaks of 1,3,5-trimethoxybenzene are 3.75 and 6.08 ppm.³ The integration number of the peak at 6.08 ppm represents the equivalent of the internal standard relative to substrate.

Copies of Crude ¹H NMR Spectrum of photocatalyzed selective oxidative coupling of benzylamines



Fig. S39. Crude ¹H NMR Spectrum for 2a.⁴



Fig. S40. Crude ¹H NMR Spectrum for 2b.⁴



Fig. S41. Crude ¹H NMR Spectrum for 2c.⁴



Fig. S42. Crude ¹H NMR Spectrum for 2d.⁴



Fig. S43. Crude ¹H NMR Spectrum for 2e.⁴



Fig. S44. Crude ¹H NMR Spectrum for 2f.⁴



Fig. S45. Crude ¹H NMR Spectrum for 2g.⁴



Fig. S46. Crude ¹H NMR Spectrum for 2h.⁴



Fig. S47. Crude ¹H NMR Spectrum for 2i.⁴



Fig. S48. Crude ¹H NMR Spectrum for 2j.⁴



Fig. S49. Crude ¹H NMR Spectrum for 2k.⁵



Fig. S50. Crude ¹H NMR Spectrum for 21.⁴

Copies of Crude 1H NMR Spectrum of Selective oxidation of thioethers by photocatalysis



Fig. S51. Crude ¹H NMR Spectrum for 4a.⁶



Fig. S52. Crude ¹H NMR Spectrum for 4b.⁶



Fig. S53. Crude ¹H NMR Spectrum for 4c.⁶



Fig. S54. Crude ¹H NMR Spectrum for 4d.⁷



Fig. S55. Crude ¹H NMR Spectrum for 4e.⁶



Fig. S56. Crude ¹H NMR Spectrum for 4f.⁷



Fig. S57. Crude ¹H NMR Spectrum for 4g.⁸



Fig. S58. Crude ¹H NMR Spectrum for 4h.⁹

5. References

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