Supporting Information

Benzothiadiazole-Based Donor-Acceptor-Type Covalent Organic Frameworks for Effective Heterogeneous Photocatalytic Aerobic Cycloaddition Reaction

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Chemicals

4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dibenzaldehyde (BTBA) and 1,3,6,8-tetrakis(4-aminophenyl)pyrene (PYTA) were purchased from Jilin Chinese Academy of Science-Yanshen Technology Co., Ltd. All the other chemicals were obtained from the chemical supplies and used without further purification.

Characterization

Powder X-ray diffraction (PXRD) patterns were measured using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer spectrometer. UV-vis and photoluminescent spectra were recorded on Shimadzu UV-3600 spectrophotometer and FLS1000 spectrofluorometer (Edinburgh Instruments), respectively. Scanning electron microscope (SEM) images were taken using a JEOLJSM-IT800(SHL). Transmission electron microscope (TEM) was performed by JEOLJEM 2100F. Thermo-gravimetric analysis (TGA) data was obtained using TGA 550 (TA Instruments) analyzer and the samples were heated from room temperature to 800 °C at a ramp rate of 10 °C / min. Nuclear magnetic resonance (NMR) data was collected using 400 MHz JEOL JNM-ECZ400S. The solid-state ^{13}C cross polarization magic angle spinning NMR spectra were measured on a Bruker AVANCE III 600 M. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on an Agilent GC 8890 gas chromatograph equipped with an Agilent 5977B GC/MSD mass spectrometer using an Agilent (HP-5 MS) capillary column (30 m × 250 μm × 0.25 μm). The standard analysis conditions: injector temperature: 250 °C, detector temperature: 250 °C, and column temperature program: 50 °C (hold 3 min) raised up to 200 °C (hold 3 min), and raised up to 300°C (hold 9 min) at a rate of

10°C min^{-1}.

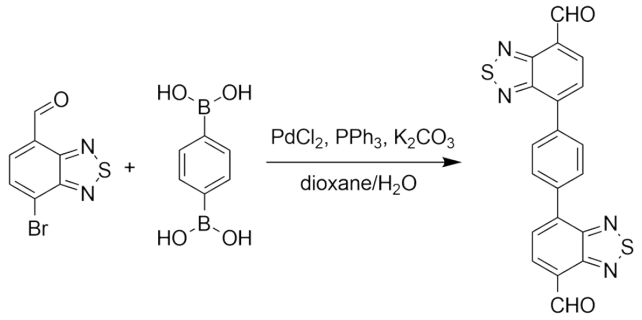
Photoelectrochemical measurements

Photoelectrochemical measurements were conducted with a CHI660E (CH Instrument Corp, Shanghai) electrochemical workstation. Firstly, 5 mg COFs were added into a mixed solution of 1 mL ethanol and 10 μL 5 wt% Nafion, which was ultra-sonicated for two hours to get homogeneous suspension. Then suspension was dropped on the surface of ITO glass and dried at room temperature. A standard three-electrode system was used with the photocatalyst-coated ITO glass as the working electrode, Pt wire as the counter electrode and an Ag/AgCl as a reference electrode. 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte. Mott-Schottky measurement was carried out at frequency of 1200, 1500, 1800 Hz with amplitude of 5 mV.

General procedure for photocatalytic cycloaddition reaction

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with 5 mg COFs, 0.50 mmol N, N, 4-trimethylaniline (1a) and 0.25 mmol N-phenylmaleimide (2a) were dispersed in 3 mL dimethyl formamide. Then the mixture was stirred under air at room temperature for 30 min in the dark. Then the above mixture was irradiated using 40 W white LED. After a certain reaction time, a mixed solution of ethyl acetate and petroleum ether was used to diagnose whether the reaction was complete. The conversion of N-phenylmaleimide was determined by GC-MS.

Synthesis of 7,7'-(1,4-phenylene)dibenzo[c][1,2,5]thiadiazole-4-carbaldehyde (PBTCA)



7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde (8.4 mmol, 2.05 g), 1,4-phenylenediboronic acid (4.0 mmol, 0.66 g), $PdCl_2$ (0.4 mmol, 70.0 mg), PPh_3 (0.8 mmol, 0.22 g) and K_2CO_3 (16.0 mmol, 2.20 g) were added in a solution containing 120 mL dioxane and 30 mL water. The reaction solution was degassed four times. Then the mixture was heated to reflux at 105 °C for 18 h under nitrogen atmosphere. Then the formed precipitates were filtrated to obtain 7,7'-(1,4-phenylene)dibenzo[c][1,2,5]thiadiazole-4-carbaldehyde (PBTCA) as a yellow solid (1.36 g, yield: 84.6%). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 10.71 (2H), 8.36 (2H), 8.27 (4H), 8.17 (2H).

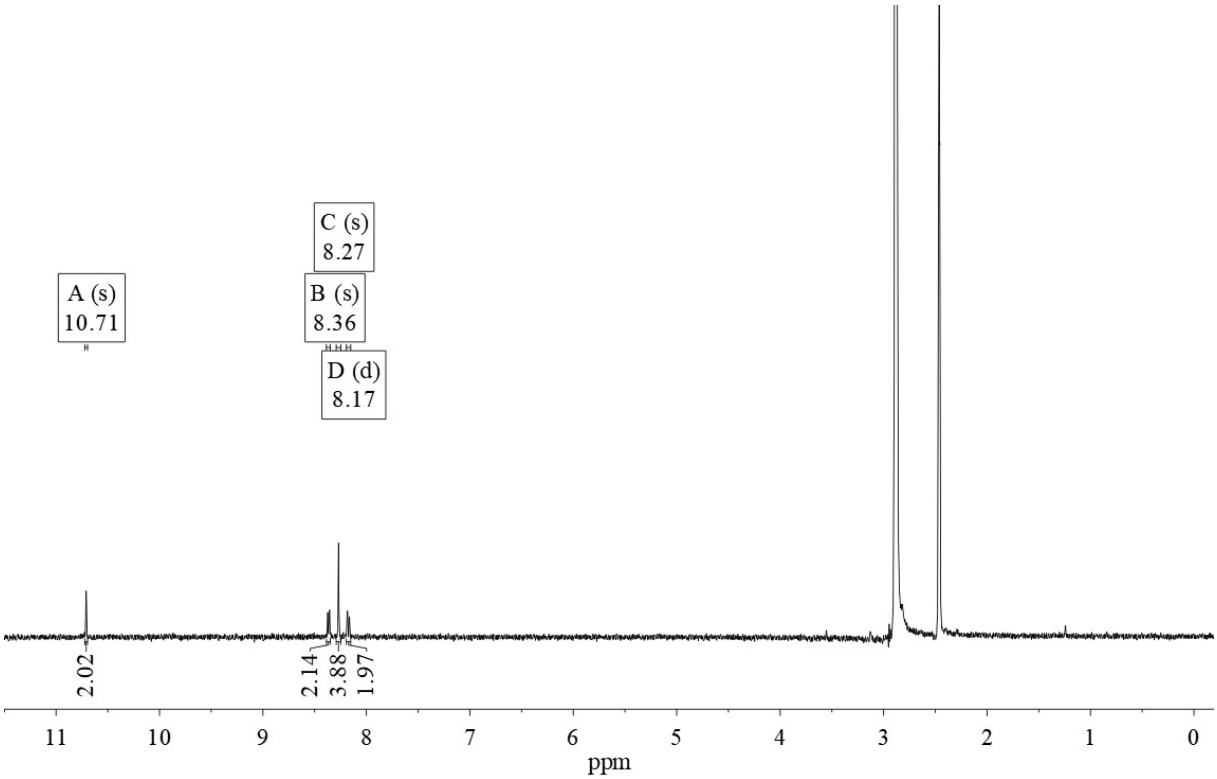


Figure S1. ^{1}H NMR spectrum of 7,7'-(1,4-phenylene)dibenzo[c][1,2,5]thiadiazole-4-carbaldehyde (PBTCA) in DMSO-d_6.

Synthesis of HIAM-0015

HIAM-0015 was synthesized according to our previous work. [1,2] PYTA (0.04 mmol, 22.64 mg) and BTBA (0.08 mmol, 27.52 mg) were dispersed in *o*-dichlorobenzene/*n*-BuOH (1mL/1mL) in the presence of AcOH (6 M, 0.2 mL). The mixture was placed in a 10 mL Pyrex tube and sonicated for 10 min. The tube was degassed through three freeze-pump-thaw cycles and then kept at 120 °C for 3 days. After the reaction was complete, the obtained mixture was cooled to room temperature, then the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF and dried under vacuum at 100 °C overnight to afford HIAM-0015.

Synthesis of HIAM-0035

PYTA (0.04 mmol, 22.64 mg) and PBTCA (0.08 mmol, 32.16 mg) were dispersed in *o*-dichlorobenzene/*n*-BuOH (1mL/1mL) in the presence of AcOH (6 M, 0.2 mL). The mixture was placed in a 10 mL Pyrex tube and sonicated for 10 min. The tube was degassed through three freeze-pump-thaw cycles and then kept at 120 °C for 3 days. After the reaction was complete, the obtained mixture was cooled to room temperature, then the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF and dried under vacuum at 100 °C overnight to afford HIAM-0035.

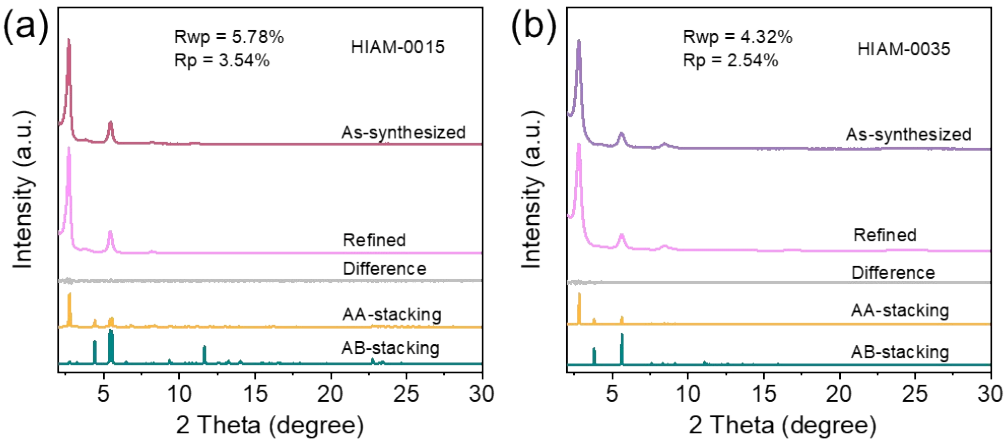


Figure S2. Experimental and simulated powder X-ray diffraction patterns for HIAM-0015 and HIAM-0035.

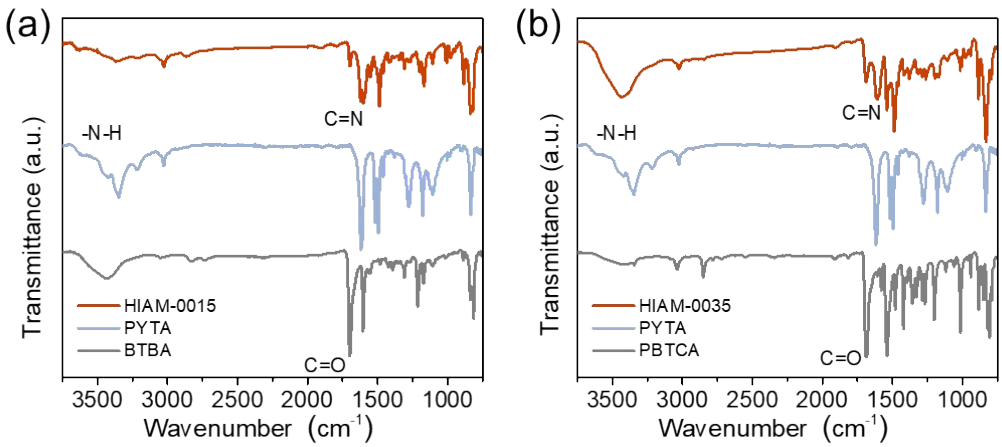


Figure S3. FT-IR spectrum of HIAM-0015 (a), HIAM-0035 (b) and the corresponding organic building units.

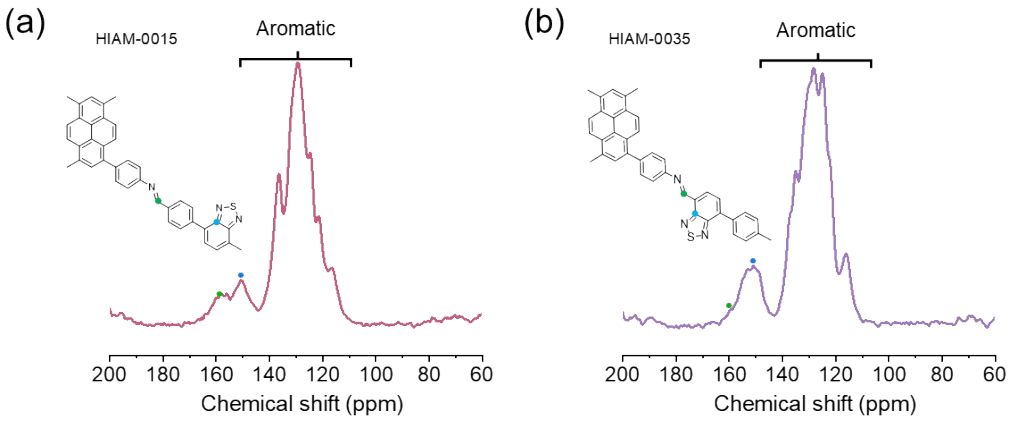


Figure S4. The solid state ^{13}C NMR of HIAM-0015 and HIAM-0035.

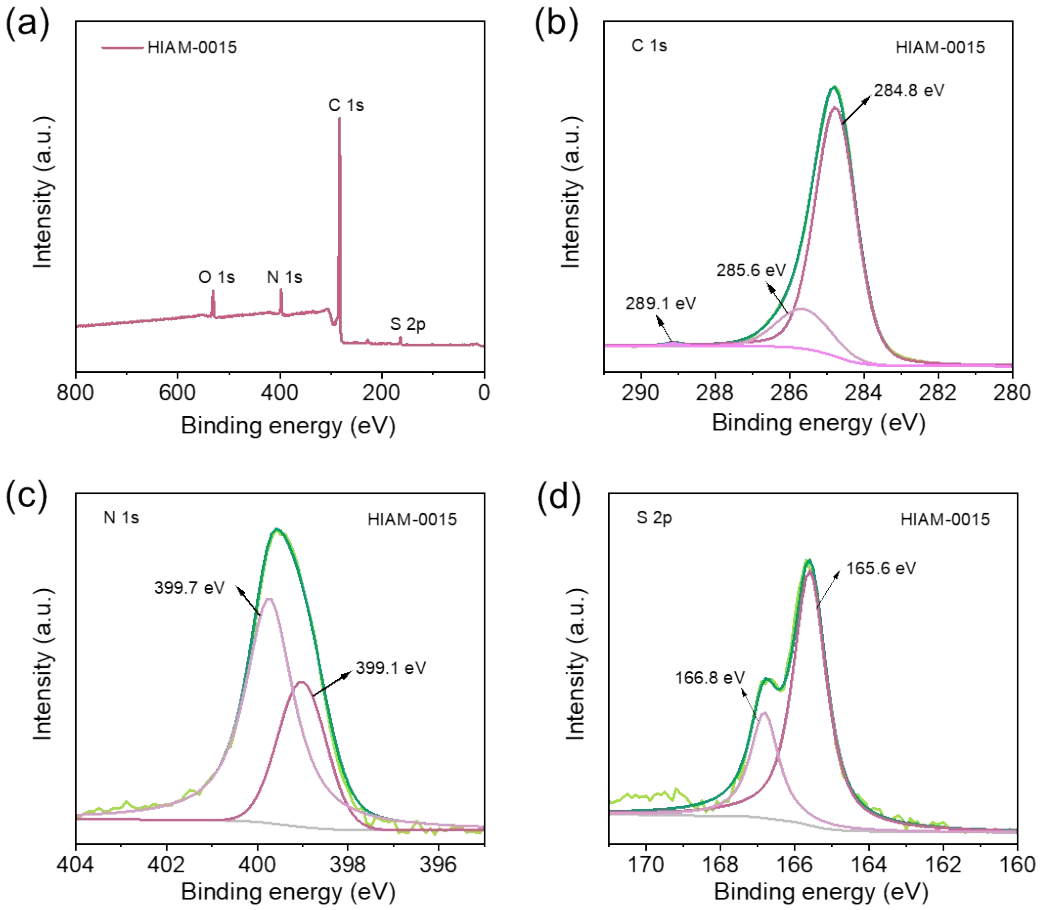


Figure S5. XPS (a) overall, (b) C 1s, (c) N 1s, (d) S 2p spectra of HIAM-0015.

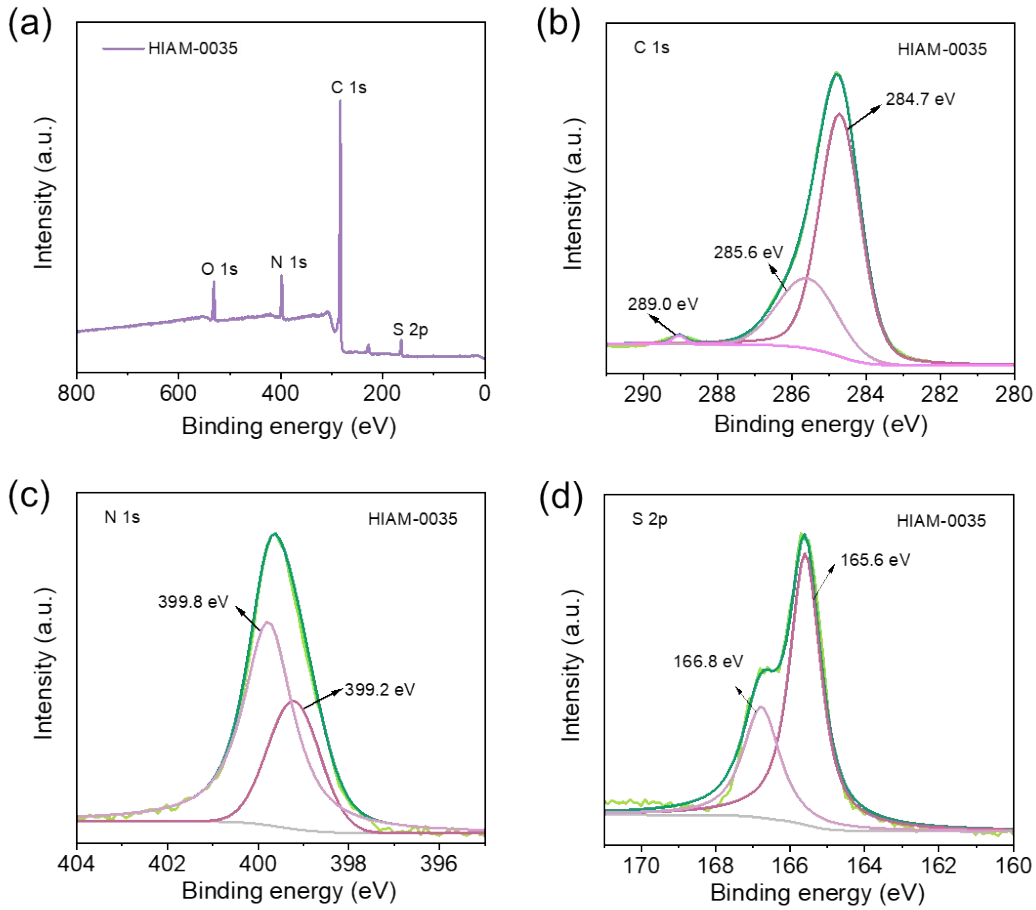


Figure S6. XPS (a) overall, (b) C 1s, (c) N 1s, (d) S 2p spectra of HIAM-0035.

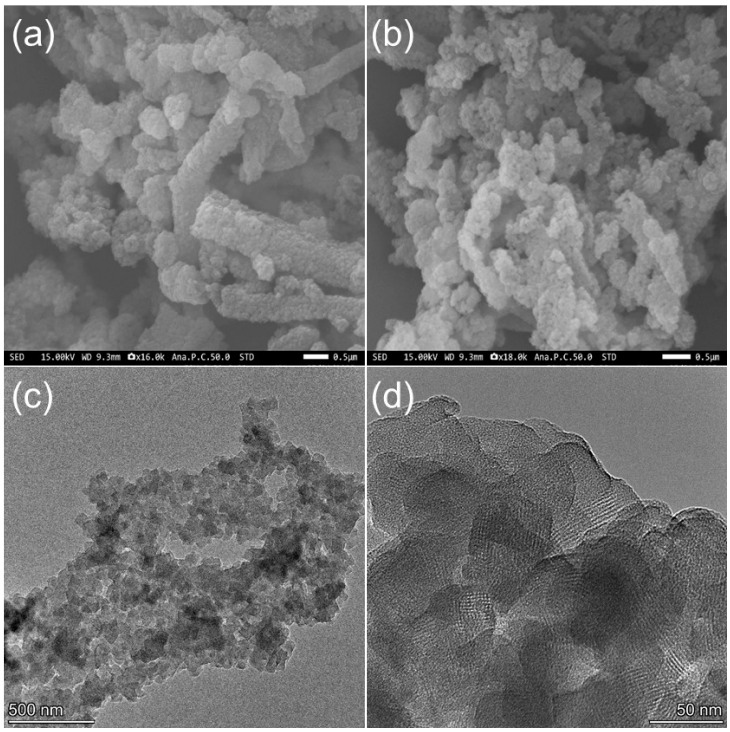


Figure S7. SEM images (a-b) and TEM images (c-d) of HIAM-0015.

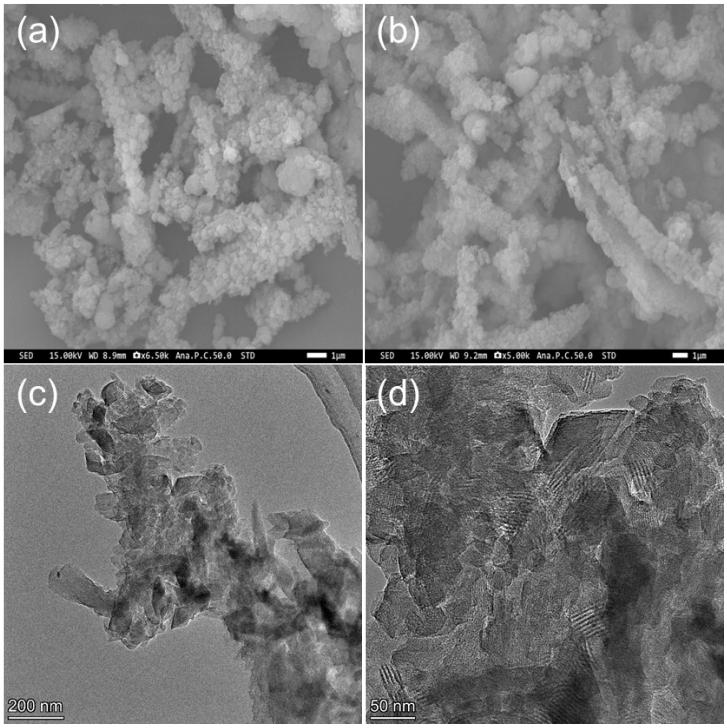


Figure S8. SEM images (a-b) and TEM images (c-d) of HIAM-0035.

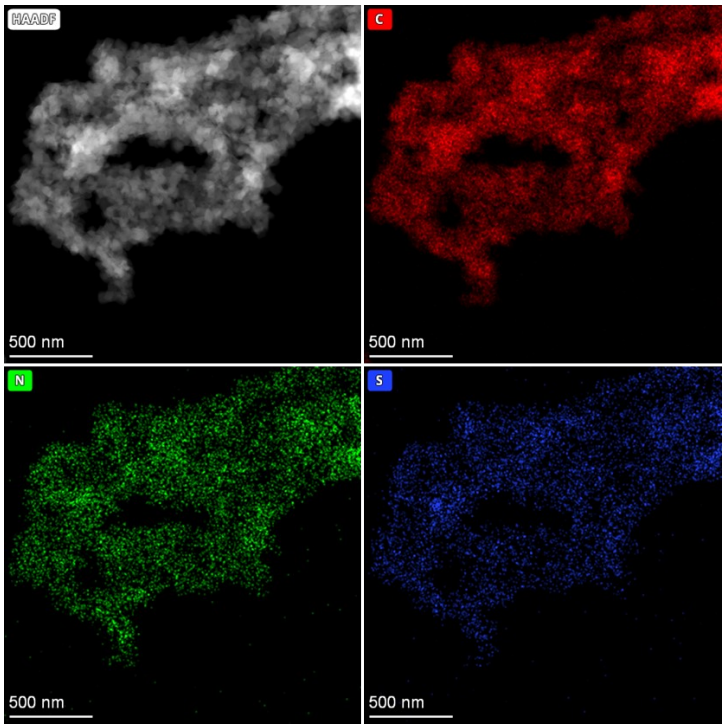


Figure S9. HAADF and elemental mapping images for C, N, S of HIAM-0015.

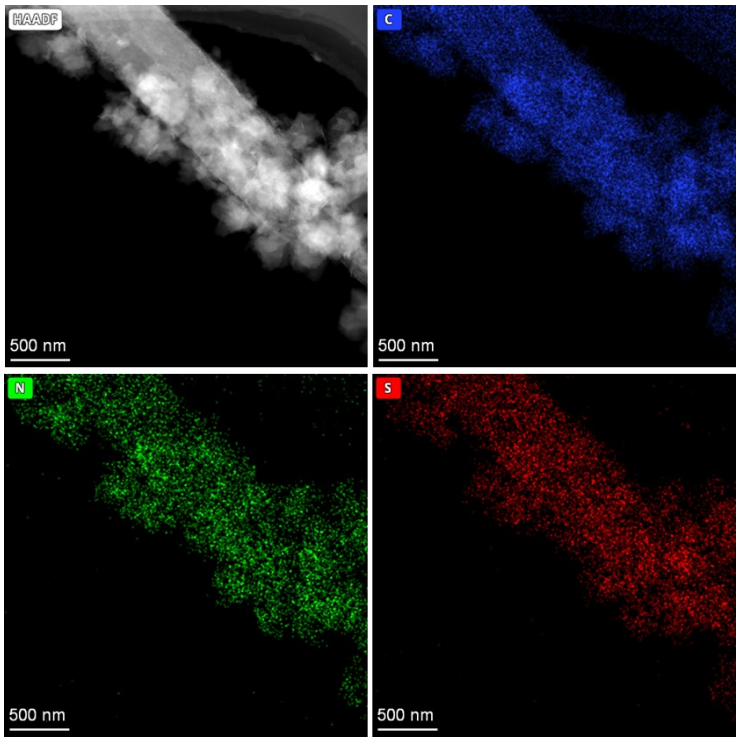


Figure S10. HAADF and elemental mapping images for C, N, S of HIAM-0035.

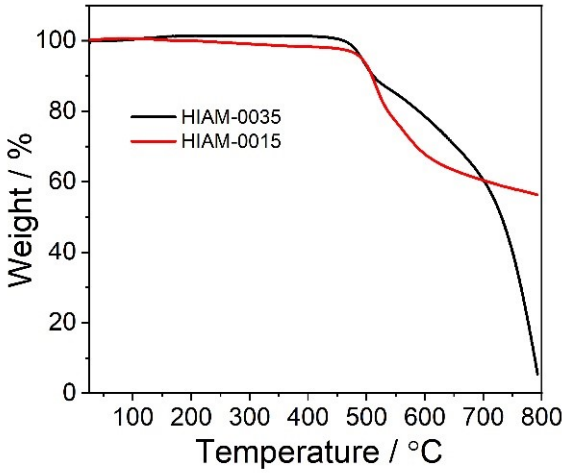


Figure S11. TGA curves of HIAM-0015 and HIAM-0035.

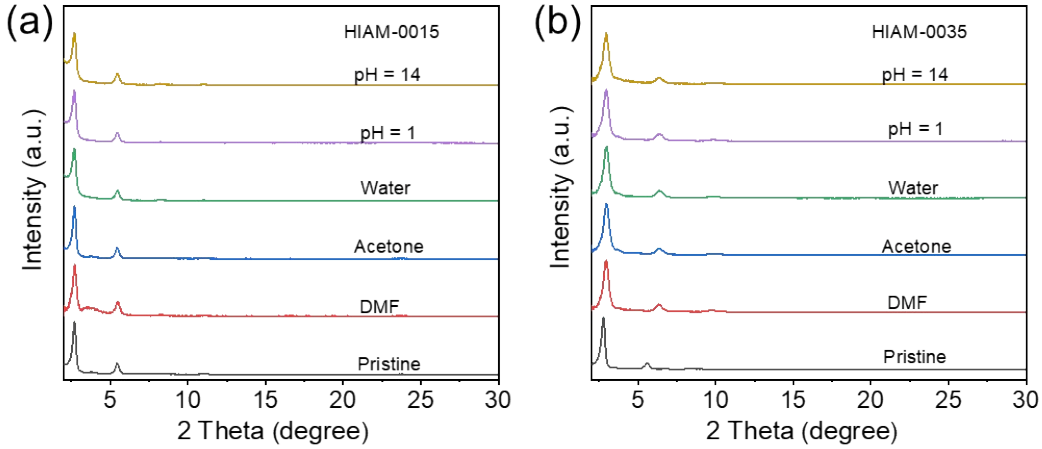


Figure S12. PXRD patterns of HIAM-0015 (a) and HAIM-0035 (b) after being immersed in different solutions for 3 days.

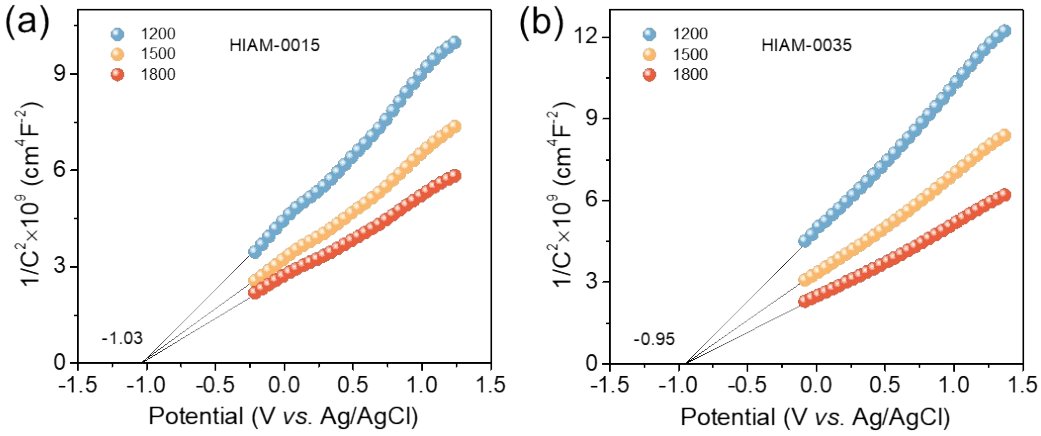


Figure S13. The Mott-Schottky plots for HIAM-0015 (a) and HIAM-0035 (b) in 0.1 M Na_2SO_4.

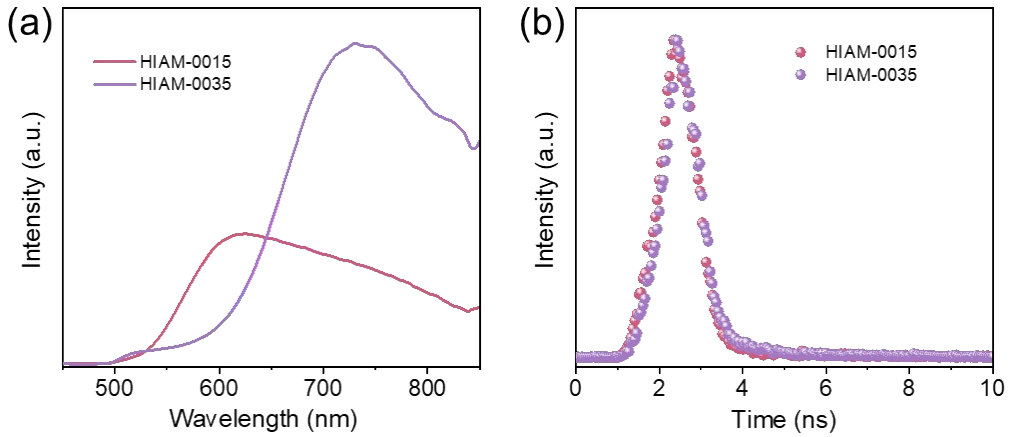


Figure S14. Photoluminescence spectra (a) and time-resolved photoluminescence decay (b) of HIAM-0015 and HIAM-0035.

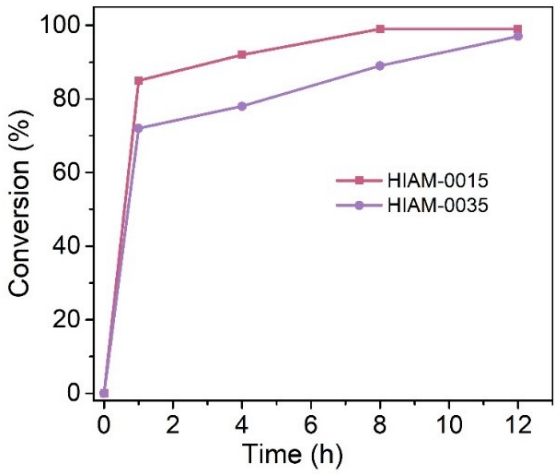


Figure S15. The photocatalytic activity of HIAM-0015 and HIAM-0035 for the cycloaddition reaction of N, N, 4-trimethylaniline and N-phenylmaleimide at different reaction times.

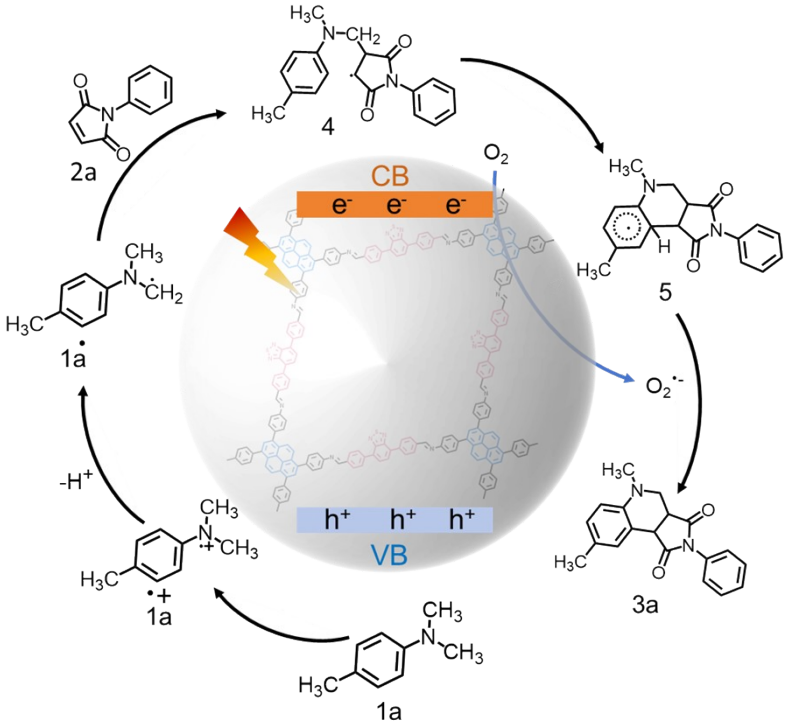


Figure S16. Proposed mechanism for photocatalytic oxidative cycloaddition reaction .

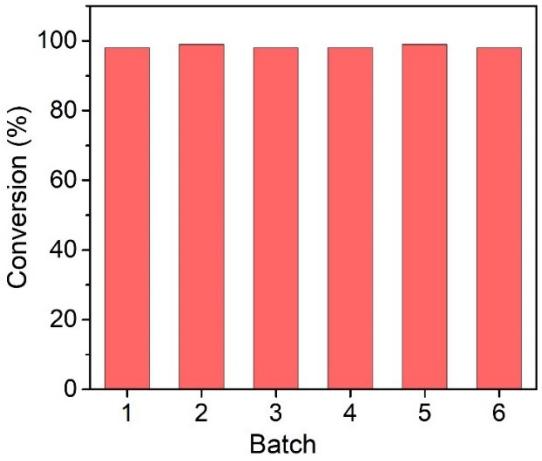


Figure S17. Repeatability test of HIAM-0015 for photocatalytic oxidative cycloaddition reaction.

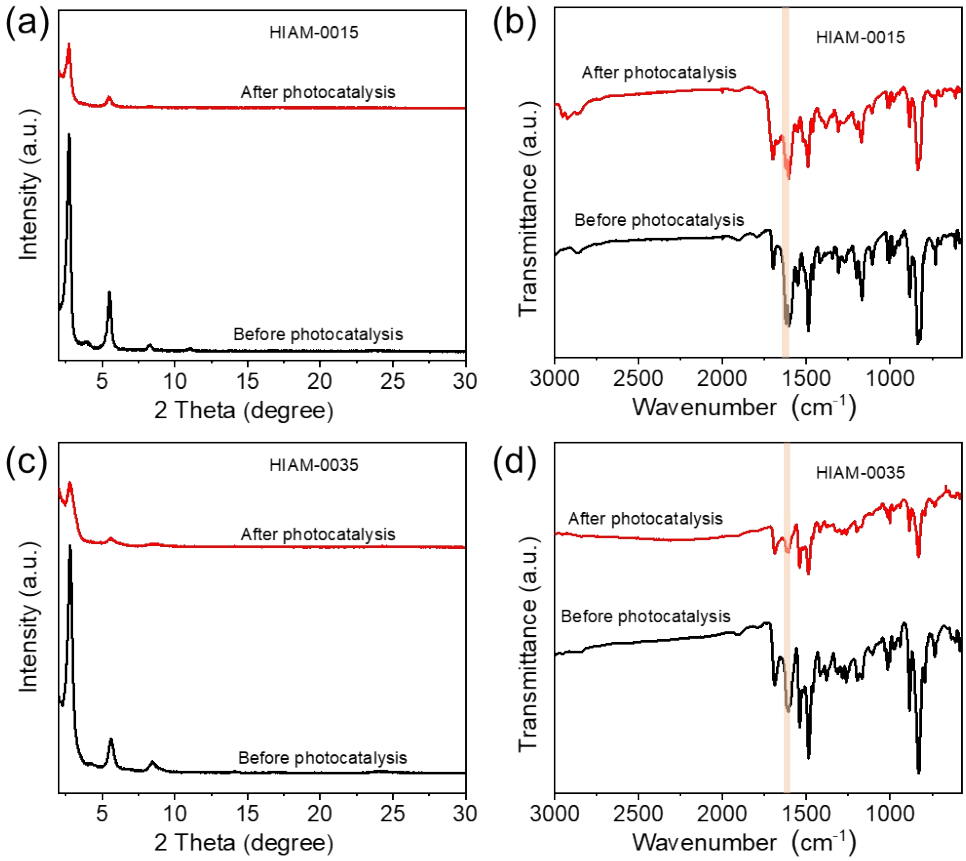


Figure S18. PXRD patterns and FT-IR spectra for HIAM-0015 (a, b) and HIAM-0035 (c, d) before and after photocatalysis.

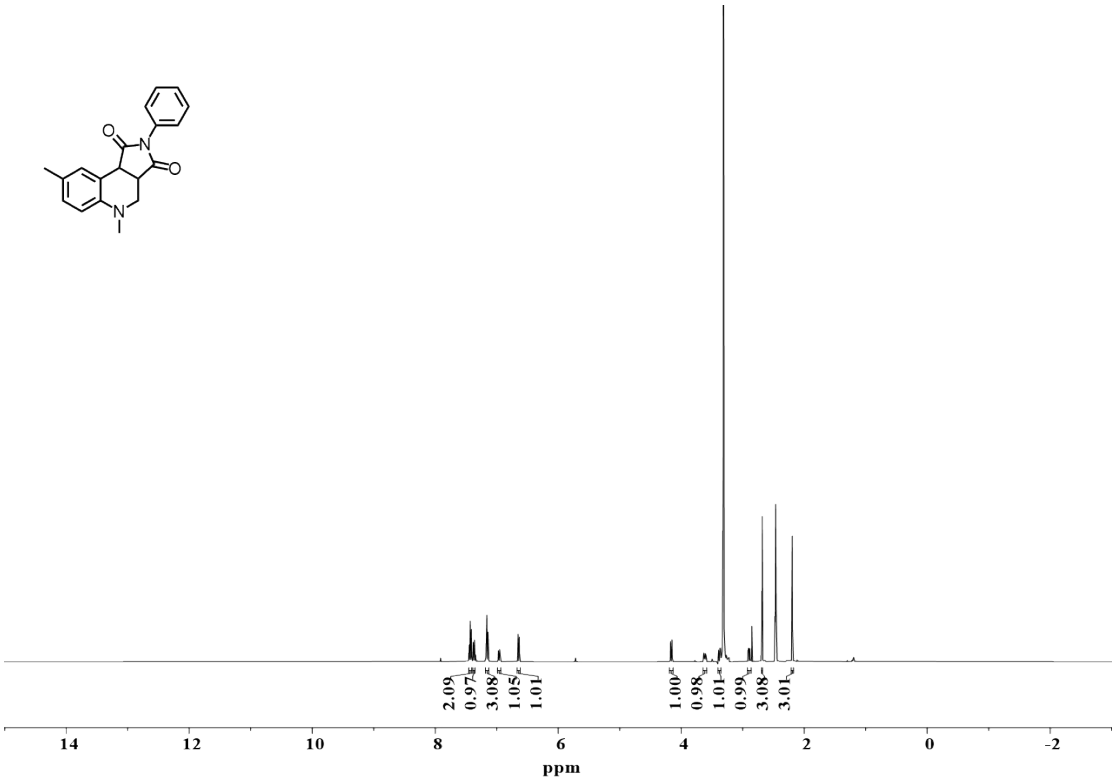


Figure S19. ^{1}H NMR spectrum of 3a in DMSO-d_6.

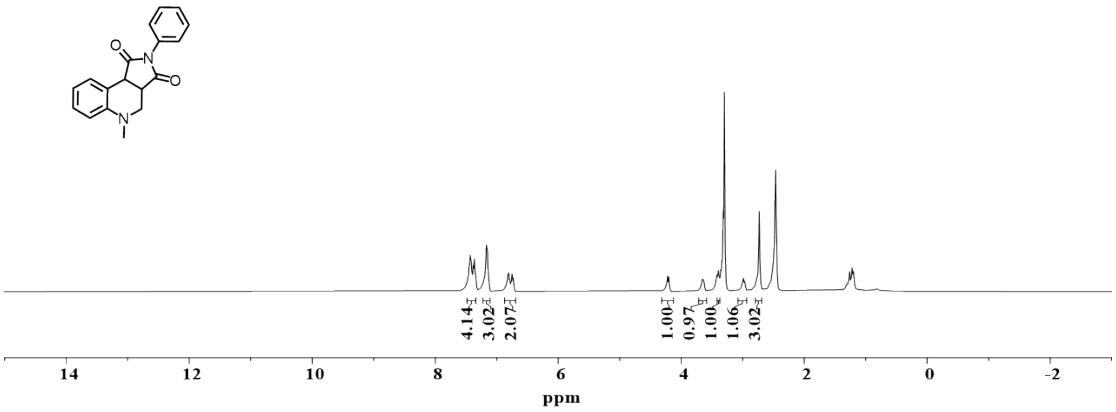


Figure S20. ^{1}H NMR spectrum of 3b in DMSO-d_6.

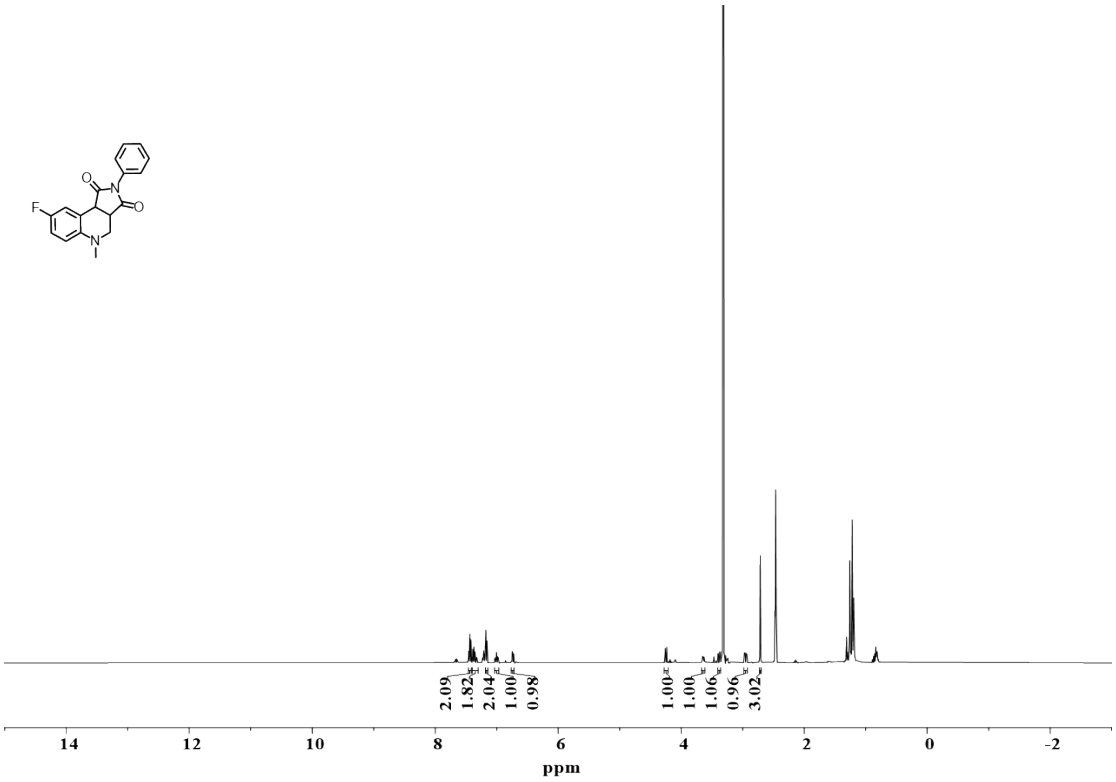


Figure S21. ^{1}H NMR spectrum of 3c in DMSO-d_6.

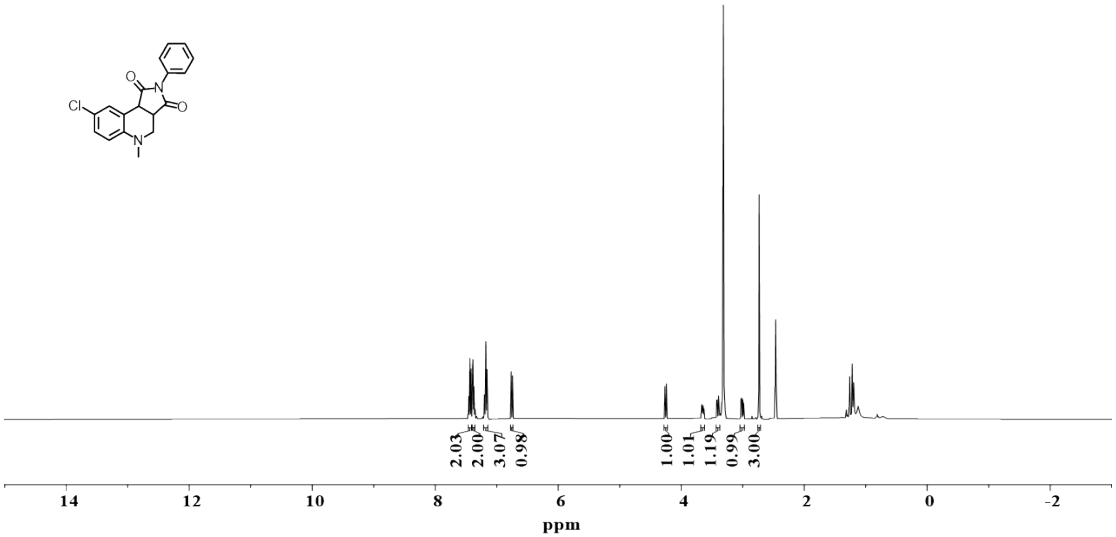


Figure S22. ^{1}H NMR spectrum of 3d in DMSO-d_6.

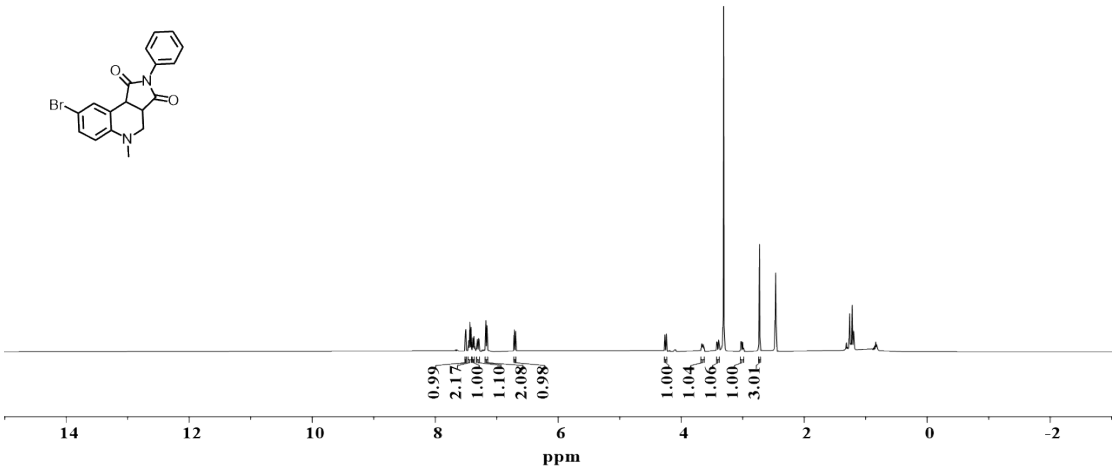


Figure S23. ^{1}H NMR spectrum of 3e in DMSO-d_6.

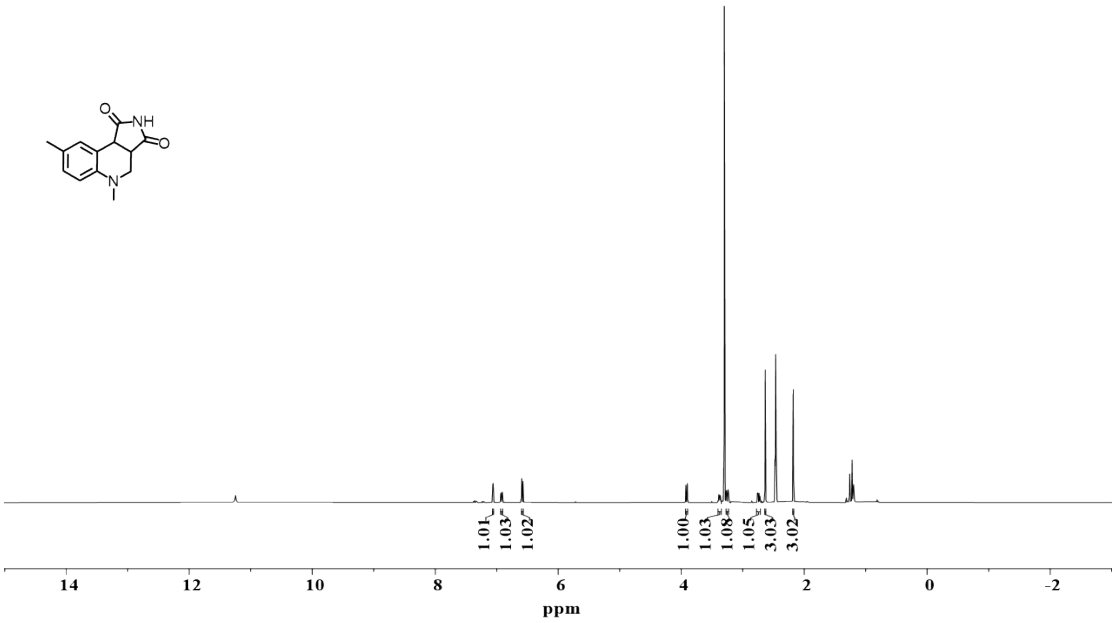


Figure S24. ^{1}H NMR spectrum of 3f in DMSO-d_6.

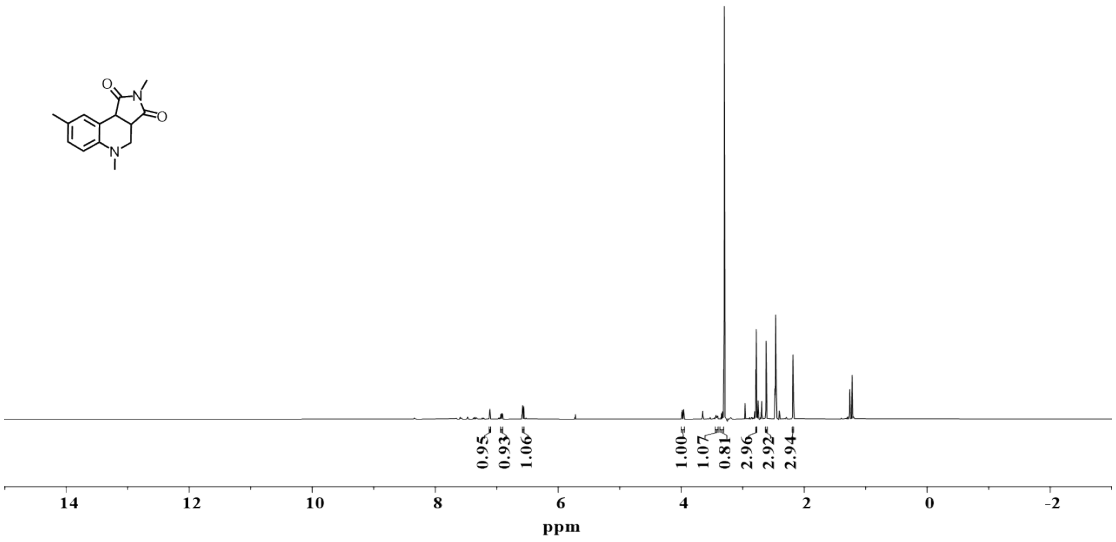


Figure S25. ^{1}H NMR spectrum of 3g in DMSO-d_6.

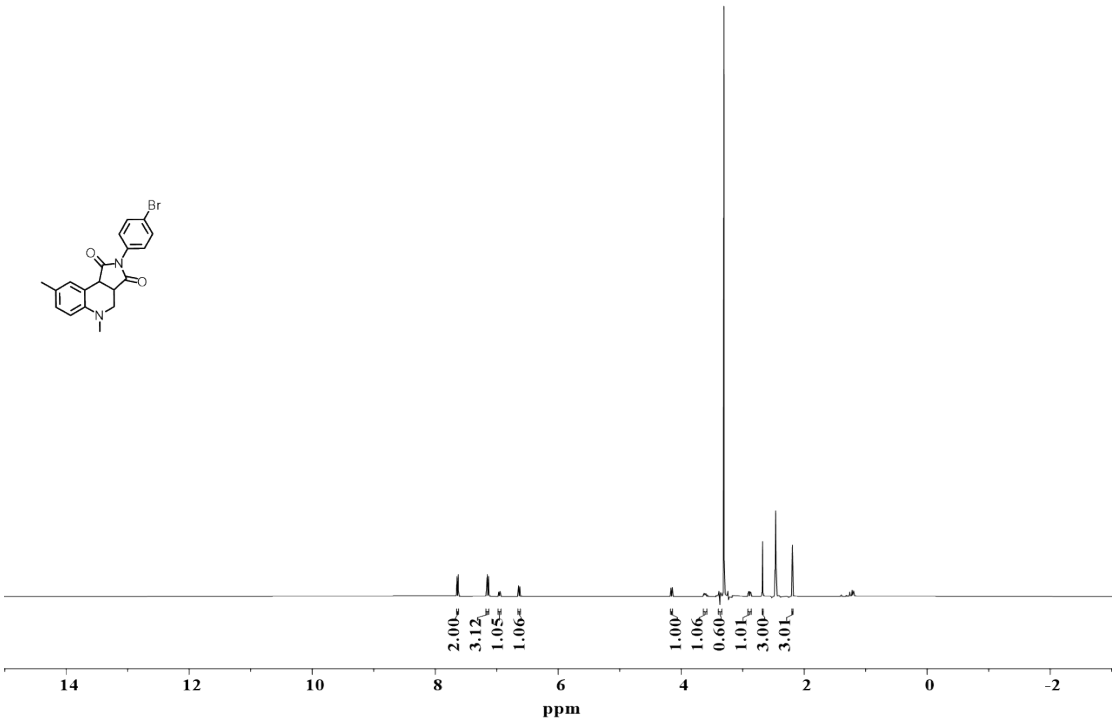


Figure S26. ^{1}H NMR spectrum of 3h in DMSO-d_6.

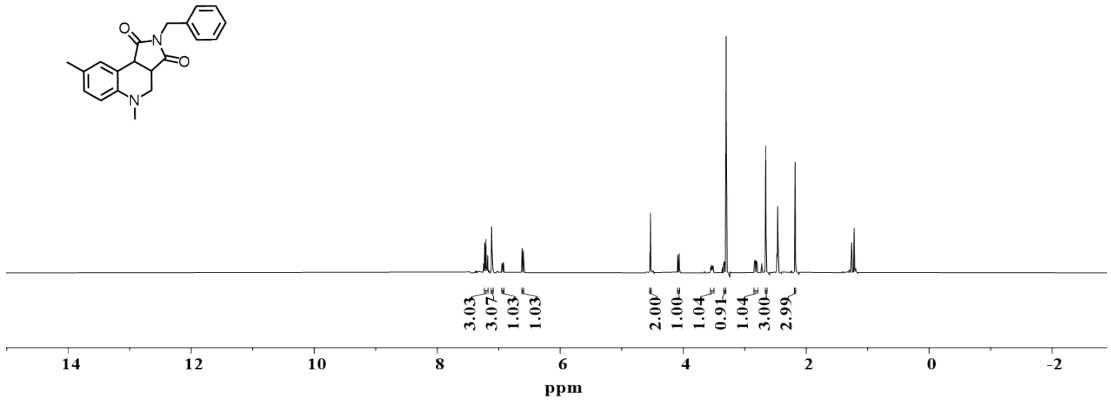


Figure S27. ^{1}H NMR spectrum of 3i in DMSO-d_6.

Table S1. Unit cell parameters and fractional atomic coordinates for HIAM-0035.

Space group: *C2/M* **a = 46.5523 Å, b = 42.5523 Å, and c = 3.7883 Å, α =γ = 90.0000°, β= 92.0675°**				
C1	C	0.4403	0.97436	0.32846
C2	C	0.47016	0.97425	0.4115
C3	C	0.48543	0.9493	0.46088
C4	C	0.42071	0.94909	0.33719
C5	.C	0.57119	0.92459	0.85412
C6	C	0.59038	0.90162	0.84166
C7	C	0.61865	0.90301	0.65218
C8	C	0.62716	0.92764	0.46494
C9	C	0.60765	0.95025	0.46934
N10	N	0.36236	0.12111	0.34897
C11	C	0.78698	0.35125	0.58927
C12	C	0.77083	0.32707	0.59891
C13	C	0.78345	0.30172	0.46983
C14	C	0.81356	0.30206	0.32722
C15	C	0.83015	0.32695	0.31754
C16	C	0.81697	0.35206	0.45061
C17	C	0.834	0.3784	0.45019
H18	H	0.47543	0.9291	0.44032
H19	H	0.55021	0.92314	1.01631
H20	H	0.58349	0.88288	0.98893

H21	H	0.64833	0.92945	0.30517
H22	H	0.61463	0.96866	0.31581
N23	N	0.77126	0.37313	0.72921
H24	H	0.82421	0.28316	0.22004
H25	H	0.85318	0.32648	0.2053
N26	N	0.75717	0.16957	0.25128
C27	C	1.23379	1.27527	0.51457
C28	C	1.2211	1.25041	0.40394
C29	C	1.23715	1.22543	0.38887
S30	S	1.26405	1.36393	0.12347
H31	H	0.82222	0.39728	0.53557
H32	H	1.19892	1.25042	0.32254
H33	H	1.22697	1.20678	0.29561
C34	C	0.48512	0	0.45289
C35	C	0.42676	0	0.27183
H36	H	0.09574	0.5	0.8011

References

(1) Han, C.-Q.; Wang, Z.-Y.; Sun, S.; Guo, J.-X.; Huang, X.; Liu, X.-Y., Linker Length Engineering toward Enhanced Photocatalytic Aerobic Oxidation in Benzothiadiazole-Based Covalent Organic Frameworks. *ACS Materials Letters* **2024,** *7* (2), 393-400.

(2) Han, C. Q.; Guo, J. X.; Sun, S.; Wang, Z. Y.; Wang, L.; Liu, X. Y., Impact of Imine Bond Orientations and Acceptor Groups on Photocatalytic Hydrogen Generation of Donor-Acceptor Covalent Organic Frameworks. *Small* **2024,** *20*, 2405887.