Supplementary Information (SI) for Journal of Materials Chemistry C.

Linker Engineering of Benzothiadiazole and Its Derivatives-based Covalent Organic Frameworks for Efficient Photocatalytic Oxidative Amine Coupling and Hydrogen Peroxide Generation

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Materials

Butanol (n-BuOH), dioxane, dimethylacetamide (DMAc), acetic acid (AA), o-dichlorobenzene (o-DCB), p-Phenylenediamine (PPDA) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. 5',5''''-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (BT-TDA), 5',5''''-(benzo[c][1,2,5]selenadiazole-4,7-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (BS-TDA) and 5',5''''-(naphtho[2,3-c][1,2,5]thiadiazole-4,9-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (NT-TDA) was synthesized according to the reported work[1]. All commercially available reagents were used without further purification.

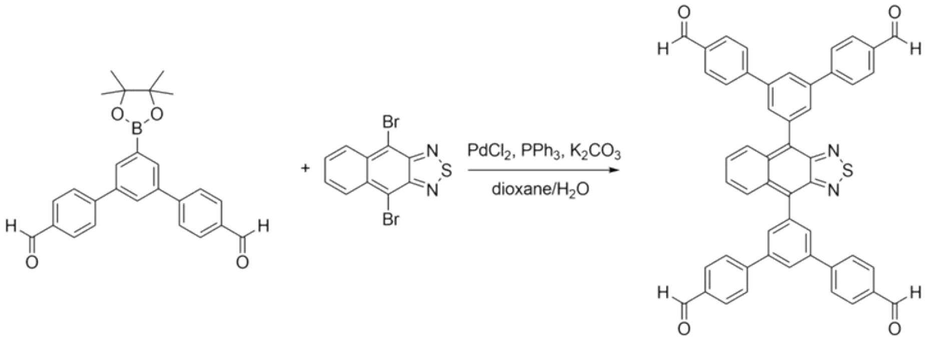
Characterization

Powder X-ray diffraction (PXRD) patterns for synthesized COFs were measured using Bruker D8Advance X-ray diffractometer with Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded from 500 to 4000 cm^{-1} on a PerkinElmer spectrometer. The solid-state ^{13}C cross polarization magic angle spinning NMR spectra were measured on a Bruker AVANCE Ш 600 M. The Steady-state photoluminescent spectra were recorded on FLS1000 spectrofluorometer (Edinburgh Instruments). The UV-vis spectra were measured on Shimadzu UV-3600 spectrophotometer. Scanning electron micrographs (SEM) images were taken using a JEOLJSM-IT800 (SHL). The thermogravimetric data was collected using TGA 550 analyzer and the samples were heated from room temperature to 800°C at a ramp rate of 10°C / min. Transmission electron microscope (TEM) was performed by JEOLJEM 2100F. Nitrogen sorption isotherms were collected by automated volumetric adsorption apparatus (Micromeritics, 3Flex). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area and the nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size distribution. The electron paramagnetic resonance (EPR) measurements were performed by Bruker EMX PLUS.

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 0.5 mL of ethanol and 8 μL of 5 wt% Nafion, which was ultra-sonicated to get homogeneous suspension. Then HIAM-00X 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, and Mott-Schottky measurement was carried out at frequency of 1000-1500 Hz with amplitude of 5 mV.

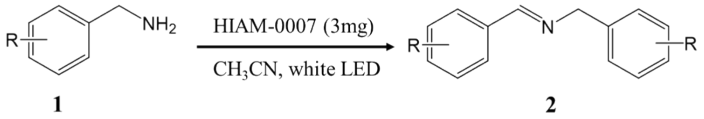
Synthesis of 5',5''''-(naphtho[2,3-c][1,2,5]selenadiazole-4,9-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (NS-TDA)



4,9-dibromonaphtho[2,3-c][1,2,5]selenadiazole (2.0 mmol, 0.78 g), 5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde (4.4 mmol, 1.82 g), $PdCl_2$ (0.2 mmol, 35.0 mg), PPh_3 (0.4 mmol, 0.11 g) and K_2CO_3 (8.0 mmol, 1.10 g) were added into one 250 mL round-bottle flask containing 80 mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 105°C for 6 hours. During the reaction, red precipitates gradually generated. After cooling down to room temperature, the precipitate was filtrated to offer 5',5''''-(naphtho[2,3-c][1,2,5]selenadiazole-4,9-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) as a red solid (1.53 g, 95.4%).

Photocatalytic Oxidative coupling of amine

General procedure for photocatalysis



3 mg HIAM-0007 and amine (0.3 mmol) were dispersed in 1 mL CH_3CN, then the mixture was stirred under air at room temperature for 30 minutes in the dark. Then the above mixture was irradiated using white LED. After a certain period of time, a mixed solution of ethyl acetate and petroleum ether was used to diagnose whether the reaction was complete. The mixture liquid was diluted with dichloromethane and centrifuged, then the supernatant was separated and the solvent was evaporated to afford a crude product. Chlorobenzene and $CHCl_2CHCl_2$ are used as the internal standards to calculate the yield of products by GC-MS and ^{1}H NMR spectroscopy[2].

H_2O_2 detection by iodometry method

According to previous reported method[3], 1 mL of 0.1 mol·L^{-1} potassium hydrogen phthalate ($C_8H_5KO_4$) aqueous solution and 1 mL of 0.4 mol·L^{-1} potassium iodide (KI) aqueous solution were added to 0.5 mL different concentration with 30%vol diluted H_2O_2 solution, which was then kept for 30 mins. H_2O_2 molecules react with iodine ions (I^-) under acidic conditions to generate I_3^- ($H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$), which have strong absorption near 350 nm and is measured by means of ultraviolet spectrophotometer. The concentration of H_2O_2 is calculated based on the calibration curve.

Photocatalytic H_2O_2 production

5 mg of photocatalyst was dispersed in 10 mL of deionized water and dispersed by ultrasonication for 30 mins. A 300 W Xe lamp (CEL-PF300-T6, Au-Light, China) with a 420 nm cutoff filter was used as the light source during the measurement. After the sample reaction interval of 30 mins, 0.5 mL 0.22 μm filtered solution was taken and the amount of H_2O_2 was detected by above iodometry.

Rotating disk electrode (RDE) measurements

The rotating disk electrode served as the substrate for the working electrode. 5 mg of COFs were dispersed in a mixture containing 0.5 mL of ethanol and 8 μL of 5 wt% Nafion solution, and sonicated to form a homogeneous catalyst suspension. 20 μL slurry was placed on the disk electrode, which was dried at room temperature. Carbon rods and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. Linear sweep voltammograms (LSVs) were acquired in O_2-saturated 0.1 M phosphate-buffered saline (PBS, pH = 7) solutions at room temperature with a scan rate of 10 mV s^{-1} and different rotational speeds. Calculate the average number of electrons (n) by the Koutecky-Levich equation:

$$\frac{1}{J}=\frac{1}{JK}+\frac{1}{JL}=\frac{1}{B\omega^{1/2}}+\frac{1}{JL}$$

$$B= 0.62nFC_0D_0^{2/3}\nu^{-1/6}$$

where J is the current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the rotating speed, n is transferred electron number, F is Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.26×10^{-3} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 (2.7 ×10-5 cm^2 s^{-1}), and ν is kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

Rotating ring-disk electrode (RRDE) measurements

A ring-disk electrode served as the substrate for working electrode. The working electrode was prepared as RDE measurements. The voltammograms were obtained in a 0.1 M phosphate buffer solution (pH = 7) at room temperature in Ar atmosphere with a scan rate of 10 mV s^{-1} and a rotation rate of 1600 rpm. The potential of ring electrode was set to -0.23 V (vs. Ag/AgCl) to detect O_2. The potential of ring electrode was set to 0.60 V (vs. Ag/AgCl) to detect H_2O_2.

Detection of $\bullet O_2^-$ by NBT

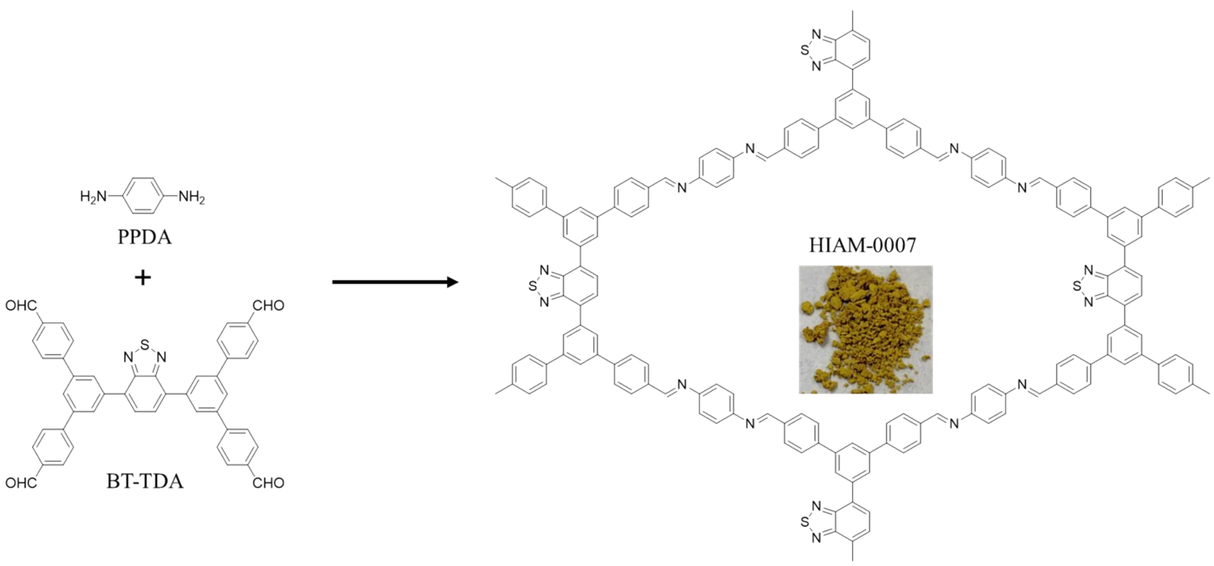
5 mg of COFs and 10 mL of NBT solution (2×10^{-5} M) were mixed and dispersed in a tube. The tube was illuminated by a Xe lamp with a 420 nm cutoff filter. After irradiation at different times (0 min, 30 min, 90 min, and 120 min, respectively), the supernatant was collected by 0.22 μm membrane filtration, which was used by UV-Vis spectrophotometer measurements.

$H_2^{18}O$ isotope mass spectrometry

According to reported literature[4], 1 mL of $H_2^{18}O$, 4 mL of H_2O and 5 mg of HIAM-0009 were mixed well, and then irradiated with a 300 W xenon lamp ($\lambda > 420$ nm) for 1 h. Then 200 μL H_2O_2 solution by photocatalytic production mixed with 200 μL of 100 μM 4-carboxyphenylboronic acid solution, and left standing for 30 min. Finally, the mass spectrum was detected.

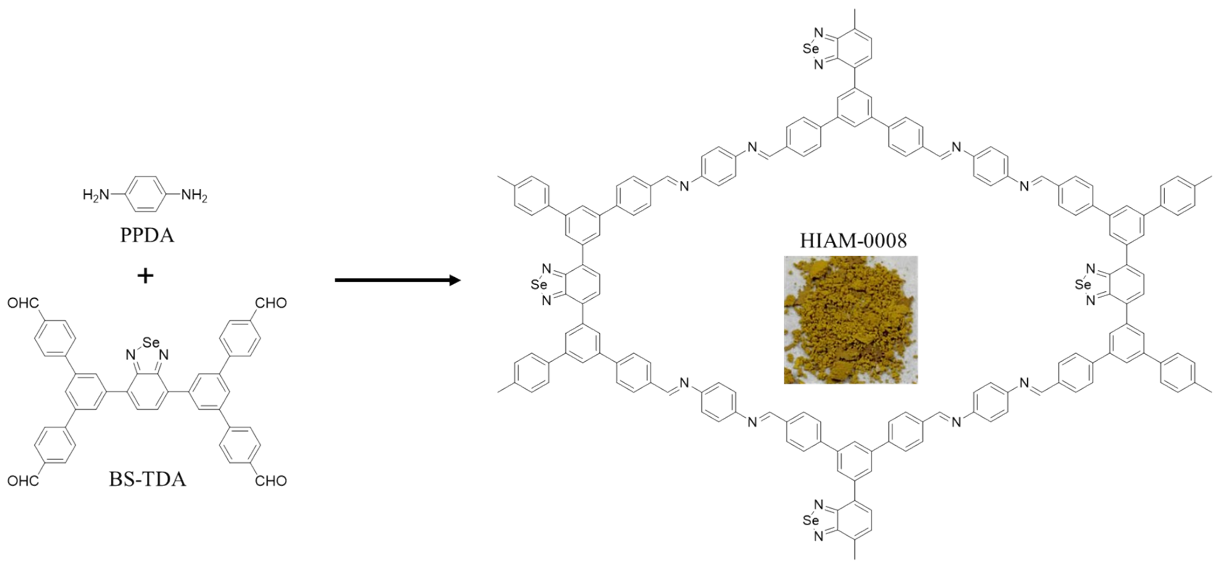
Synthesis of HIMA-COFs

Synthesis of HIAM-0007



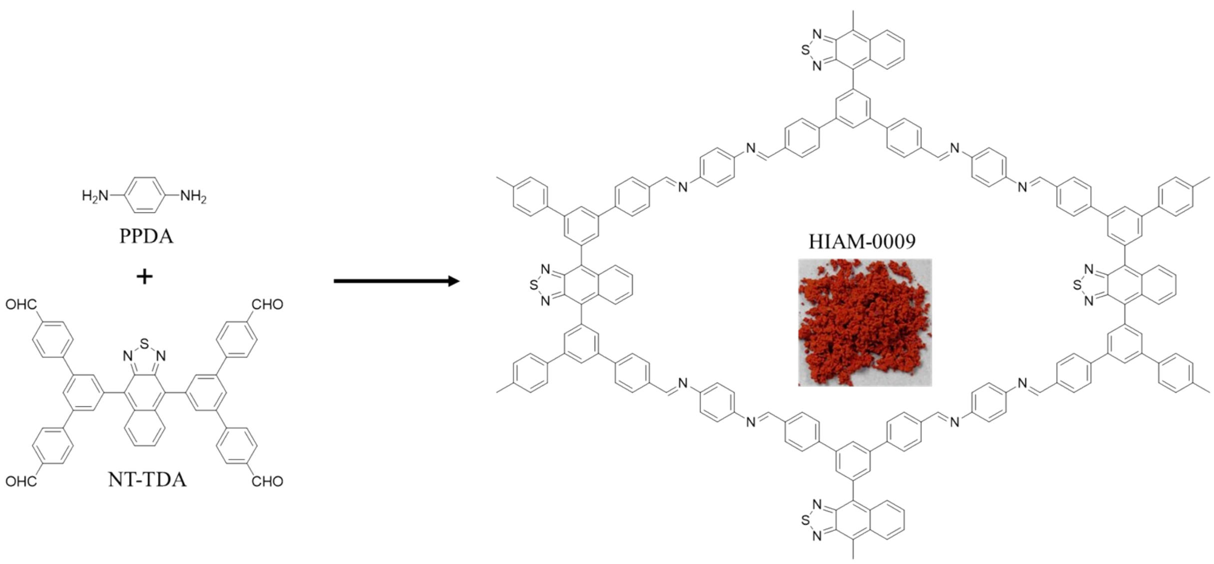
5',5''''-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (BT-TDA) (14.08 mg, 0.02 mmol), *p*-Phenylenediamine (PPDA) (4.32 mg, 0.04 mmol) and 50 μL 6M AA in butanol / dioxane (1 mL, 1/1) were added to 10 mL Pyrex tube. The above mixture was sonicated for 10 min, then the tube was degassed through three freeze-pump-thaw cycles and then kept at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF for 24 h and dried under 60 °C vacuum to afford yellow powder.

Synthesis of HIAM-0008



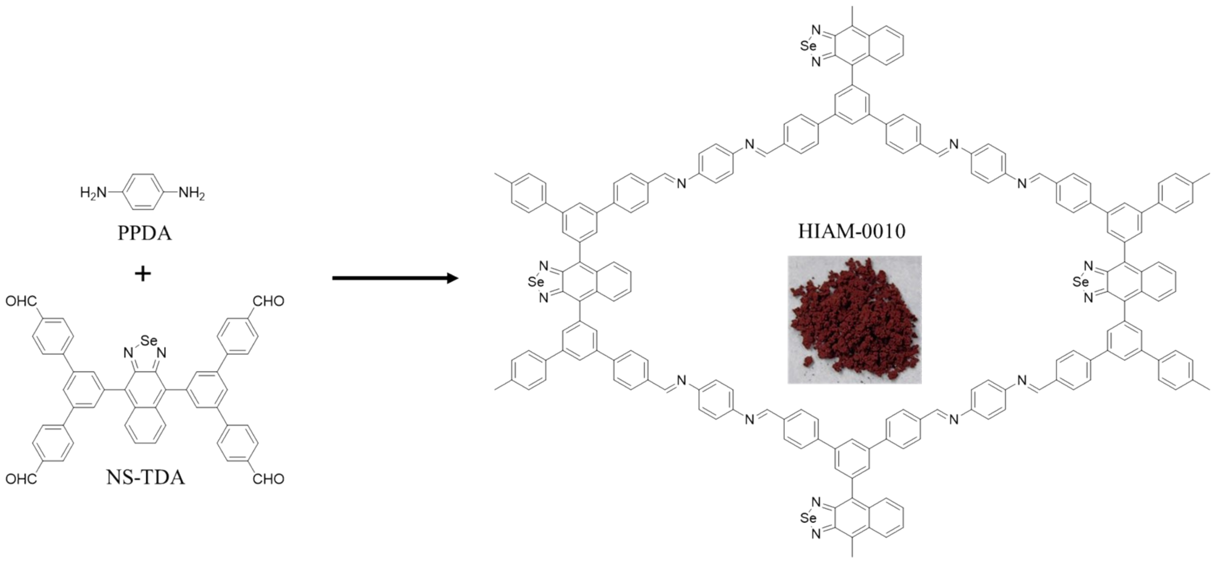
5',5""'-(benzo[c][1,2,5]selenadiazole-4,7-diyl)bis(([1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde)) (BS-TDA) (15.02 mg, 0.02 mmol), *p*-Phenylenediamine (PPDA) (4.32 mg, 0.04 mmol) and 50 μL 6M AA in *o*-dichlorobenzene / butanol (1 mL, 1/1) were added to 10 mL Pyrex tube. The above mixture was sonicated for 10 min, then the tube was degassed through three freeze-pump-thaw cycles and then kept at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF for 24 h and dried under 60 °C vacuum to afford yellow powder.

Synthesis of HIAM-0009



5',5""-(naphtho[2,3-c][1,2,5]thiadiazole-4,9-diyl)bis(([1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde)) (NT-TDA) (15.08 mg, 0.02 mmol), *p*-Phenylenediamine (PPDA) (4.32 mg, 0.04 mmol) and 50 μL 6M AA in *o*-dichlorobenzene / butanol (1 mL, 1/1) were added to 10 mL Pyrex tube. The above mixture was sonicated for 10 min, then the tube was degassed through three freeze-pump-thaw cycles and then with kept at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF for 24 h and dried under 60 °C vacuum to afford red powder.

Synthesis of HIAM-0010



5',5''''-(naphtho[2,3-c][1,2,5]selenadiazole-4,9-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarbaldehyde)) (NS-TDA) (16.04 mg, 0.02 mmol), *p*-Phenylenediamine (PPDA) (4.32 mg, 0.04 mmol) and 50 µL 6M AA in *o*-dichlorobenzene / butanol (1 mL, 1/1) were added to 10 mL Pyrex tube. The above mixture was sonicated for 10 min, then the tube was degassed through three freeze-pump-thaw cycles and then with kept at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with THF for several times. The product was Soxhlet extracted in THF for 24 h and dried under 60 °C vacuum to afford purple powder.

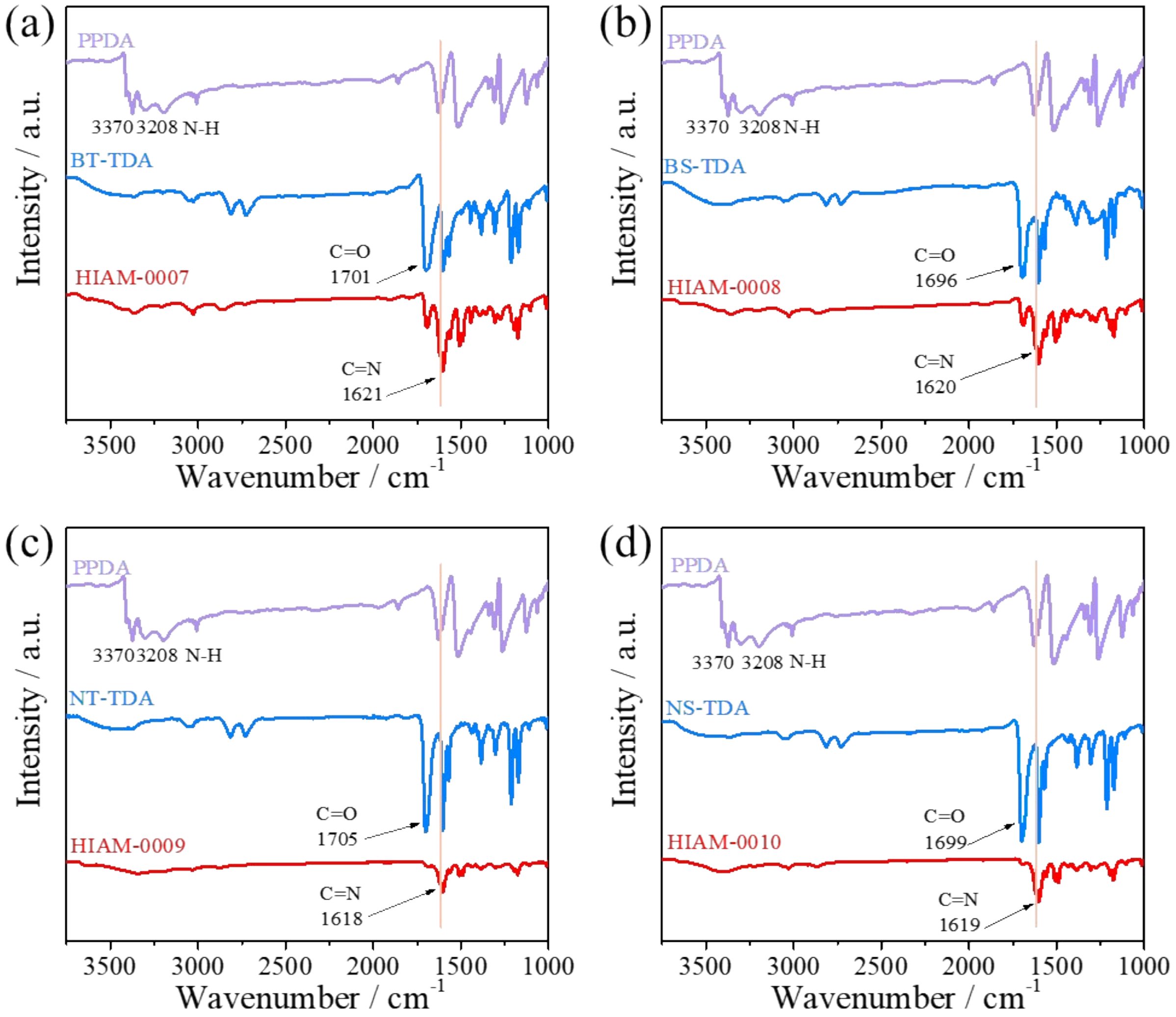


Figure S1. FT-IR spectra of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) compared with corresponding to monomers.

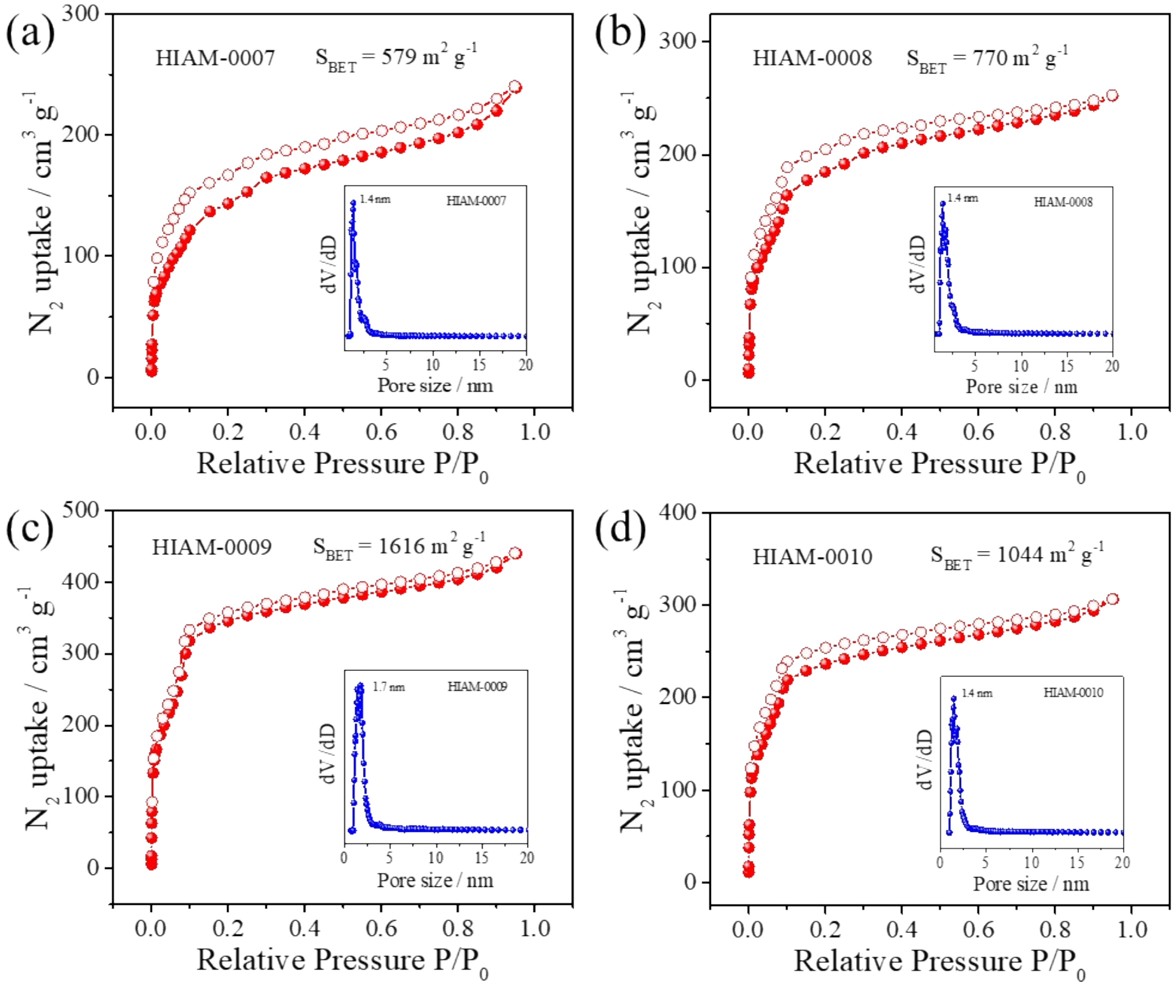


Figure S2. N_2 adsorption (closed circles) and desorption (open circles) isotherm curves in 77 K of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-00010 (d), inset: the pore size distribution corresponding to COFs.

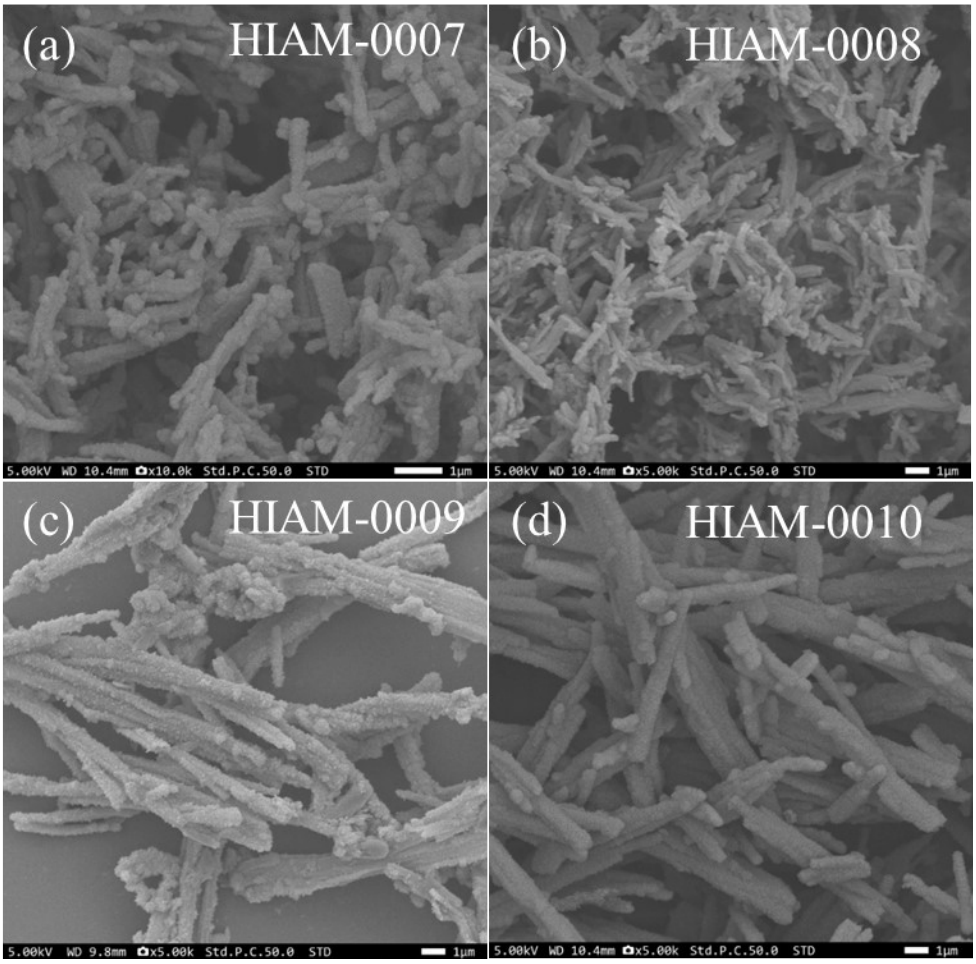


Figure S3. SEM images of (a) HIAM-0007, (b) HIAM-0008, (c) HIAM-0009 and (d) HIAM-0010.

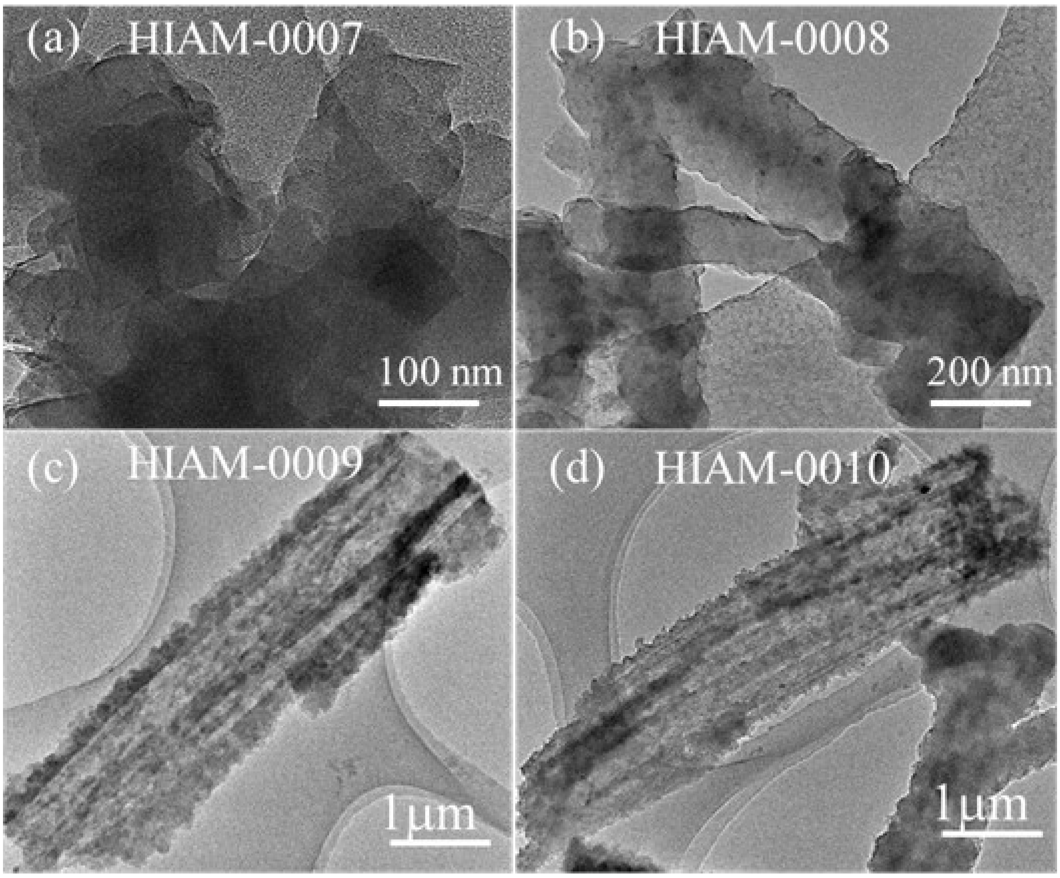


Figure S4. TEM images of (a) HIAM-0007, (b) HIAM-0008, (c) HIAM-0009 and (d) HIAM-0010.

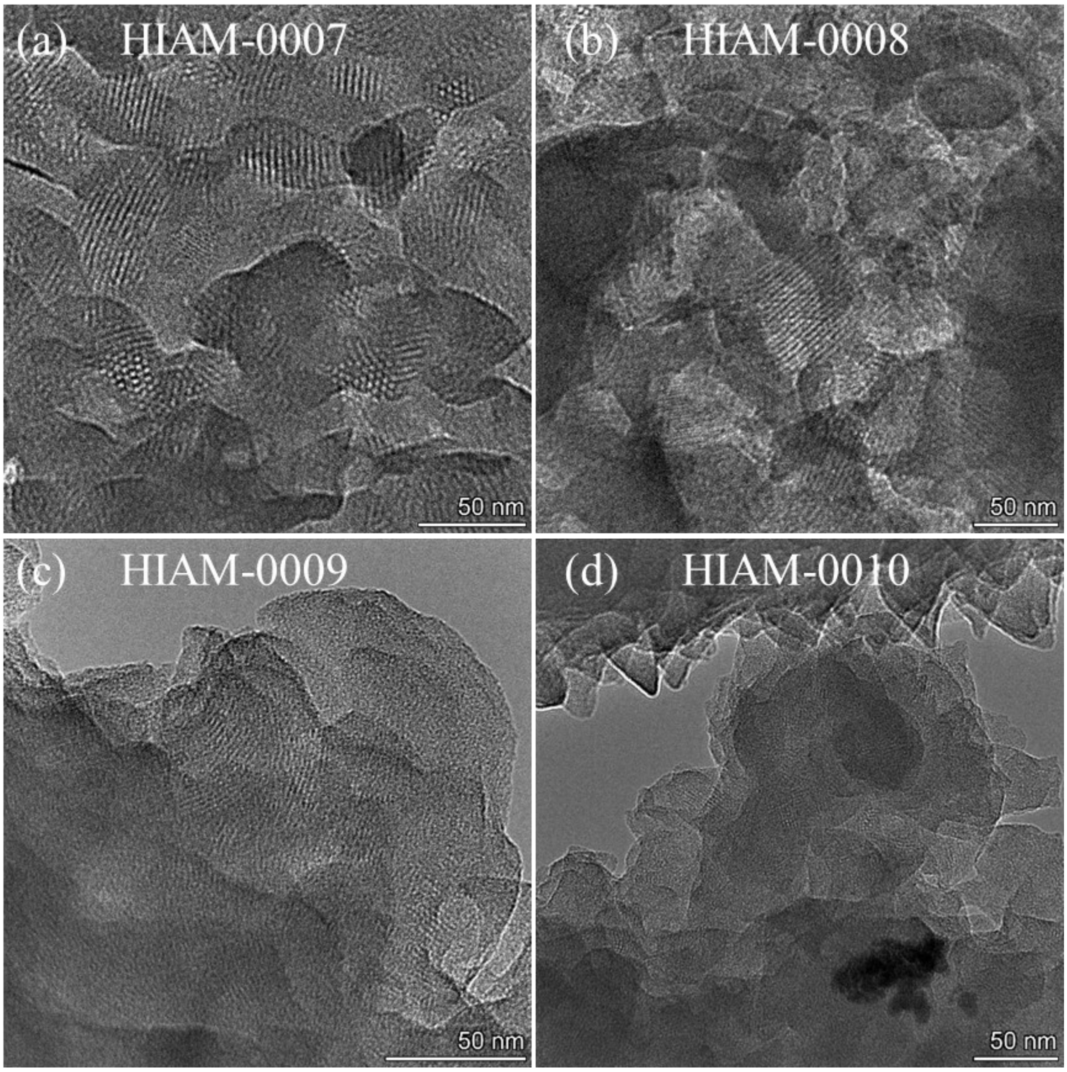


Figure S5. HR-TEM images of (a) HIAM-0007, (b) HIAM-0008, (c) HIAM-0009 and (d) HIAM-0010.

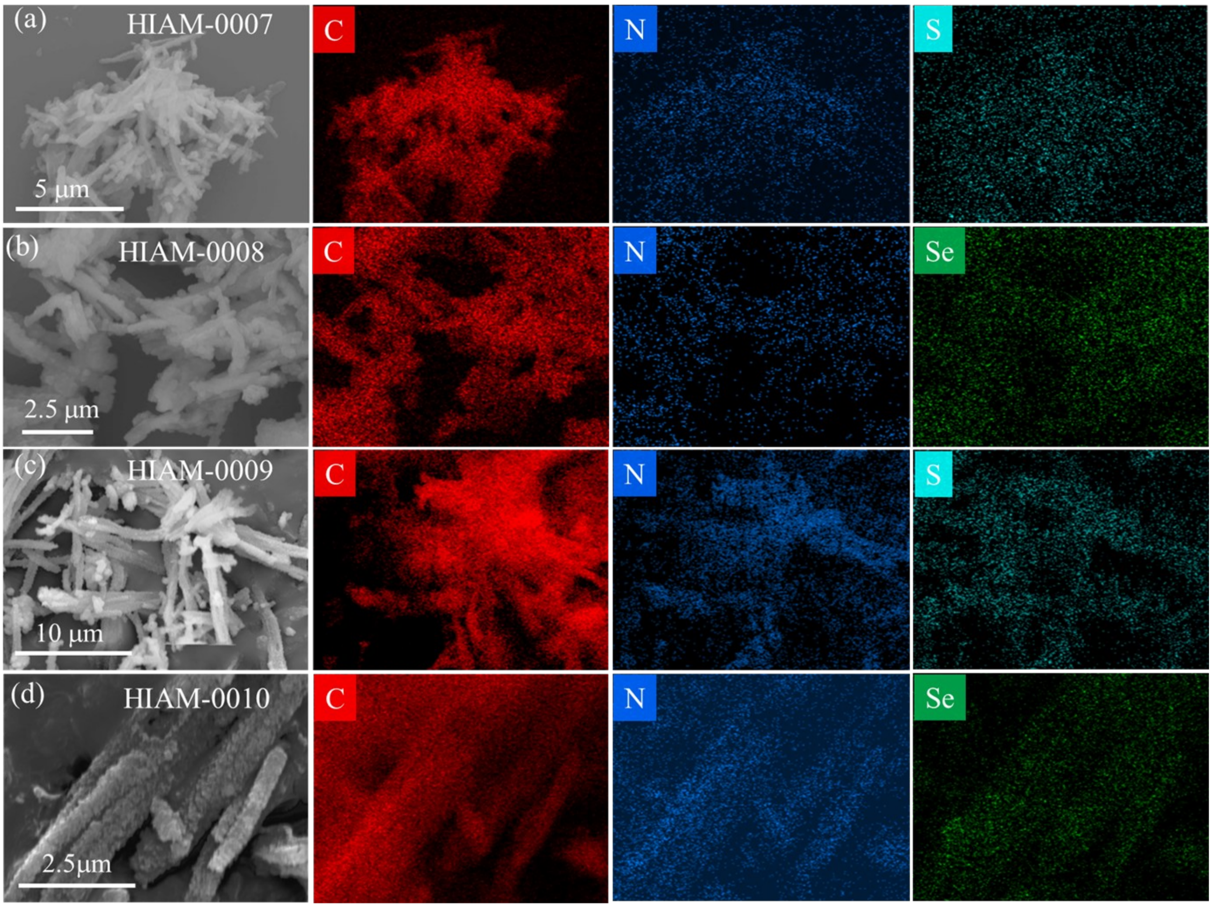


Figure S6. SEM and Elemental mapping images for C, N, S of HIAM-0007 (a) and HIAM-0009 (c); C, N, Se for HIAM-0008 (b) and HIAM-0010 (d).

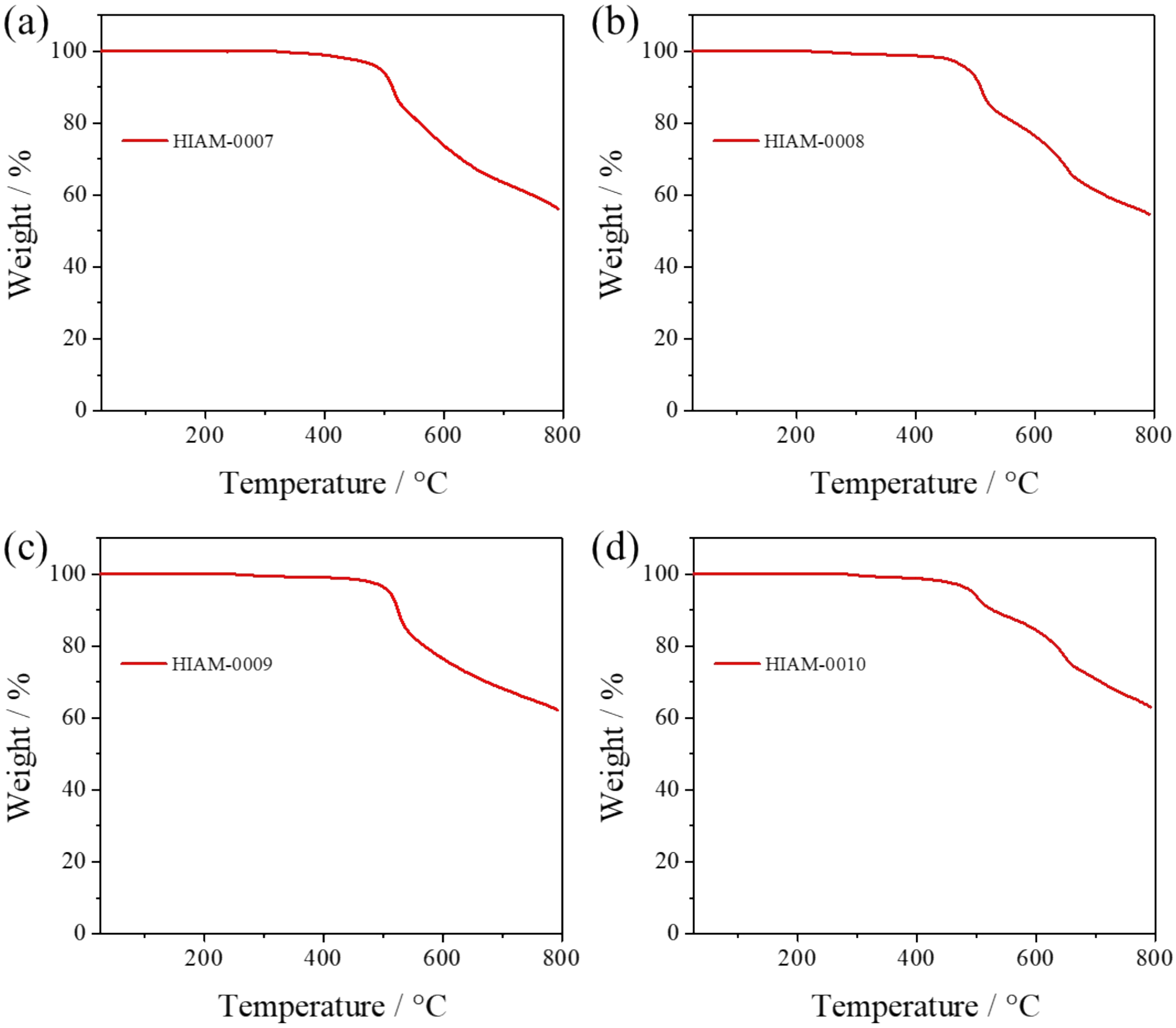


Figure S7. TGA curves of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d).

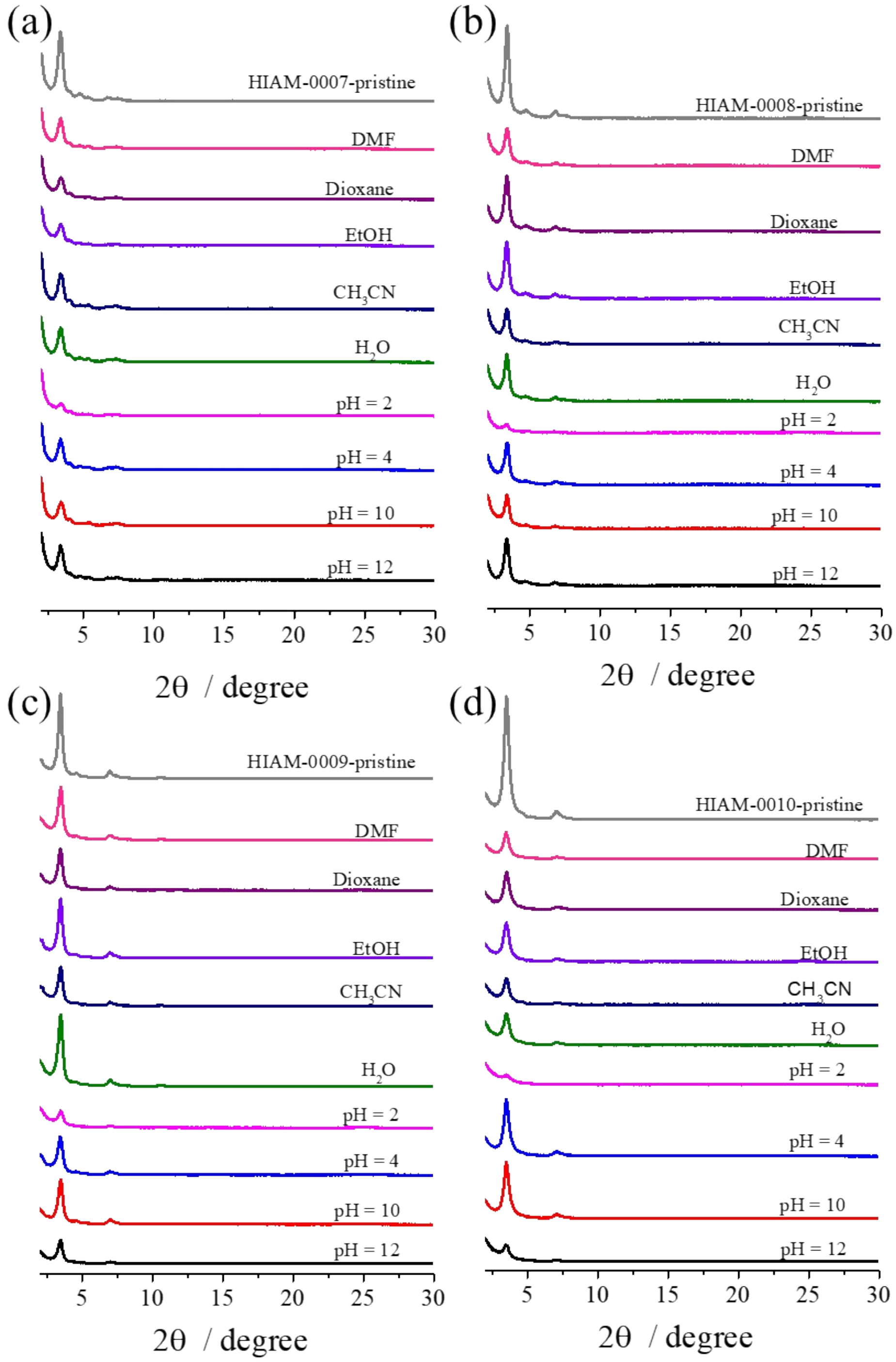


Figure S8. PXRD patterns for HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) after soaking in various kinds of organic solvents, H_2O (25 °C), pH = 2, pH = 4, pH = 10 and pH = 12 for 24 hours.

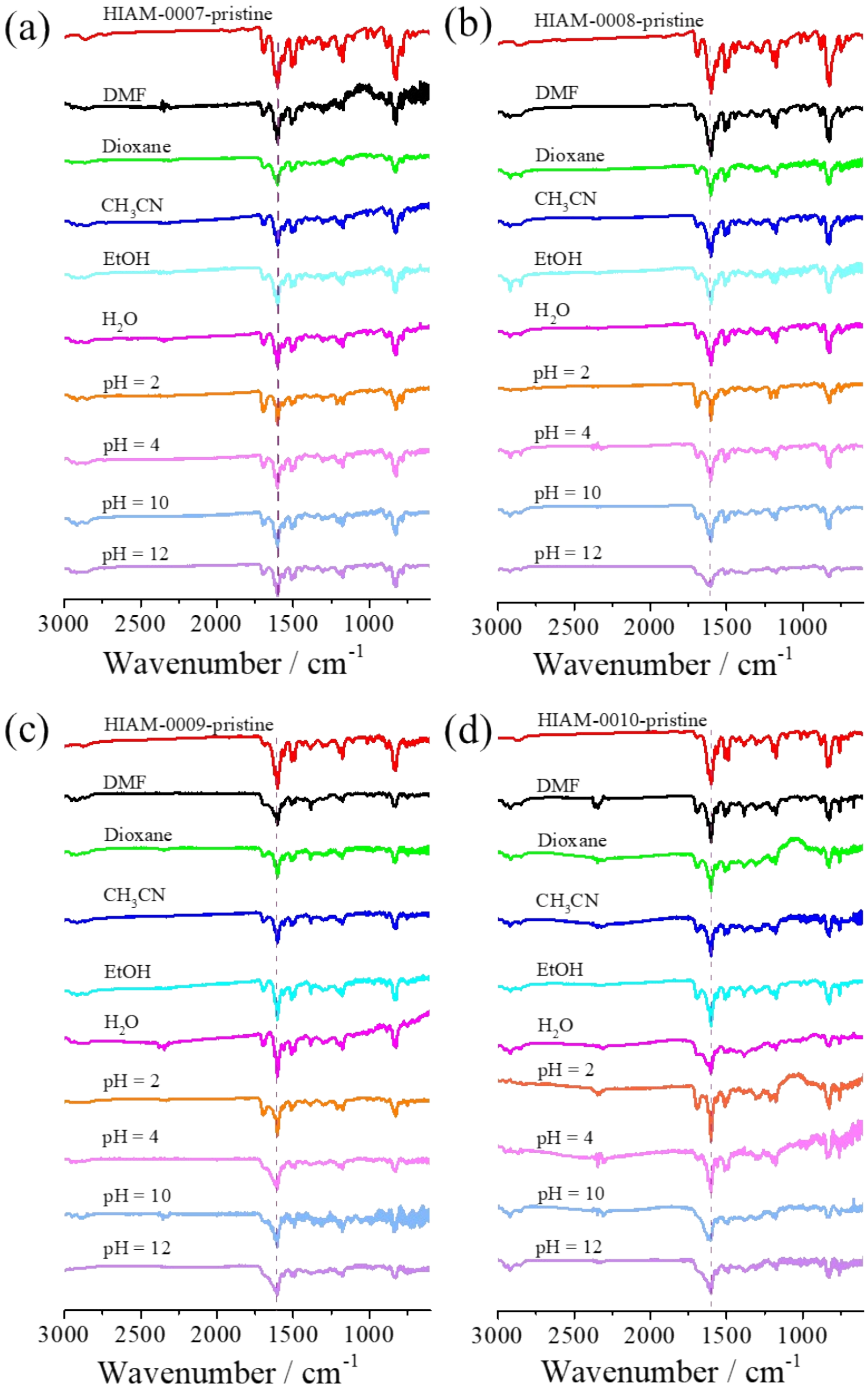


Figure S9. FITR patterns for HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) after soaking in various kinds of organic solvents, H_2O (25 °C), pH = 2, pH = 4, pH = 10 and pH = 12 for 24 hours.

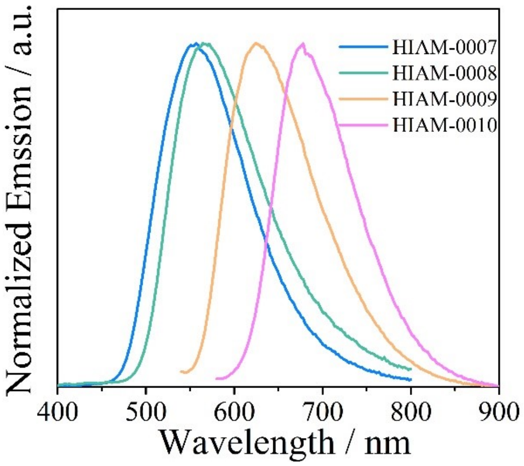


Figure S10. Normalized solid-state emission spectra for HIAM-0007, HIAM-0008, HIAM-0009 and HIAM-0010.

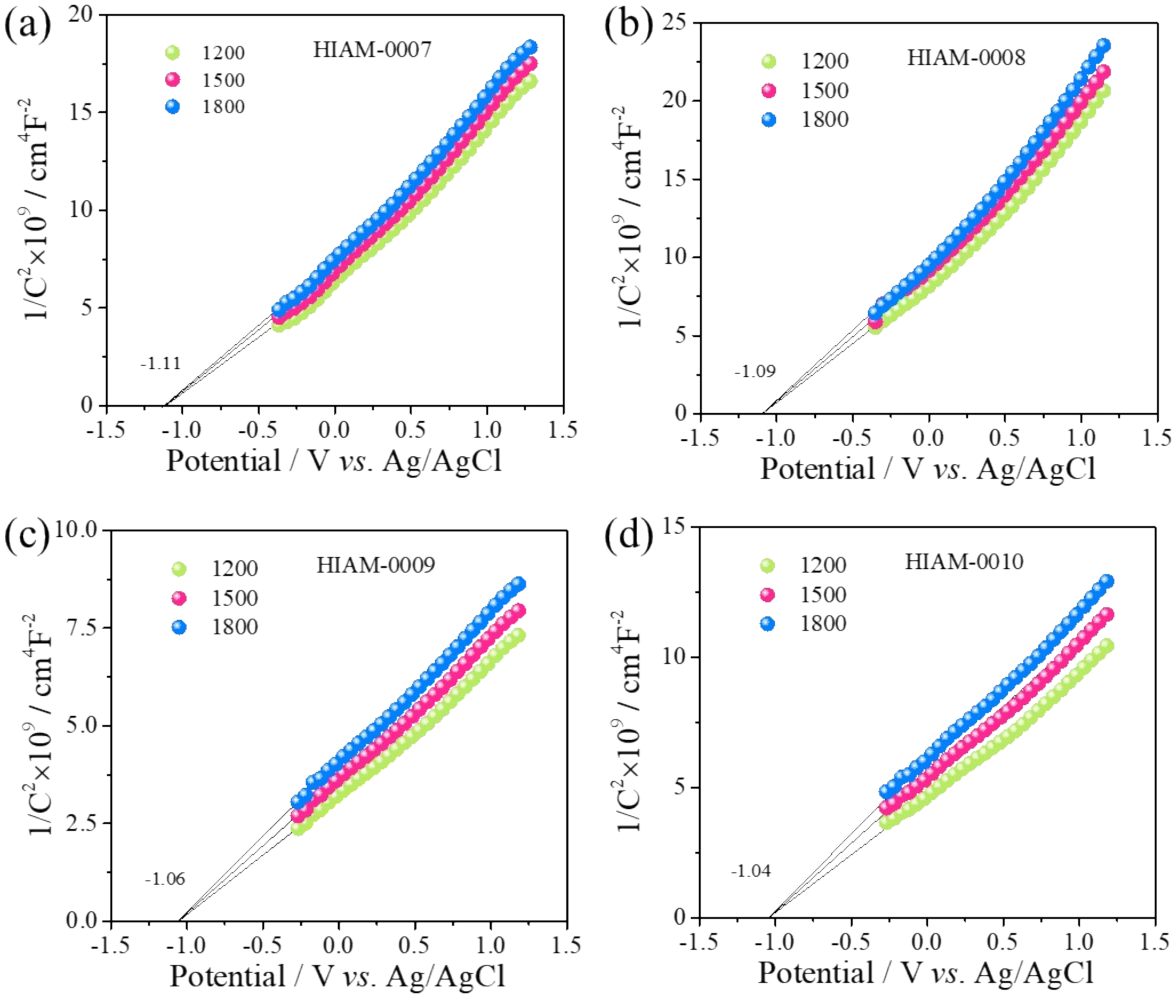


Figure S11. Mott-Schottky plots of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d).

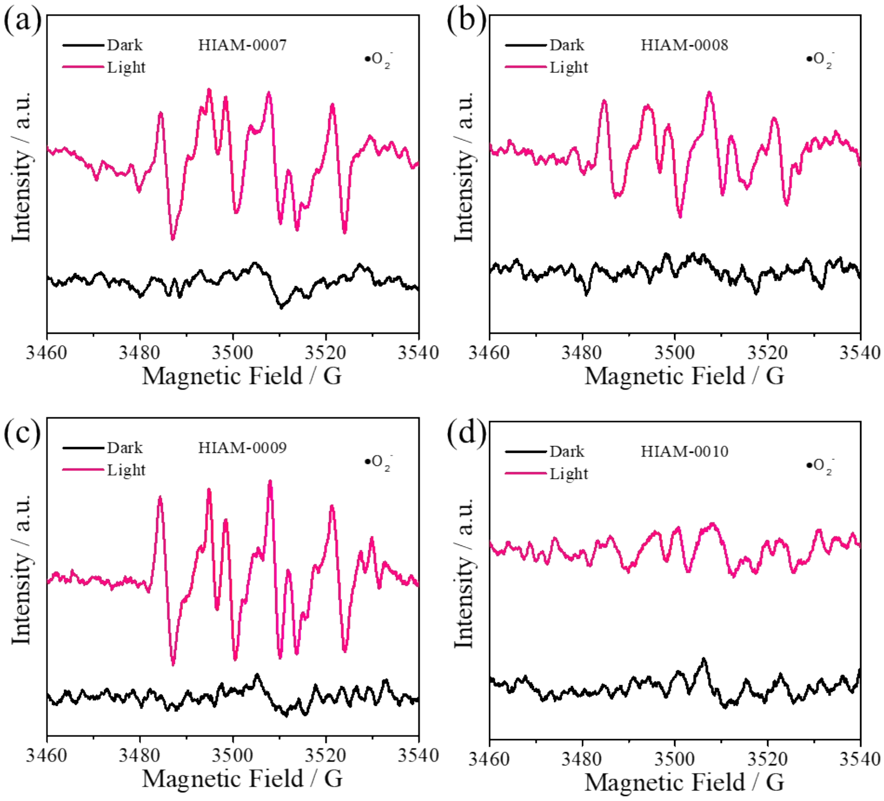
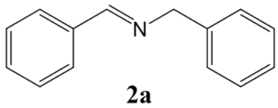


Figure S12. The DMPO spin trapping EPR spectra of HIAM-0007 (a), HIAM-0008 (b) , HIAM-0009 (c) and HIAM-0010 (d) for $\cdot O_2^-$ detection under dark and visible light.

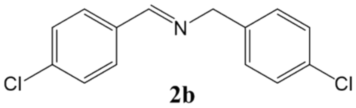
^{1}H-NMR analysis of the photocatalytic products



2a

N-benzyl-1-phenylmethanimine (2a)

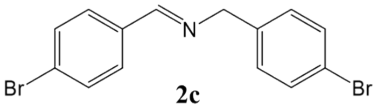
NMR yield: 99%. ^{1}H NMR (400 MHz, *d$_6$*-DMSO): δ = 8.48 (s, 1H), 7.76-7.73 (m, 2H), 7.44-7.42 (m, 4H), 7.31-7.30 (m, 4H), 4.74 (s, 2H) ppm.



2b

N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (2b)

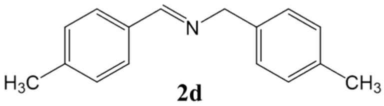
NMR yield: 95%. ^{1}H NMR (400 MHz, *d$_6$*-DMSO): δ= 8.47 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 4.72 (s, 2H) ppm.



2c

N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (2c)

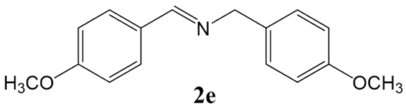
NMR yield: 94%. ^{1}H NMR (400 MHz, *d$_6$*-DMSO): δ= 8.46 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.27(d, J = 8.4 Hz, 2H), 4.70 (s, 2H) ppm.



2d

N-(4-methylbenzyl)-1-(4-methylbenzyl)methanimine (2d)

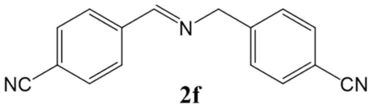
NMR yield: 81%. ^{1}H NMR (400 MHz, *d$_6$*-DMSO): δ= 8.39 (s, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 4.66 (s, 2H), 2.30 (s, 3H), 2.24 (s, 3H) ppm.



2e

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

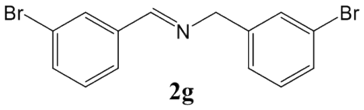
NMR yield: 88%. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 8.34 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.61 (s, 2H), 3.76 (s, 3H), 3.69 (s, 3H) ppm.



2f

N-(4-cyanobenzyl)-1-(4- cyanobenzyl)methanimine (2f)

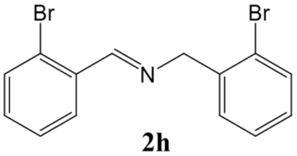
NMR yield: 70%. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 8.60 (s, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 4.88 (s, 2H) ppm.



2g

N-(3-bromobenzyl)-1-(3-bromophenyl)methanimine (2g)

NMR yield: 93%. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 8.47 (s, 1H), 7.93 (s, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 7.0 Hz, 1H), 7.50 (s, 1H), 7.42-7.39 (m, 2H), 7.32-7.28 (m, 2H), 4.75 (s, 2H) ppm.



2h

N-(2-bromobenzyl)-1-(2-bromophenyl)methanimine (2h)

NMR yield: 93%. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 8.74 (s, 1H), 7.99-7.96 (m, 1H), 7.69-7.61 (m, 2H), 7.44-7.38 (m, 4H), 7.25-7.20 (m, 1H), 4.87 (s, 2H) ppm.

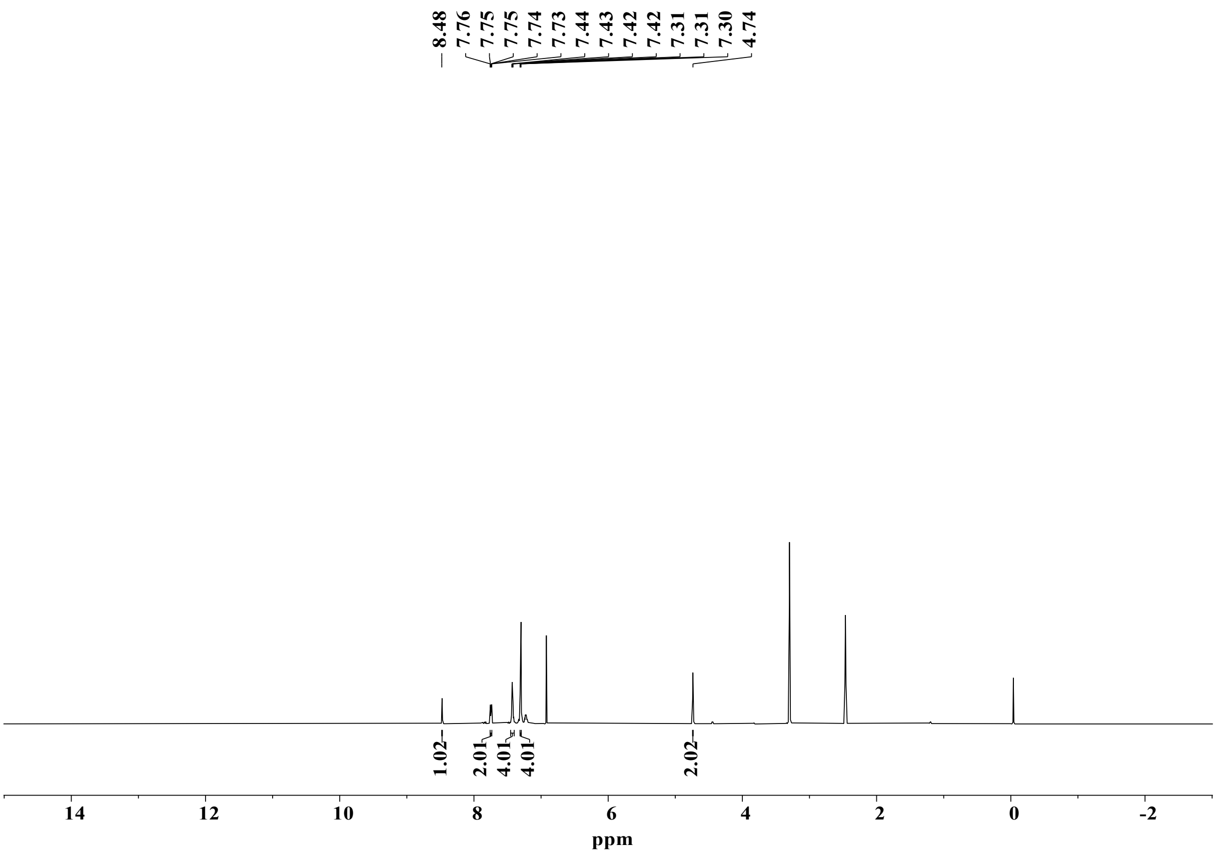


Figure S13. ^{1}H NMR spectrum of N-benzyl-1-phenylmethanimine (2a) (400 MHz, d_6-DMSO).

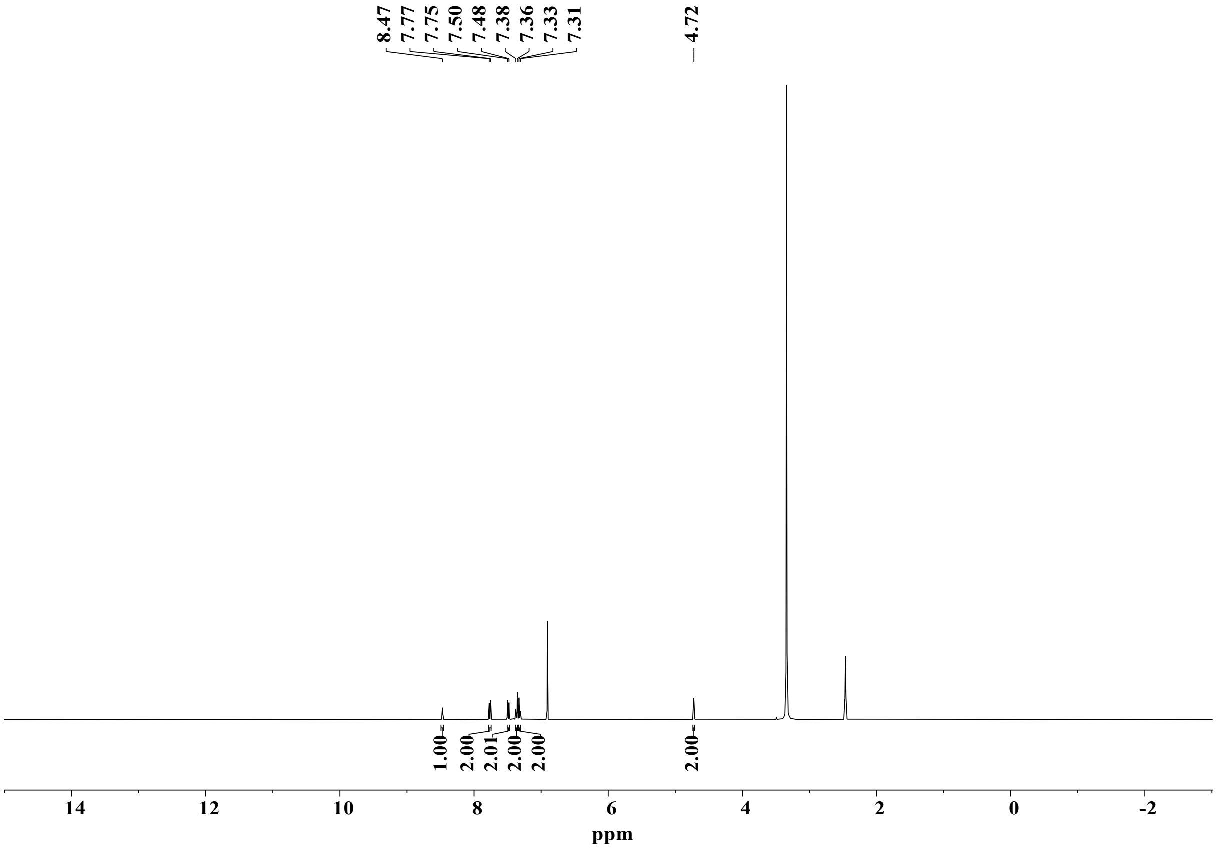


Figure S14. ^{1}H NMR spectrum of N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (2b) (400 MHz, d_6-DMSO).

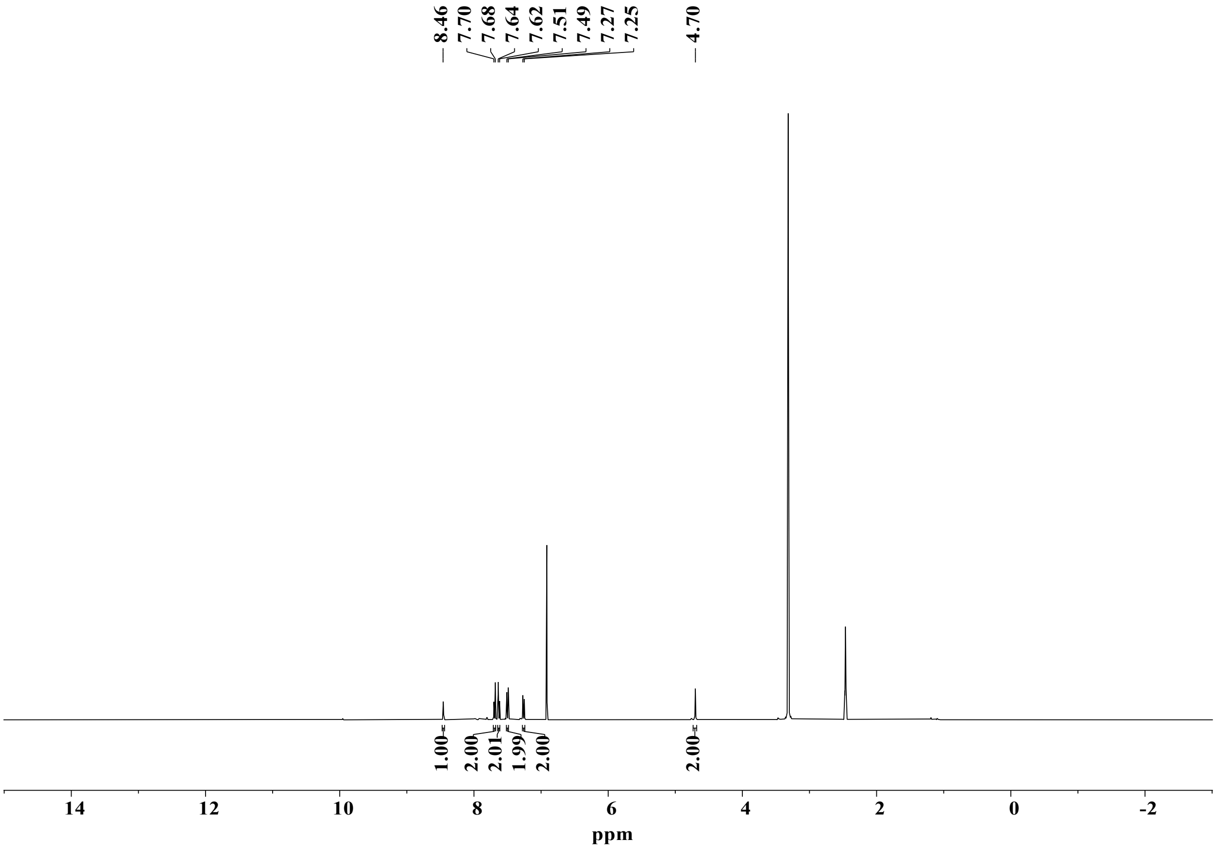


Figure S15. ^{1}H NMR spectrum of N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (2c) (400 MHz, d_6-DMSO).

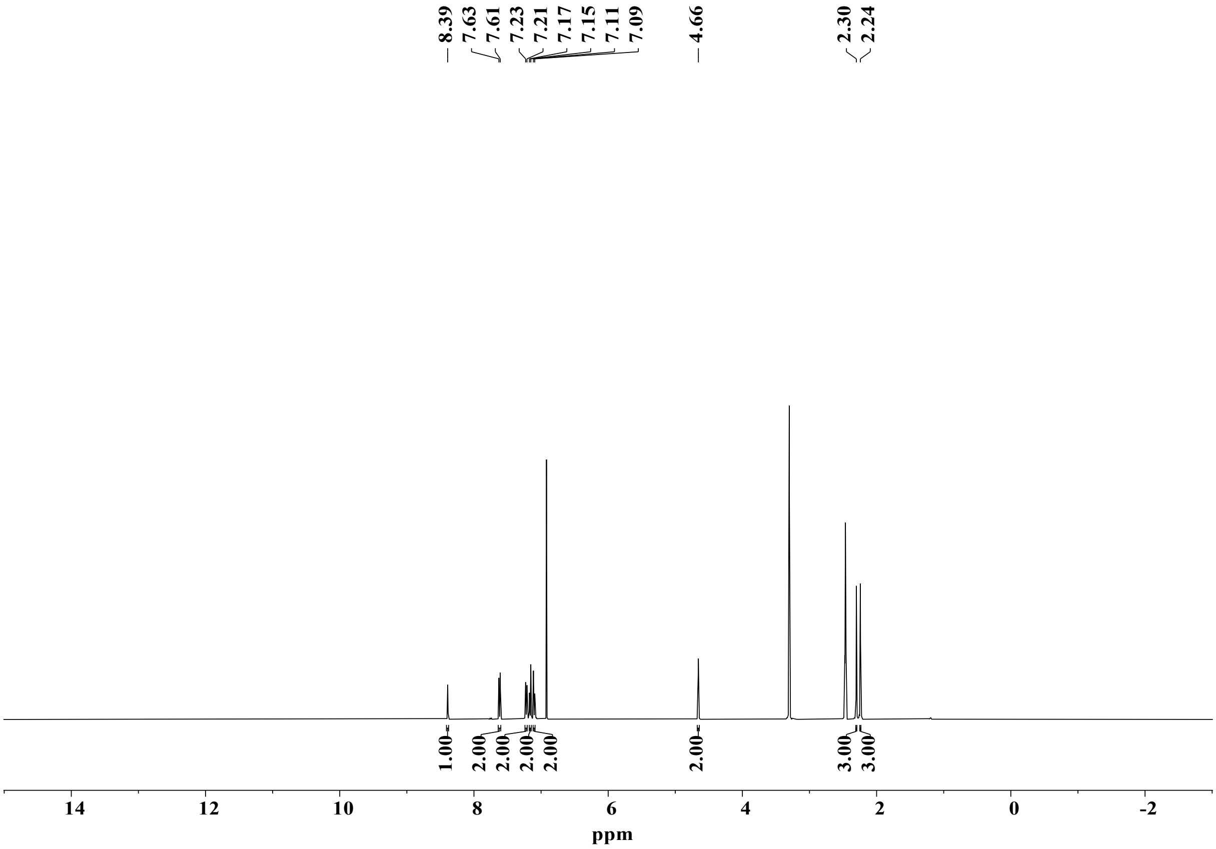


Figure S16. ^1H NMR spectrum of N-(4-methylbenzyl)-1-(4-methylbenzyl)methanimine (2d) (400 MHz, d_6-DMSO).

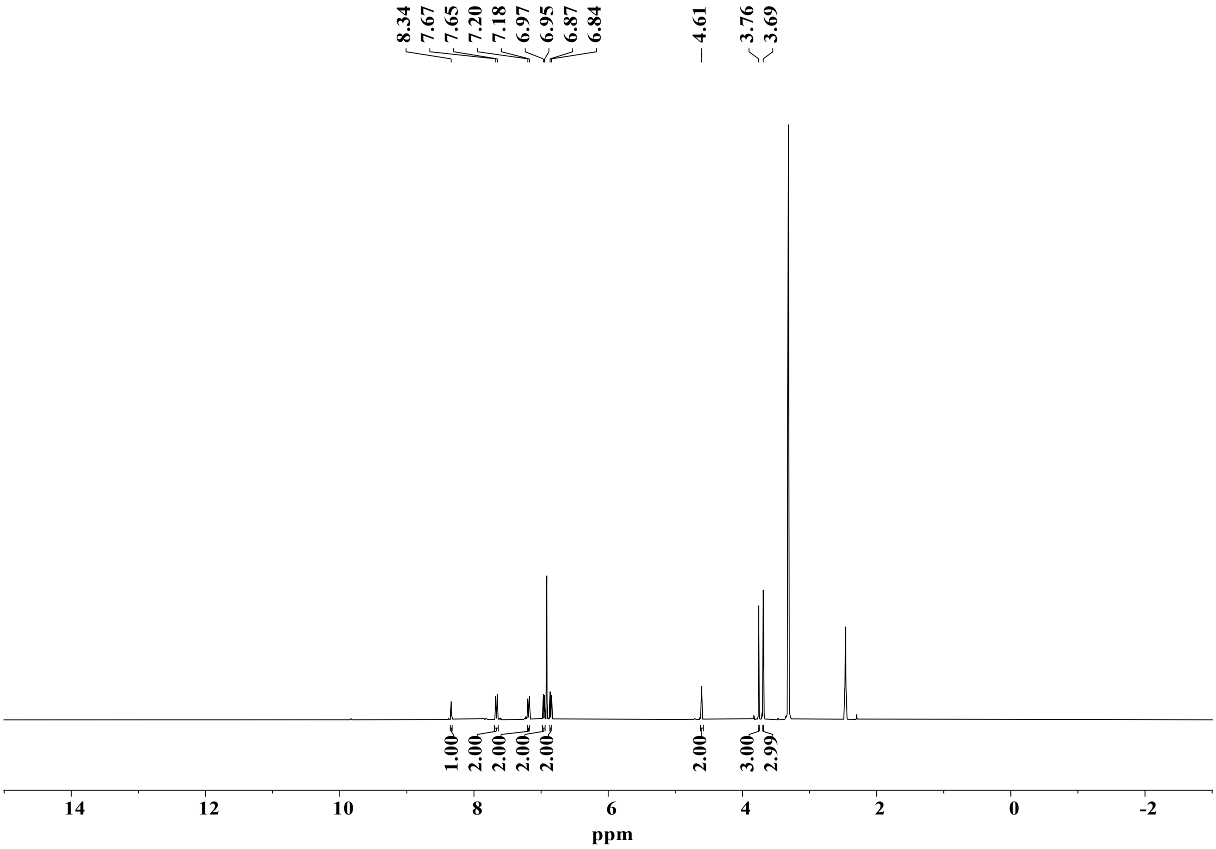


Figure S17. ^{1}H NMR spectrum of N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (2e)

(400 MHz, d_6-DMSO).

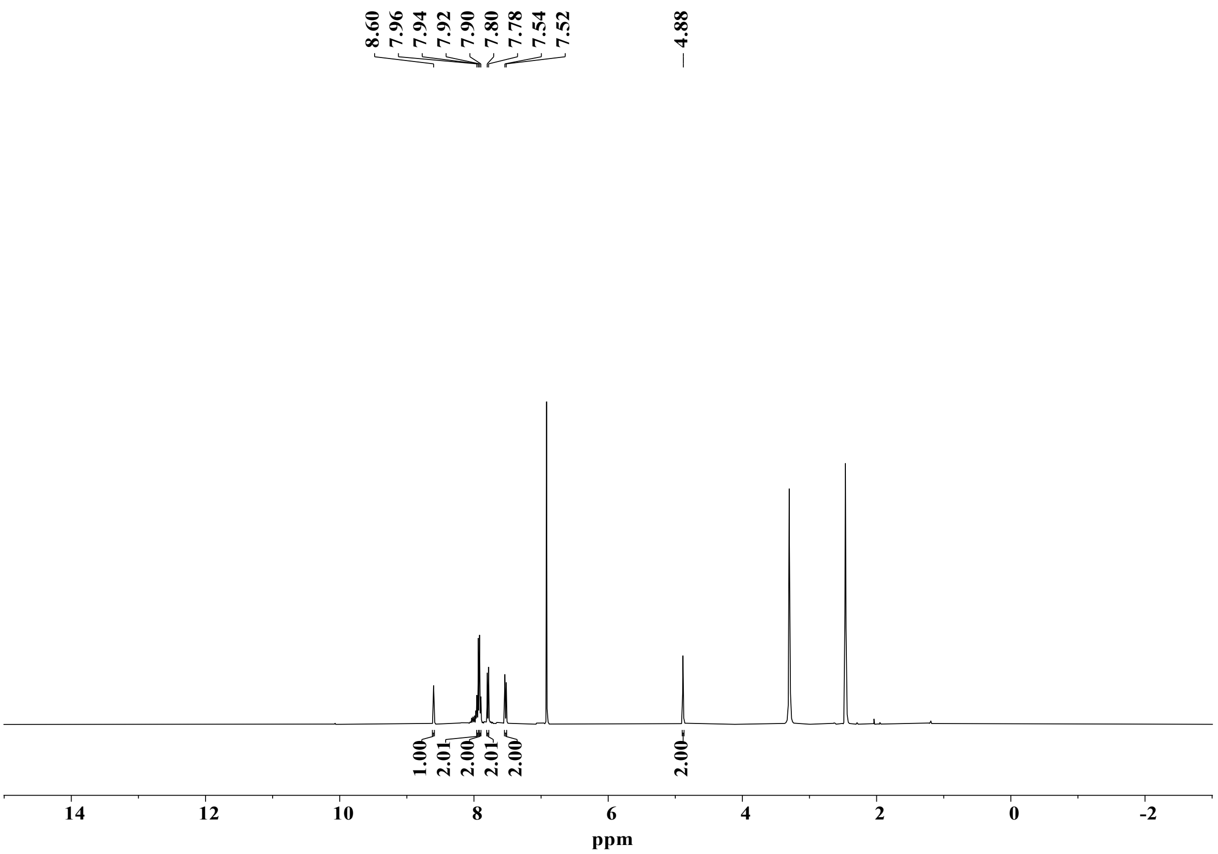


Figure S18. ^{1}H NMR spectrum of N-(4-cyanobenzyl)-1-(4- cyanobenzyl)methanimine (2f) (400 MHz, d_6-DMSO).

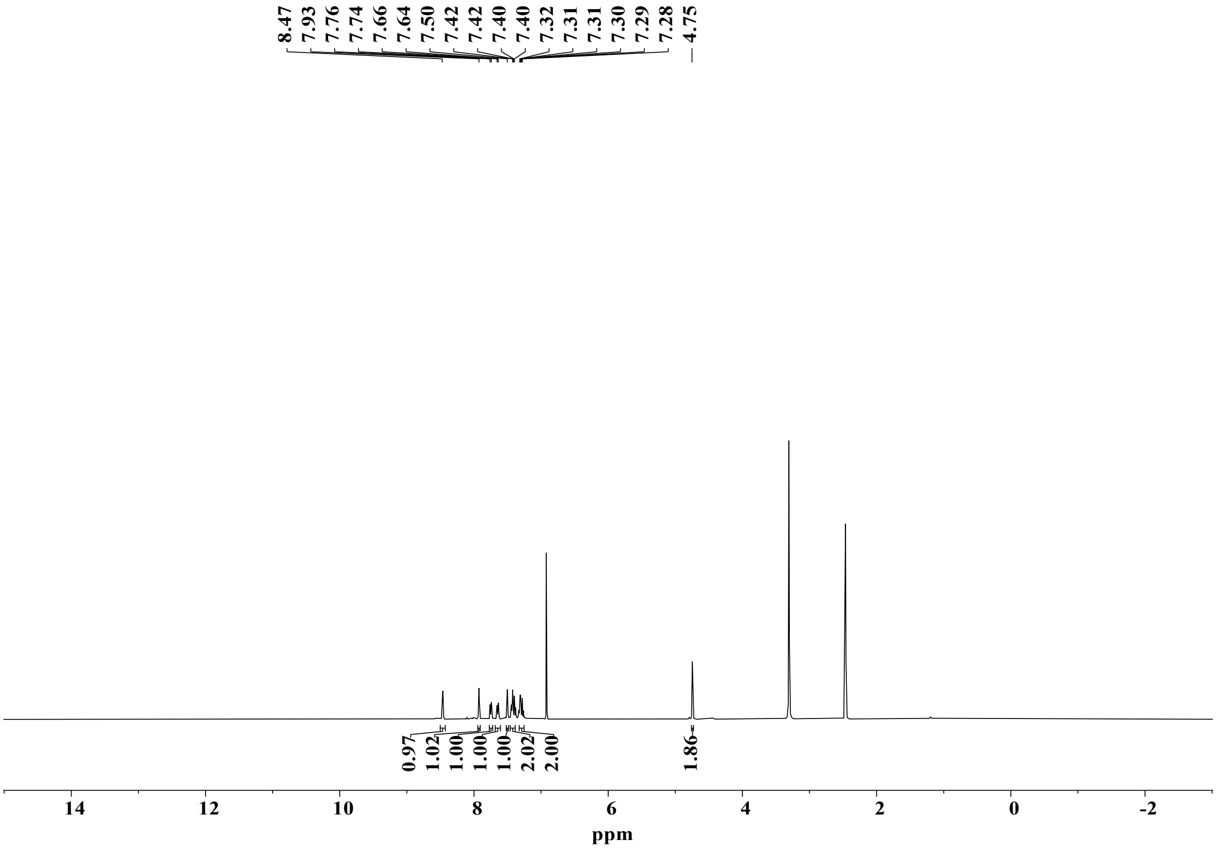


Figure S19. ^{1}H NMR spectrum of N-(3-bromobenzyl)-1-(3-bromophenyl)methanimine (2g) (400 MHz, *d*$_6$-DMSO).

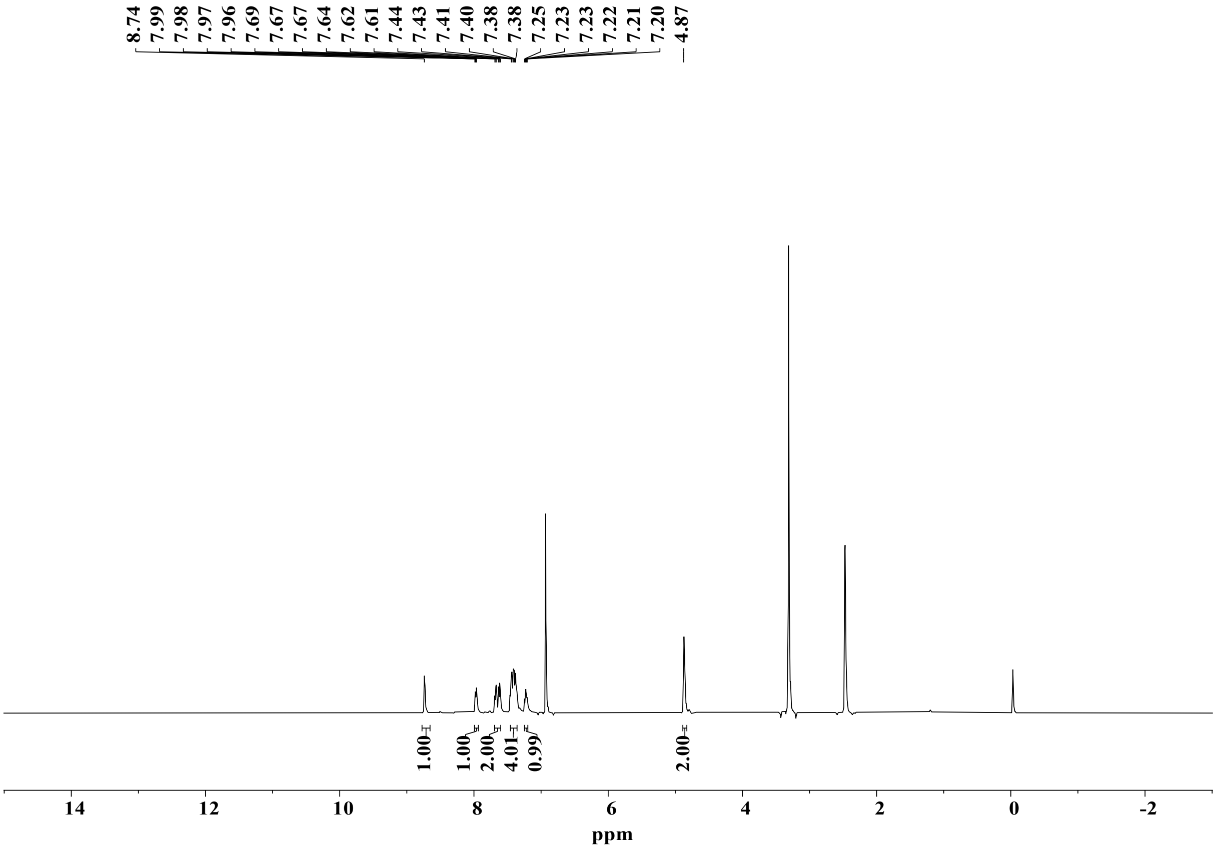


Figure S20. ^{1}H NMR spectrum of N-(2-bromobenzyl)-1-(2-bromophenyl)methanimine (2h) (400 MHz, d_6-DMSO).

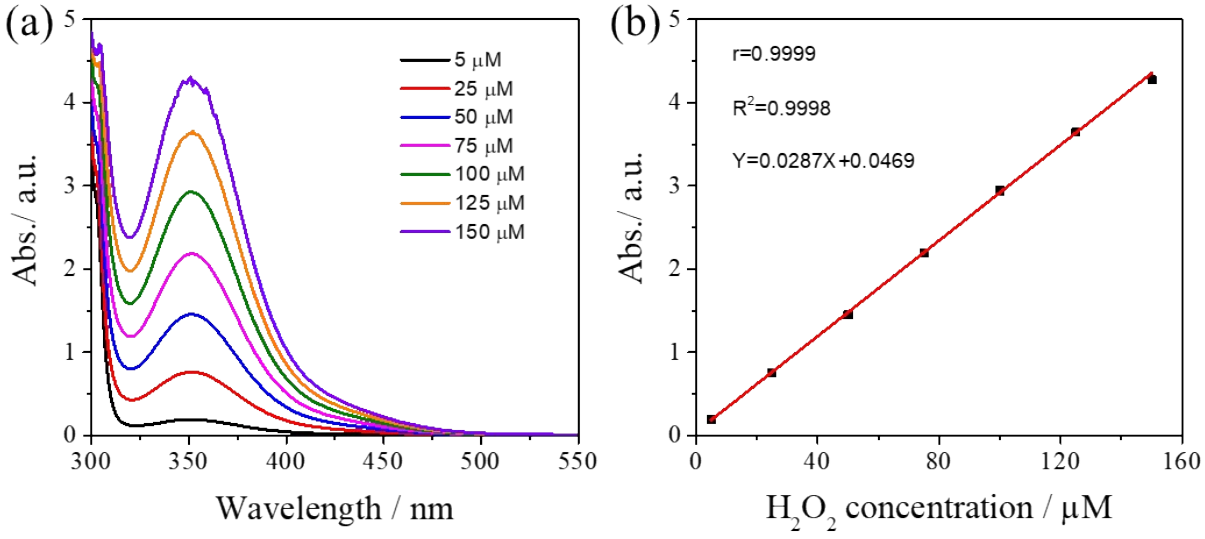


Figure S21. The absorption spectra of different concentrations of H_2O_2 at wavelengths of 300-550 nm by iodometry (a). The standard curve of H_2O_2 concentration-absorbance by the iodometry method (b).

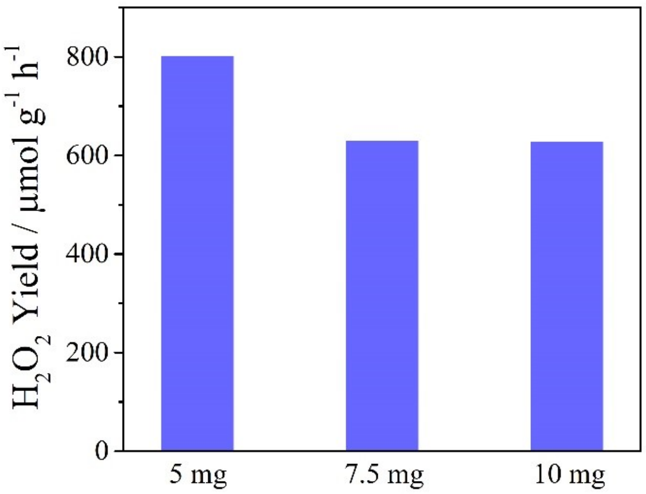


Figure S22. The effect of catalyst dosage on the photocatalytic H_2O_2 performance of HIAM-0009.

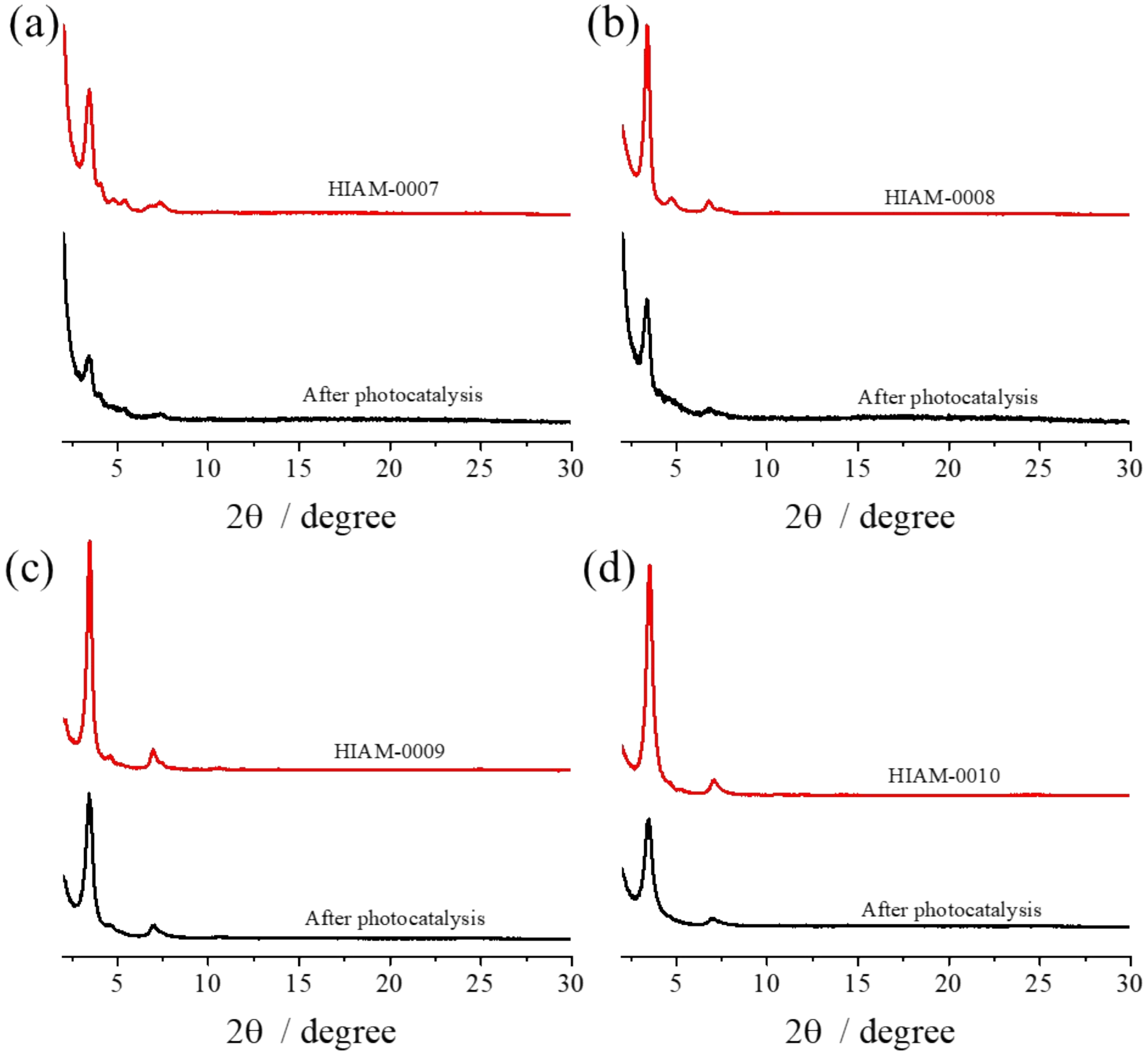


Figure S23. PXRD patterns of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) before and after photocatalysis H_2O_2 production.

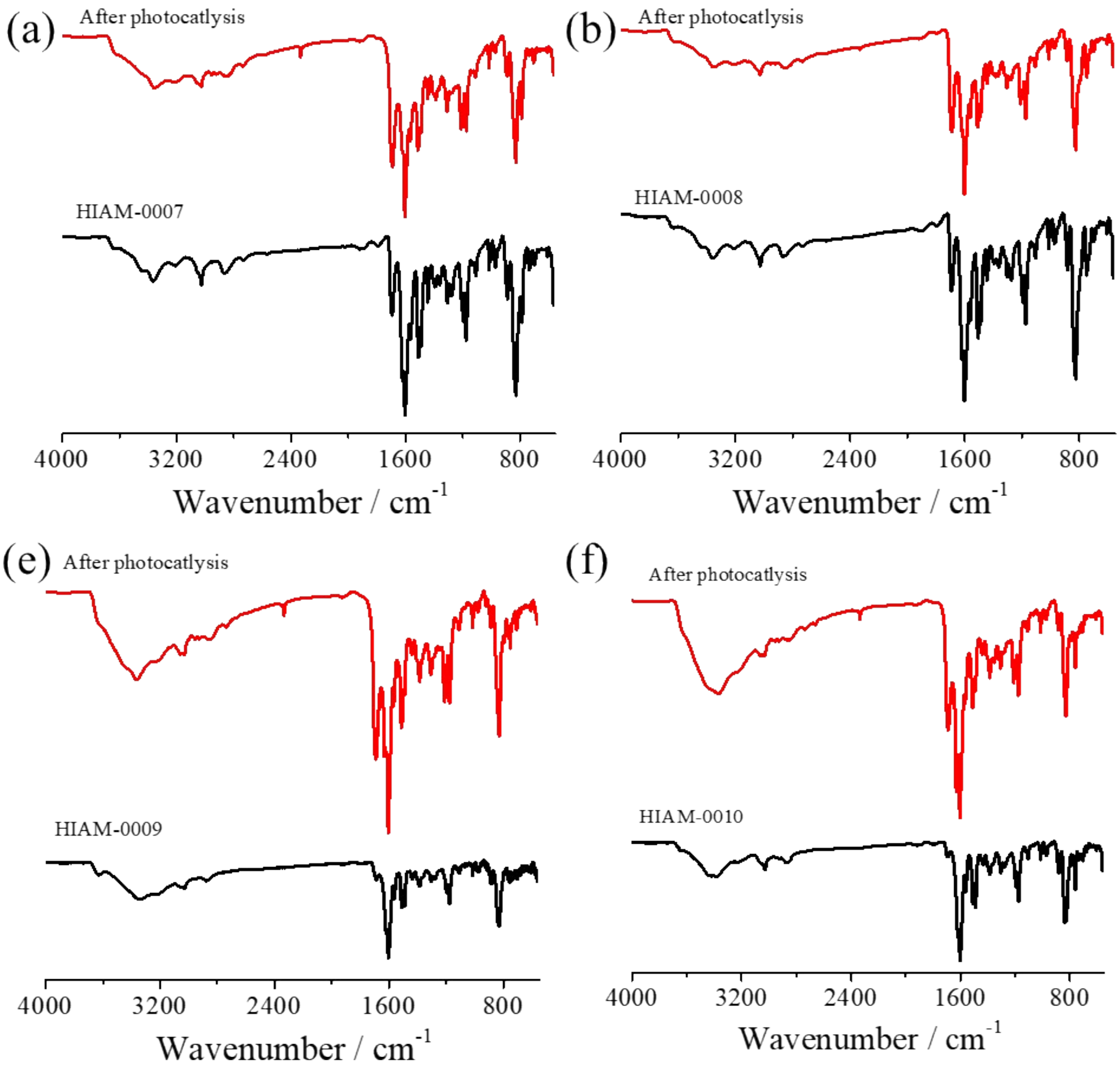


Figure S24. FT-IR spectra of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) before and after photocatalysis H_2O_2 production.

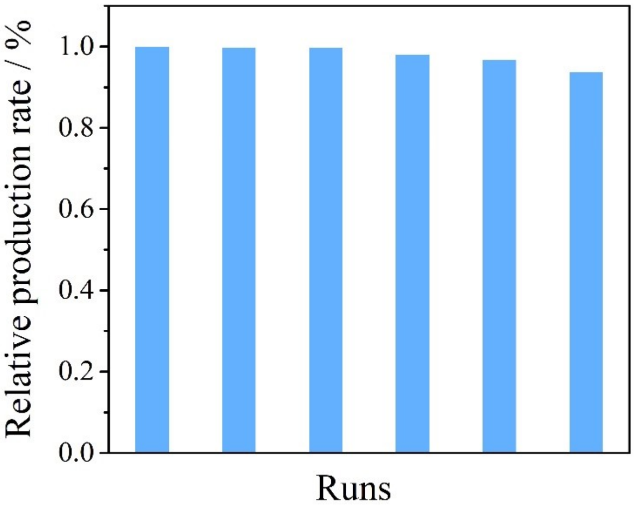


Figure S25. Photocatalytic cycle stability tests toward H_2O_2 production using HIAM-0009 as photocatalyst.

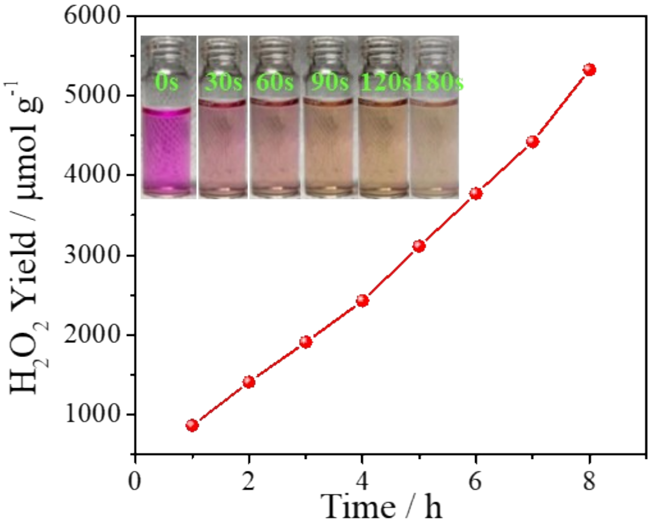


Figure S26. Long-term photocatalytic reaction for HIAM-0009, inset: RhB degradation experiments.

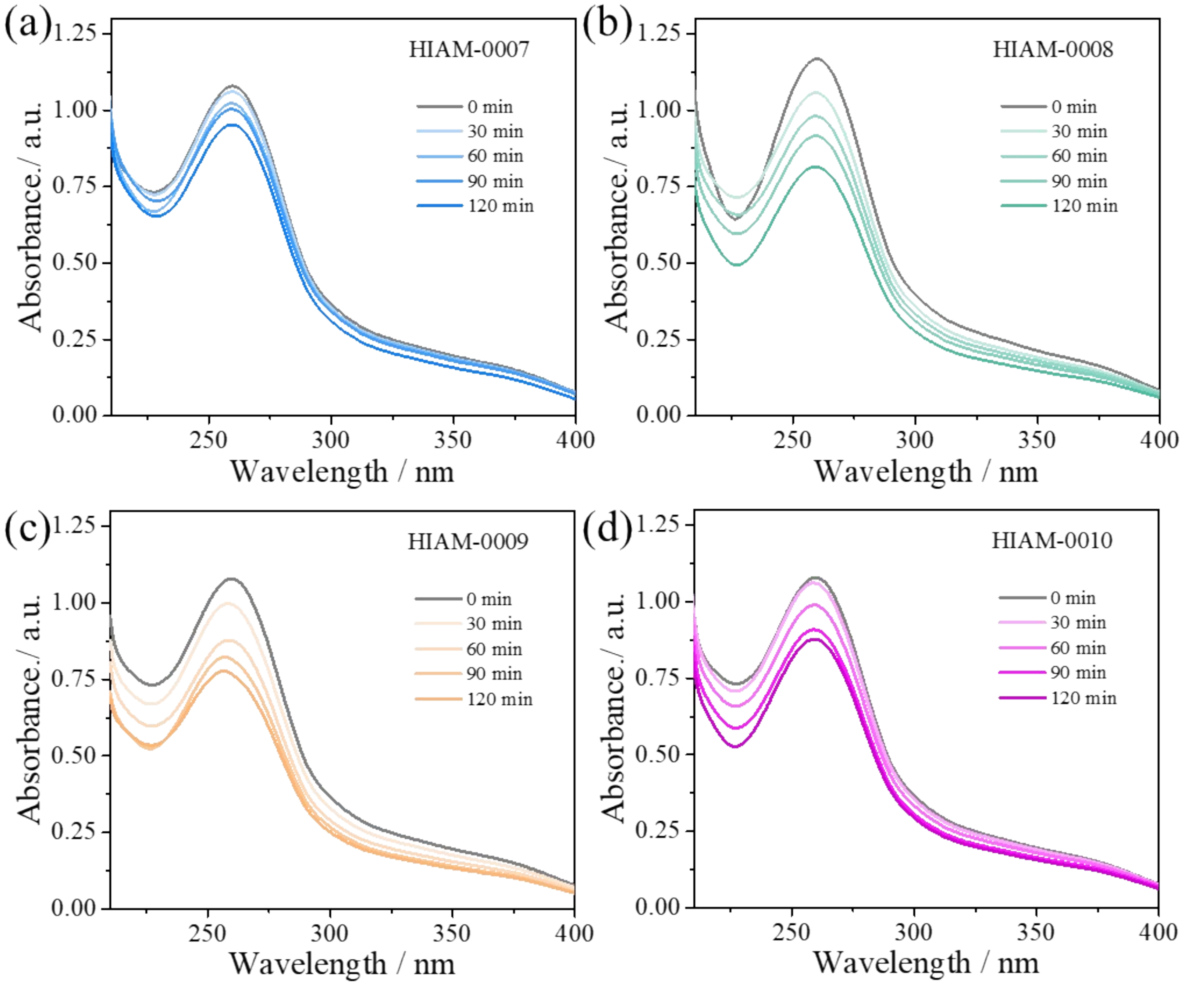


Figure S27. Absorbance changes in NBT degradation using HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d).

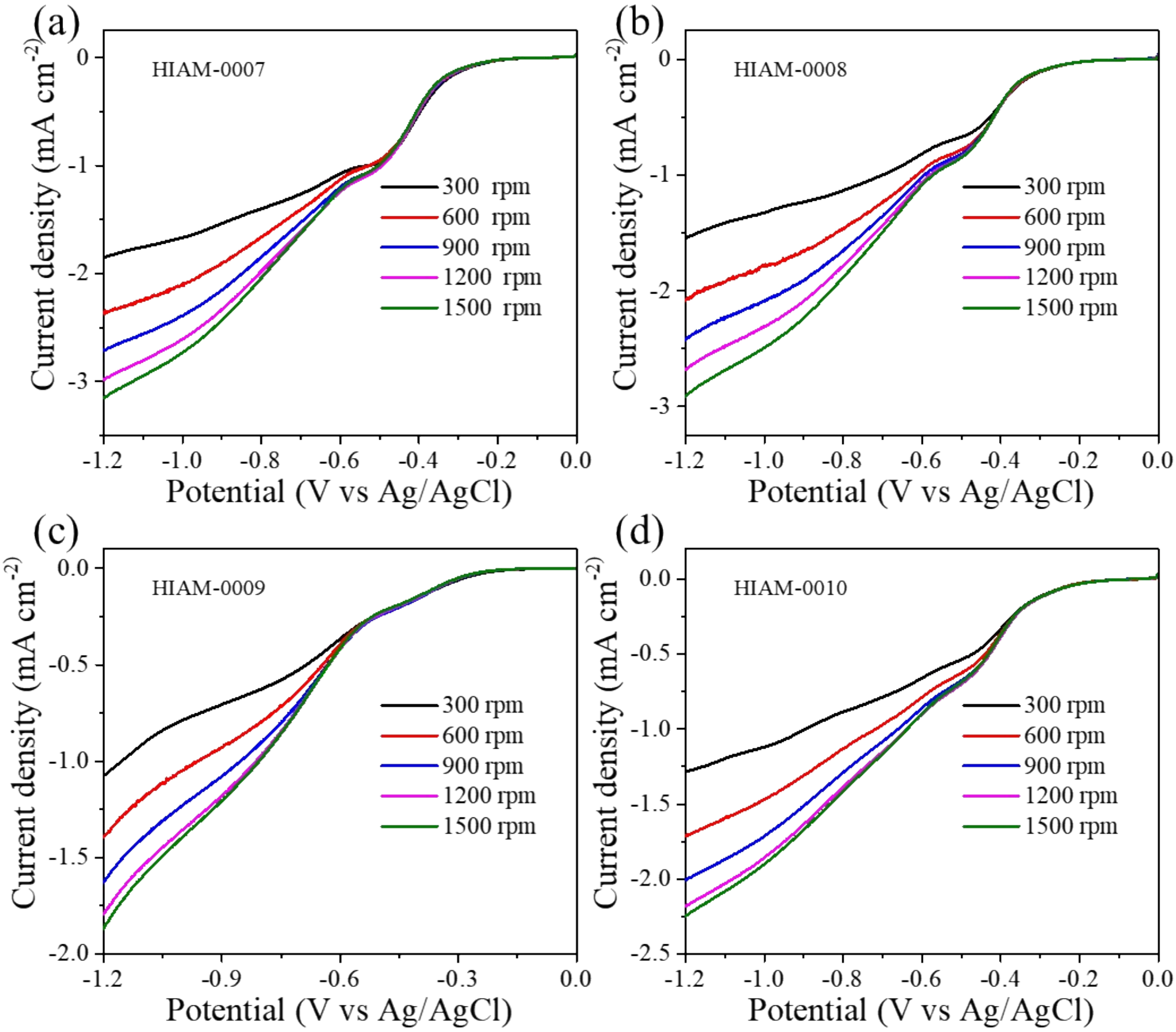


Figure S28. Linear-sweep RDE voltammograms of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) measured at different rotating speeds.

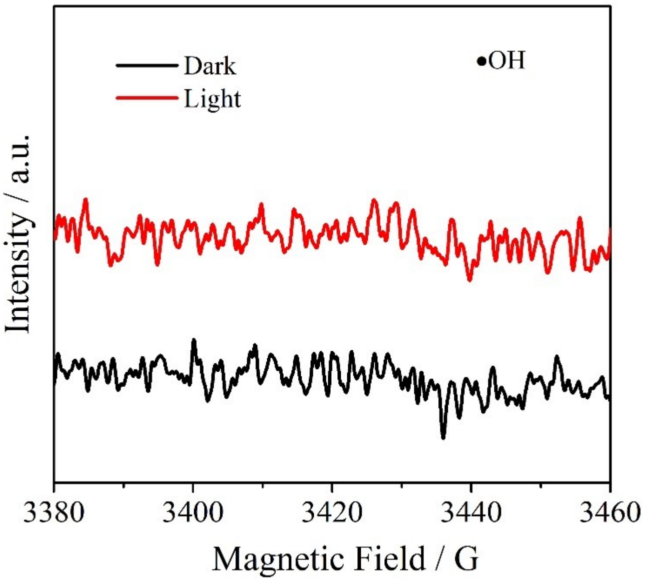


Figure S29. The DMPO spin trapping EPR spectra of HIAM-0007 for ·OH detection under dark and visible light.

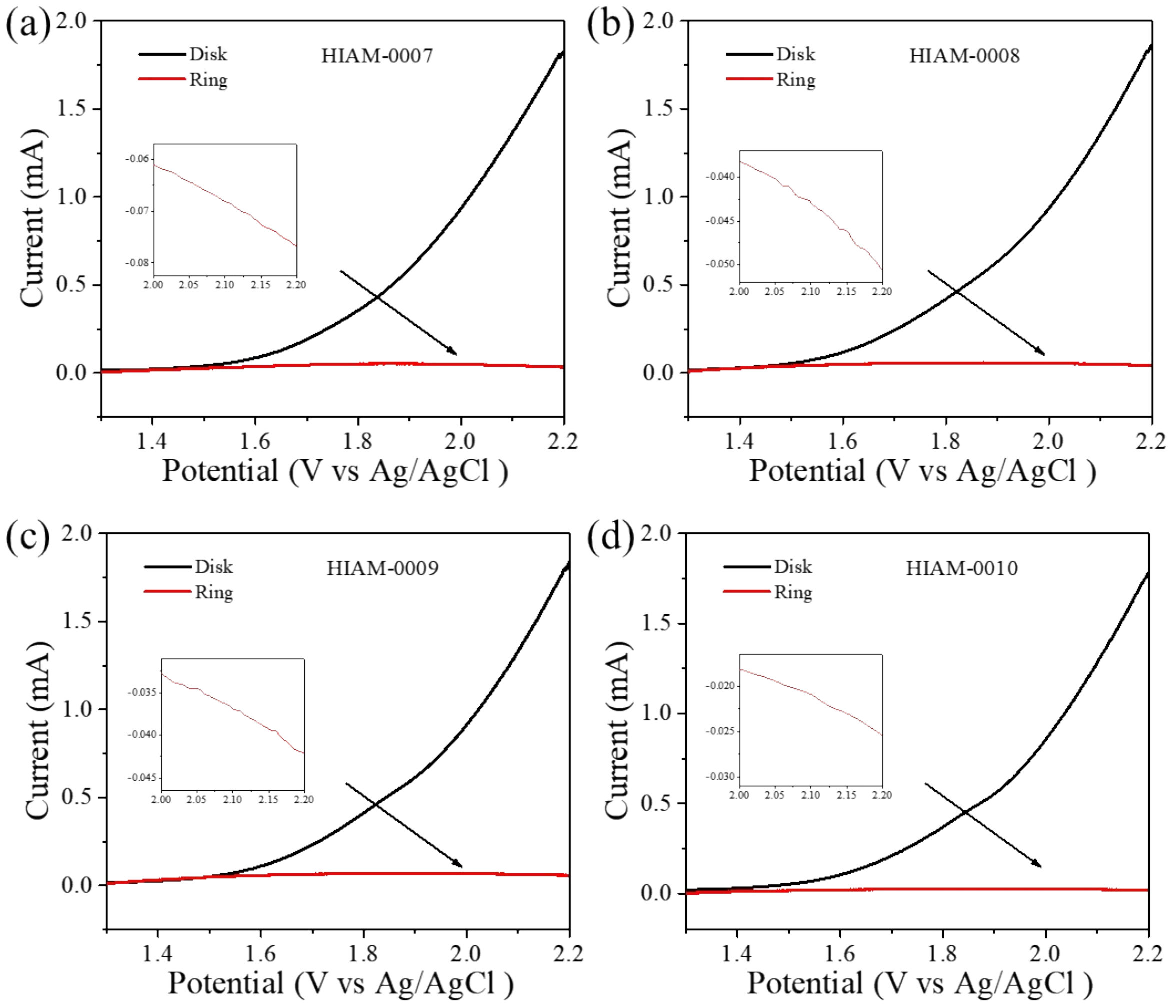


Figure S30. The RRDE measurements of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) with rotating speed of 1000 rpm, the potential of the Pt ring electrode was set at -0.23 V (vs. Ag/AgCl) to detect O_2.

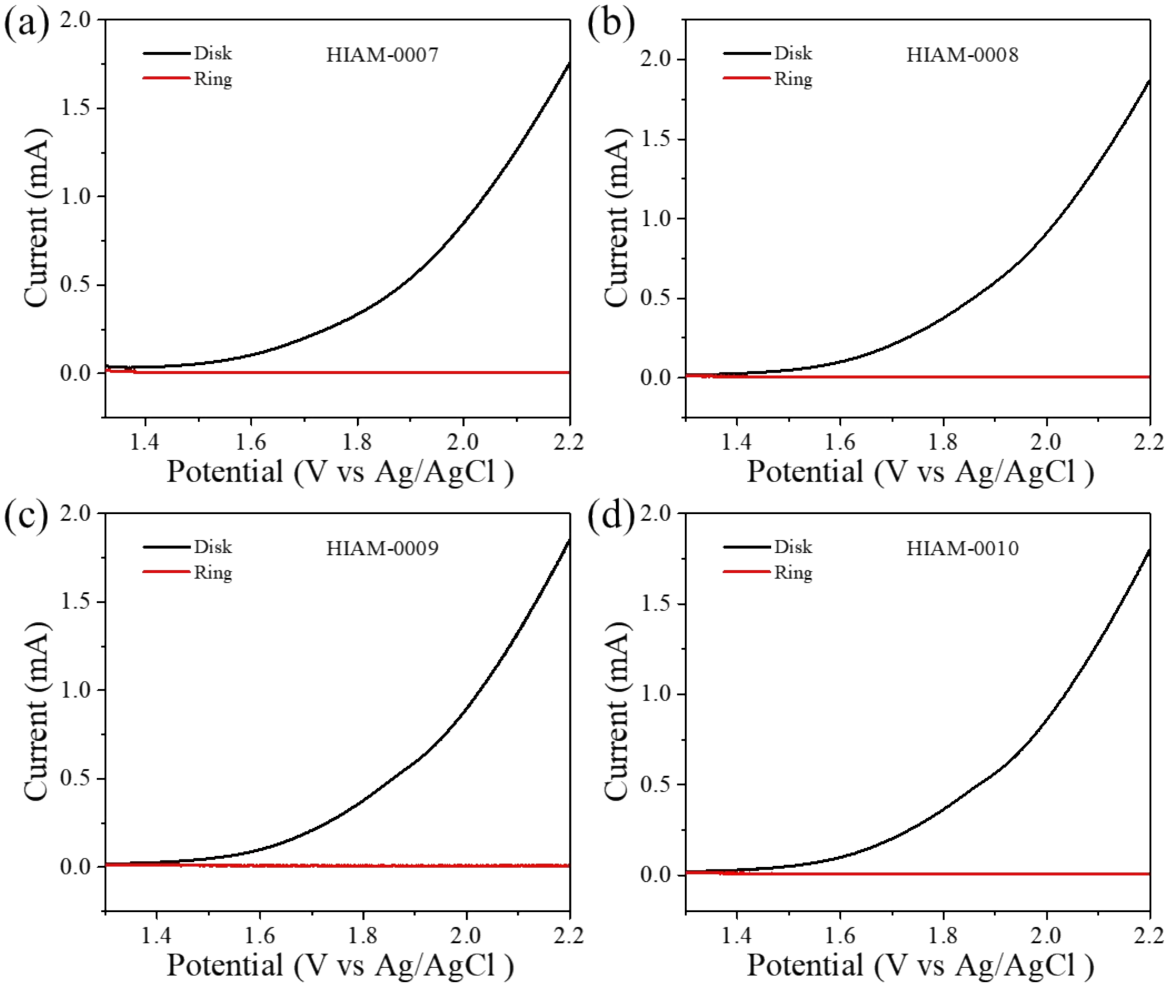


Figure S31. The RRDE measurements of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d) with rotating speed of 1000 rpm, the potential of the Pt ring electrode was set at 0.6 V (vs. Ag/AgCl) to detect H_2O_2.

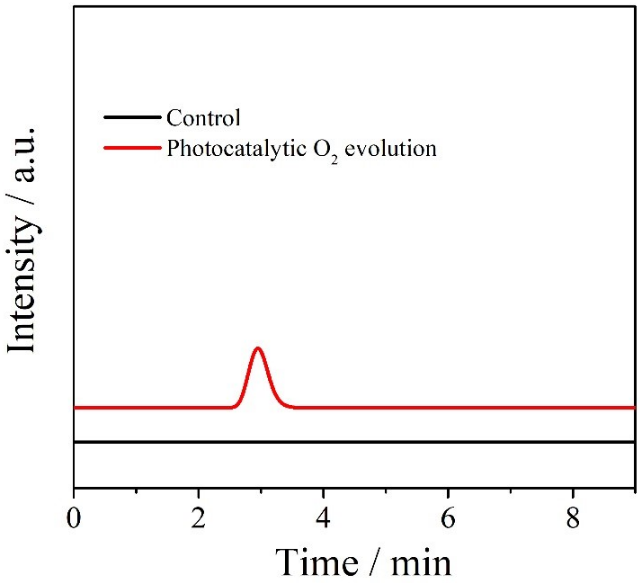


Figure S32. GC chromatogram of photocatalytic O_2 generation using HIAM-0009 as photocatalyst (λ > 420 nm; 30 mM $AgNO_3$; 50 mg COFs in 50 mL solution).

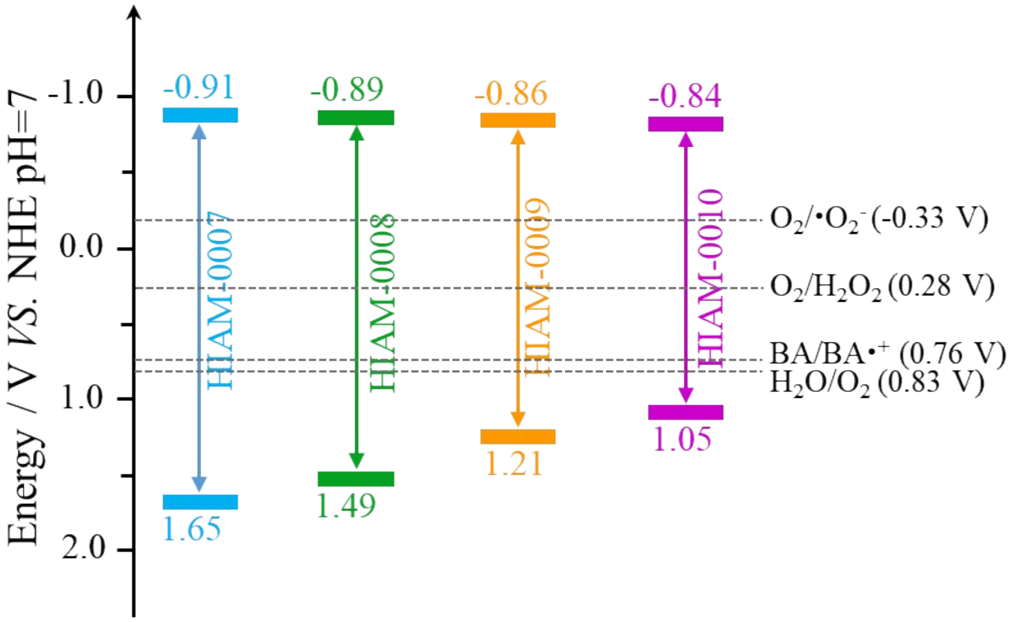


Figure S33. The energy band structure of HIAM-0007, HIAM-0008, HIAM-0009 and HIAM-0010 and redox potentials of benzylamine (BA), molecular oxygen into superoxide and hydrogen peroxide in the photocatalytic reaction.

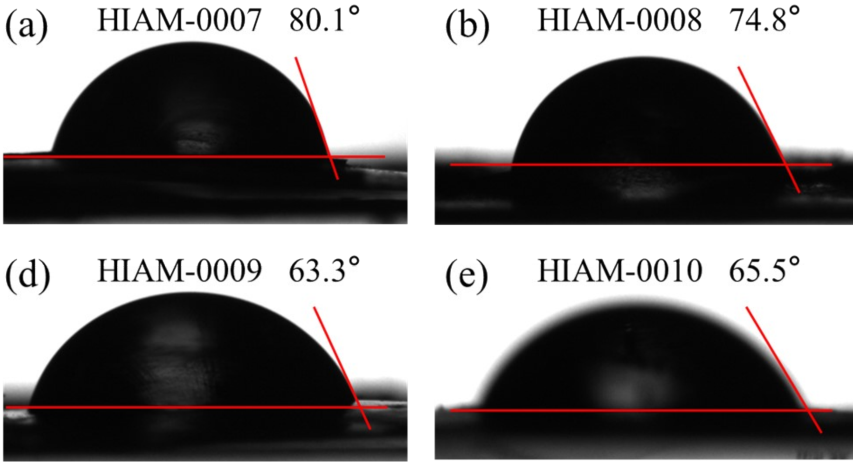


Figure S34. Water contact angles of HIAM-0007 (a), HIAM-0008 (b), HIAM-0009 (c) and HIAM-0010 (d).

Table S1. Fractional atomic coordinates and the unit cell of HIAM-0007 from the Rietveld refinement AA-stacking mode.

Space group: ***pm*** **a = 26.2379 Å, b = 3.4871 Å, and c = 26.2460 Å, α = γ = 90°, and β =92°**				
C1	C	0.21768	0	0.69501
C2	C	0.26573	0	0.67599
C3	C	0.27539	0	0.62503
C4	C	0.23358	0	0.59074
C5	C	0.1827	0	0.60668
C6	C	0.17585	0	0.65979
C7	C	0.13875	0	0.56739
C8	C	0.14913	0	0.51516
C9	C	0.11128	0	0.47739
C10	C	0.05906	0	0.48784
C11	C	0.04821	0	0.54038
C12	C	0.08623	0	0.57832
C13	C	0.0197	0	0.44395
C14	C	0.03555	0	0.39306
C15	C	1.00109	0	0.34908
C16	C	0.95012	0	0.35882
C17	C	0.93121	0	0.40691
C18	C	0.96651	0	0.44866
C19	C	0.21344	0	0.75165

C20	C	0.32947	0	0.60923
C21	C	0.87458	0	0.41129
C22	C	0.01693	0	0.29723
C23	C	0.37058	0	0.64637
C24	C	0.42003	0	0.63265
C25	C	0.43082	0	0.58185
C26	C	0.39203	0	0.5438
C27	C	0.34166	0	0.5573
C28	C	0.16552	0	0.77354
C29	C	0.16227	0	0.82586
C30	C	0.20682	0	0.85744
C31	C	0.2541	0	0.83715
C32	C	0.25773	0	0.78536
C33	C	0.84075	0	0.3671
C34	C	0.78896	0	0.37087
C35	C	0.76881	0	0.41821
C36	C	0.80052	0	0.46266
C37	C	0.85282	0	0.45927
C38	C	0.06885	0	0.28495
C39	C	0.08227	0	0.23457
C40	C	0.04416	0	0.19586
C41	C	0.99326	0	0.2045

C42	C	0.97961	0	0.25394
C43	C	0.48332	0	0.57045
C44	C	0.05547	0	0.14335
C45	C	0.20441	0	0.91175
C46	C	0.71451	0	0.42081
N47	N	0.00164	0	0.55952
S48	S	0.00294	0	0.62374
N49	N	0.06718	0	0.62493
C50	C	0.16832	0	0.07058
C51	C	0.18438	0	0.02116
C52	C	0.14766	0	-0.01933
C53	C	0.09616	0	-0.01085
C54	C	0.08015	0	0.03795
C55	C	0.11638	0	0.07917
N56	N	0.10203	0	0.13029
N57	N	0.1599	0	0.9295
N58	N	0.69693	0	0.46538
N59	N	0.49626	0	0.52387
C60	C	0.54735	0	0.50938
C61	C	0.58868	0	0.54548
C62	C	0.63744	0	0.52932
C63	C	0.64576	0	0.47781

C64	C	0.60515	0	0.44122
C65	C	0.55578	0	0.45743
H66	H	0.29647	0	0.70149
H67	H	0.24188	0	0.55192
H68	H	0.13893	0	0.67424
H69	H	0.18636	0	0.50005
H70	H	0.12631	0	0.44014
H71	H	0.07436	0	0.38469
H72	H	0.92456	0	0.32813
H73	H	0.95214	0	0.48561
H74	H	0.36816	0	0.68701
H75	H	0.45015	0	0.66229
H76	H	0.40052	0	0.50377
H77	H	0.31381	0	0.52608
H78	H	0.1299	0	0.7517
H79	H	0.12467	0	0.84141
H80	H	0.28857	0	0.86149
H81	H	0.29683	0	0.77515
H82	H	0.85087	0	0.32798
H83	H	0.76452	0	0.33648
H84	H	0.78507	0	0.50029
H85	H	0.87475	0	0.49482

H86	H	0.10013	0	0.31276
H87	H	0.12231	0	0.22602
H88	H	0.96357	0	0.17442
H89	H	0.93897	0	0.25644
H90	H	0.51053	0	0.60224
H91	H	0.02361	0	0.11623
H92	H	0.23886	0	0.9358
H93	H	0.69034	0	0.38645
H94	H	0.19613	0	0.10225
H95	H	0.22486	0	0.01546
H96	H	0.0683	0	-0.04255
H97	H	0.03947	0	0.04154
H98	H	0.5852	0	0.58616
H99	H	0.66923	0	0.55708
H100	H	0.61074	0	0.40073
H101	H	0.52402	0	0.4297

Table S2. Fractional atomic coordinates and the unit cell of HIAM-0008 from the Pawley refinement AA-stacking mode.

Space group: ***pm*** **a = 25.7358 Å, b = 3.5620 Å, and c = 26.0727 Å, α = γ = 90°, and β =93°**				
C1	C	0.22933	0	0.73947
C2	C	0.27676	0	0.71734
C3	C	0.28288	0	0.66569
C4	C	0.23832	0	0.63409
C5	C	0.18766	0	0.65268
C6	C	0.18393	0	0.70654
C7	C	0.14111	0	0.61481
C8	C	0.14929	0	0.5643
C9	C	0.10918	0	0.52407
C10	C	0.05793	0	0.53137
C11	C	0.04397	0	0.5864
C12	C	0.0852	0	0.62772
C13	C	0.02039	0	0.4848
C14	C	0.03982	0	0.43493
C15	C	1.01106	0	0.38613
C16	C	0.95862	0	0.39185
C17	C	0.93587	0	0.43841
C18	C	0.96886	0	0.48339
C19	C	0.23016	0	0.79669

C20	C	0.33621	0	0.64584
C21	C	0.87791	0	0.43728
C22	C	0.02829	0	0.33808
C23	C	0.38087	0	0.68023
C24	C	0.42967	0	0.66262
C25	C	0.43604	0	0.61056
C26	C	0.39373	0	0.57517
C27	C	0.34414	0	0.59253
C28	C	0.1836	0	0.82208
C29	C	0.18488	0	0.87491
C30	C	0.23282	0	0.90362
C31	C	0.27891	0	0.87982
C32	C	0.27802	0	0.82742
C33	C	0.84685	0	0.38997
C34	C	0.79369	0	0.38903
C35	C	0.76958	0	0.43454
C36	C	0.79876	0	0.48186
C37	C	0.85216	0	0.48317
C38	C	0.08229	0	0.33012
C39	C	0.09977	0	0.28097
C40	C	0.06371	0	0.23935
C41	C	1.01406	0	0.24136

C42	C	0.9964	0	0.28951
C43	C	0.48778	0	0.59483
C44	C	0.07886	0	0.18798
C45	C	0.23455	0	0.9585
C46	C	0.71395	0	0.43325
N47	N	-0.00286	0	0.60175
Se48	Se	-0.00428	0	0.67403
N49	N	0.069	0	0.6737
C50	C	0.19703	0	0.12028
C51	C	0.21458	0	0.07097
C52	C	0.17774	0	0.02956
C53	C	0.12519	0	0.03628
C54	C	0.10777	0	0.08444
C55	C	0.14366	0	0.12717
N56	N	0.12714	0	0.17787
N57	N	0.1902	0	0.97767
N58	N	0.69539	0	0.4774
N59	N	0.49667	0	0.54684
C60	C	0.54719	0	0.52869
C61	C	0.59153	0	0.56264
C62	C	0.63953	0	0.54365
C63	C	0.64437	0	0.49144

C64	C	0.60133	0	0.45649
C65	C	0.55216	0	0.47565
H66	H	0.31	0	0.74067
H67	H	0.24487	0	0.59501
H68	H	0.14674	0	0.7226
H69	H	0.18603	0	0.54728
H70	H	0.12679	0	0.48797
H71	H	0.0796	0	0.42872
H72	H	0.93501	0	0.35906
H73	H	0.9523	0	0.5199
H74	H	0.38173	0	0.72137
H75	H	0.46276	0	0.69014
H76	H	0.39886	0	0.53418
H77	H	0.31375	0	0.56275
H78	H	0.14578	0	0.80244
H79	H	0.14795	0	0.89308
H80	H	0.31584	0	0.90183
H81	H	0.31688	0	0.8145
H82	H	0.86011	0	0.35167
H83	H	0.77139	0	0.3526
H84	H	0.78053	0	0.5184
H85	H	0.87188	0	0.52057

H86	H	0.11237	0	0.36025
H87	H	0.14124	0	0.27561
H88	H	0.98595	0	0.20887
H89	H	0.95472	0	0.28853
H90	H	0.51785	0	0.62488
H91	H	0.04777	0	0.15901
H92	H	0.27066	0	0.98162
H93	H	0.68992	0	0.39797
H94	H	0.22465	0	0.15302
H95	H	0.25593	0	0.0657
H96	H	0.09746	0	0.00353
H97	H	0.06615	0	0.08586
H98	H	0.59137	0	0.60384
H99	H	0.67364	0	0.56987
H100	H	0.60536	0	0.41543
H101	H	0.51805	0	0.44957

Table S3. Fractional atomic coordinates and the unit cell of HIAM-0009 from the Pawley refinement AA-stacking mode.

Space group: ***pm*** **a = 25.7638 Å, b = 3.5011 Å, and c = 25.3582 Å，α = γ = 90°, and β =96°**				
C1	C	-0.77874	0	-0.25334
C2	C	-0.72606	0	-0.25741
C3	C	-0.70749	0	-0.30624
C4	C	-0.74376	0	-0.35207
C5	C	-0.79768	0	-0.35318
C6	C	-0.81237	0	-0.30056
C7	C	-0.83755	0	-0.40605
C8	C	-0.82781	0	-0.46259
C9	C	-0.87167	0	-0.50576
C10	C	-0.92635	0	-0.49503
C11	C	-0.93119	0	-0.43915
C12	C	-0.89117	0	-0.39956
C13	C	-0.97817	0	-0.53659
C14	C	-0.98451	0	-0.59333
C15	C	-1.03404	0	-0.62505
C16	C	-1.07866	0	-0.5995
C17	C	-1.07598	0	-0.54546
C18	C	-1.02717	0	-0.51763
C19	C	-0.799	0	-0.20005

C20	C	-0.65036	0	-0.30969
C21	C	-1.12368	0	-0.51662
C22	C	-1.04046	0	-0.68456
C23	C	-0.61264	0	-0.26399
C24	C	-0.55964	0	-0.26923
C25	C	-0.54433	0	-0.31977
C26	C	-0.58078	0	-0.36457
C27	C	-0.6323	0	-0.35988
C28	C	-0.85336	0	-0.19562
C29	C	-0.87179	0	-0.14718
C30	C	-0.83713	0	-0.10115
C31	C	-0.78369	0	-0.10349
C32	C	-0.7646	0	-0.15226
C33	C	-1.17384	0	-0.54503
C34	C	-1.21731	0	-0.51857
C35	C	-1.21201	0	-0.46338
C36	C	-1.16388	0	-0.43402
C37	C	-1.12019	0	-0.45993
C38	C	-0.99632	0	-0.71201
C39	C	-1.00142	0	-0.76609
C40	C	-1.05095	0	-0.79612
C41	C	-1.09544	0	-0.77049

C42	C	-1.09057	0	-0.71544
C43	C	-0.49172	0	-0.33126
C44	C	-1.05358	0	-0.85372
C45	C	-0.85711	0	-0.05074
C46	C	-1.25805	0	-0.43806
N47	N	-0.97614	0	-0.41705
S48	S	-0.97387	0	-0.3517
N49	N	-0.90993	0	-0.35246
C50	C	-0.9328	0	0.08951
C51	C	-0.9059	0	0.04631
C52	C	-0.93347	0	-0.00439
C53	C	-0.98826	0	-0.01103
C54	C	-1.01556	0	0.03331
C55	C	-0.98678	0	0.08309
N56	N	-1.00824	0	0.13074
N57	N	-0.90712	0	-0.05006
N58	N	-1.2579	0	-0.38679
N59	N	-1.44964	0	-0.29763
C60	C	-1.40009	0	-0.31872
C61	C	-1.35295	0	-0.28515
C62	C	-1.30519	0	-0.30734
C63	C	-1.30527	0	-0.3628

C64	C	-1.35261	0	-0.39479
C65	C	-1.39775	0	-0.37395
C66	C	-0.77666	0	-0.48015
C67	C	-0.76717	0	-0.53263
C68	C	-0.80758	0	-0.57158
C69	C	-0.85795	0	-0.5585
H70	H	-0.69951	0	-0.22272
H71	H	-0.72891	0	-0.38608
H72	H	-0.84942	0	-0.2921
H73	H	-0.95383	0	-0.61523
H74	H	-1.11564	0	-0.62138
H75	H	-1.03159	0	-0.48032
H76	H	-0.62181	0	-0.2237
H77	H	-0.53117	0	-0.23445
H78	H	-0.56961	0	-0.40467
H79	H	-0.65545	0	-0.39763
H80	H	-0.88428	0	-0.22767
H81	H	-0.91374	0	-0.14616
H82	H	-0.75665	0	-0.06757
H83	H	-0.72277	0	-0.1501
H84	H	-1.18192	0	-0.58747
H85	H	-1.25538	0	-0.54157

H86	H	-1.15987	0	-0.391
H87	H	-1.08532	0	-0.43247
H88	H	-0.95663	0	-0.69393
H89	H	-0.96516	0	-0.78405
H90	H	-1.13378	0	-0.79287
H91	H	-1.12751	0	-0.69968
H92	H	-0.49098	0	-0.37259
H93	H	-1.0892	0	-0.8807
H94	H	-0.82966	0	-0.01548
H95	H	-1.29219	0	-0.46583
H96	H	-0.9114	0	0.12882
H97	H	-0.86398	0	0.05398
H98	H	-1.00938	0	-0.05039
H99	H	-1.05781	0	0.02897
H100	H	-1.35321	0	-0.2425
H101	H	-1.26868	0	-0.28176
H102	H	-1.35817	0	-0.43728
H103	H	-1.42911	0	-0.4054
H104	H	-0.73988	0	-0.45902
H105	H	-0.72754	0	-0.54335
H106	H	-0.79984	0	-0.61275
H107	H	-0.88275	0	-0.59297

Table S4. Fractional atomic coordinates and the unit cell of HIAM-0010 from the Pawley refinement AA-stacking mode.

Space group: ***pm*** **a = 26.4222 Å, b = 3.5689 Å, and c = 26.1301 Å， α = γ = 90°, and β =99°**				
C1	C	0.2405	0	0.75624
C2	C	0.29243	0	0.75191
C3	C	0.30887	0	0.70397
C4	C	0.27072	0	0.65953
C5	C	0.21701	0	0.65826
C6	C	0.20489	0	0.70978
C7	C	0.17414	0	0.60675
C8	C	0.18004	0	0.55387
C9	C	0.13338	0	0.50754
C10	C	0.08135	0	0.51482
C11	C	0.07602	0	0.57093
C12	C	0.11882	0	0.6134
C13	C	0.02948	0	0.47281
C14	C	0.02755	0	0.41862
C15	C	0.98474	0	0.38065
C16	C	0.93759	0	0.39768
C17	C	0.9337	0	0.45034
C18	C	0.97997	0	0.4861
C19	C	0.22331	0	0.8092

C20	C	0.36583	0	0.69981
C21	C	0.88135	0	0.46787
C22	C	-0.01273	0	0.32284
C23	C	0.40481	0	0.74424
C24	C	0.45686	0	0.73967
C25	C	0.47186	0	0.6909
C26	C	0.43421	0	0.64678
C27	C	0.38268	0	0.65094
C28	C	0.17064	0	0.8148
C29	C	0.15546	0	0.86333
C30	C	0.19193	0	0.90823
C31	C	0.24379	0	0.90412
C32	C	0.25936	0	0.85574
C33	C	0.83532	0	0.43141
C34	C	0.78747	0	0.44702
C35	C	0.78321	0	0.49941
C36	C	0.82758	0	0.53641
C37	C	0.87574	0	0.52112
C38	C	0.03554	0	0.30577
C39	C	0.0396	0	0.25376
C40	C	-0.00404	0	0.2157
C41	C	0.94902	0	0.23107

C42	C	0.94455	0	0.28374
C43	C	0.52633	0	0.68517
C44	C	0.00195	0	0.16075
C45	C	0.17673	0	0.95963
C46	C	0.73203	0	0.51414
N47	N	0.0324	0	0.58686
Se48	Se	0.03355	0	0.65819
N49	N	0.1039	0	0.65792
C50	C	0.11926	0	0.10415
C51	C	0.14058	0	0.05905
C52	C	0.10867	0	0.01052
C53	C	0.05532	0	0.00839
C54	C	0.03392	0	0.05397
C55	C	0.06627	0	0.10206
N56	N	0.04823	0	0.15044
N57	N	0.12863	0	0.96452
N58	N	0.72615	0	0.56252
N59	N	0.53727	0	0.63863
C60	C	0.58585	0	0.62164
C61	C	0.63283	0	0.65543
C62	C	0.67869	0	0.63511
C63	C	0.67808	0	0.58137

C64	C	0.63065	0	0.54801
C65	C	0.58525	0	0.56825
C66	C	0.23188	0	0.53602
C67	C	0.23952	0	0.48745
C68	C	0.19792	0	0.44602
C69	C	0.15012	0	0.45457
H70	H	0.32031	0	0.78578
H71	H	0.2858	0	0.62745
H72	H	0.16808	0	0.71707
H73	H	0.05916	0	0.40348
H74	H	0.90405	0	0.36956
H75	H	0.97311	0	0.52367
H76	H	0.3969	0	0.78333
H77	H	0.48542	0	0.77438
H78	H	0.44437	0	0.60822
H79	H	0.35782	0	0.61419
H80	H	0.13929	0	0.7831
H81	H	0.11486	0	0.86553
H82	H	0.27263	0	0.93863
H83	H	0.30016	0	0.85698
H84	H	0.834	0	0.39016
H85	H	0.75344	0	0.41774

H86	H	0.8252	0	0.57742
H87	H	0.90727	0	0.55267
H88	H	0.07196	0	0.33074
H89	H	0.07779	0	0.24364
H90	H	0.91472	0	0.20217
H91	H	0.90593	0	0.29186
H92	H	0.55589	0	0.71895
H93	H	-0.03113	0	0.13049
H94	H	0.2068	0	0.99278
H95	H	0.69971	0	0.48323
H96	H	0.14427	0	0.14128
H97	H	0.18182	0	0.06329
H98	H	0.03036	0	-0.02873
H99	H	-0.00732	0	0.05131
H100	H	0.6345	0	0.69701
H101	H	0.71487	0	0.66124
H102	H	0.62744	0	0.50639
H103	H	0.54907	0	0.54208
H104	H	0.26826	0	0.55696
H105	H	0.27806	0	0.47781
H106	H	0.20683	0	0.40679
H107	H	0.12908	0	0.41783

Fluorescence life-times of HIAM-0007 to HIAM-0010 were obtained by Exp. Reconvolution Fit, $R(t) = B_1*\exp(-t/\tau_1) + B_2*\exp(-t/\tau_2)$ (shown in Table S5), where τ_i is the estimated lifetime value and B_i is the corresponding amplitude.

Table S5. Fluorescence life-time measurements.

COF	λ_{em} **/ nm**	τ_1 **/ ns**	B_1 **/ %**	τ_2 **/ ns**	B_2 **/ %**	χ^2
HIAM-0007	557	0.43	49.98	2.21	51.02	1.10
HIAM-0008	565	0.11	10.91	2.30	89.09	1.22
HIAM-0009	625	0.76	25.11	2.63	74.89	1.06
HIAM-0010	678	0.30	11.39	1.62	88.61	1.06

[a] Fluorescence life-times obtained upon excitation at λ_{ex} = 450 nm with a laser.

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