Supporting Information

Facile Synthesis of Benzothiadiazole and Its Derivatives-based Covalent Organic Frameworks using "Two-in-One" Monomers for Photocatalytic Hydrogen Generation

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Chemicals

4,9-dibromonaphtho[2,3-*c*][1,2,5]thiadiazole, 4,9-dibromonaphtho[2,3-*c*][1,2,5]selenadiazole and 4,7-dibromobenzo[*c*][1,2,5]selenadiazole were purchased from Jilin Chinese Academy of Science-Yanshen Technology Co., Ltd. 4(4-formylphenyl)boronic acid, 1,3,5-tribromobenzene, neopentyl glycol, *p*-toluenesulfonic acid, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All the other chemicals were obtained from the chemical supplies and used without further purification.

Characterization

Nuclear magnetic resonance (NMR) data were collected using 400 MHz JEOL JNM-ECZ400S. Powder X-ray diffraction (PXRD) patterns were recorded using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The UV-vis spectra were recorded on Shimadzu UV-3600 spectrophotometer. The photoluminescent spectra were measured on FLS1000 spectrofluorometer (Edinburgh Instruments). The TGA data were 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. Scanning electron micrographs (SEM) images were taken using a JEOL JSM-IT800 (SHL). Fourier transform infrared (FT-IR) spectra were recorded from 400 to 4000 cm^{-1} on a PerkinElmer spectrometer. Transmission electron microscope (TEM) was performed by Thermo Scientific Talos F200S. Gas chromatographic (GC) analysis was carried out on a CEAULIGHT GC-7920 instrument equipped with a thermal conductivity detector (TCD) using high pure nitrogen as the carrier gas.

Photoelectrochemical measurements

All the photoelectrochemical measurement were obtained on an electrochemical workstation (CHI660E, CH Instrument Corp, Shanghai). 5 mg of HIAM-0011/HIAM-0012/HIAM-0013/HIAM-0014 was added to a mixed solution of 1 mL ethanol and 10 μL 5 wt% Nafion. The mixture was then ultrasonicated for two hours to get homogeneous suspension. The 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 and 1800 Hz with amplitude of 5 mV.

Stability testing of COFs

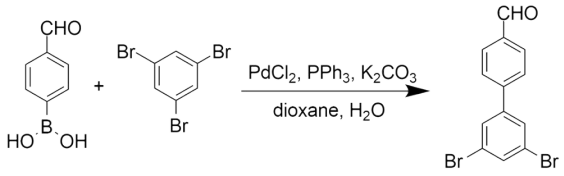
Samples of HIAM-0011/HIAM-0012/HIAM-0013/HIAM-0014 (~ 5 mg) was suspended in 1 mL HCl solution (pH = 2, pH = 4), NaOH solution (pH = 10, pH = 12), water, or boiling water. These suspensions were tightly sealed in 5 mL glass vials and stored at room temperature for 24 hours (boiling water needs to be heated at 100 °C). The samples were then washed with ethanol and dried under 100 ° C vacuum. The resultant samples were used for PXRD and IR analysis.

Photocatalytic hydrogen evolution

5 mg HIAM-0011/HIAM-0012/HIAM-0013/HIAM-0014 was well dispersed in 50 mL deionized water containing 0.1 M ascorbic acid (AA) as the sacrificial agent. Then 0.01 M chloroplatinic acid (H_2PtCl_6) aqueous solution (1 wt% Pt) was introduced into the reaction

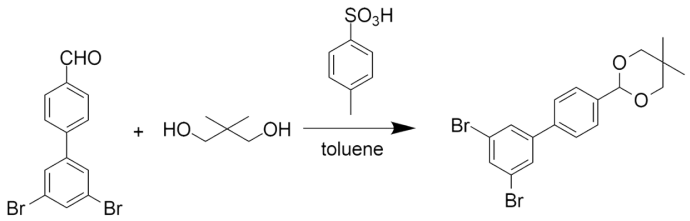
system. The reaction solution was evacuated under vacuum to completely discharge air. After that the reaction system was irradiated vertically under 300 W xenon lamp with λ＞420 nm cut-off filter. For long-term and recycled experiment, 5 mg HIAM-0011 was adopted with 50 mL deionized water containing 0.1 M AA (1 wt% Pt) and radiated under 300 W xenon lamp with λ＞420 nm cut-off filter.

Synthesis of 3,5-bromo-[1,1'-biphenyl]-4'-formaldehyde



(4-formylphenyl)boronic acid (100.0 mmol, 14.99 g), 1,3,5-tribromobenzene (200.0 mmol, 62.96 g), $PdCl_2$ (5.0 mmol, 0.88 g), PPh_3 (10.0 mmol, 2.62 g) and K_2CO_3 (200.0 mmol, 27.64 g) were added into one 1000 mL flask containing 400 mL dioxane and 100 mL water. The mixture was degassed four times and stirred at 105 ℃ overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography to offer 3',5'-dibromo-[1,1'-biphenyl]-4-carbaldehyde as a white solid (12.0 g, yield: 35.3 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.06 (1H), 7.87 (2H), 7.70 (2H), 7.69 (2H), 7.68(1H).

Synthesis of 2-(3',5'-dibromo-[1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3-dioxane



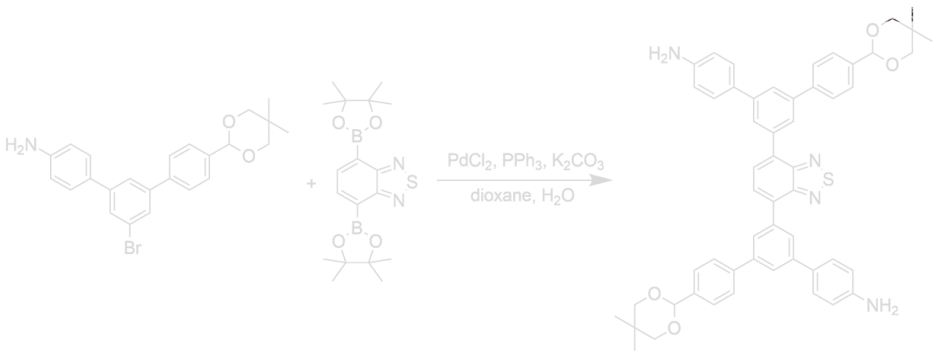
3',5'-dibromo-[1,1'-biphenyl]-4-carbaldehyde (6.00 g, 17.65 mmol), neopentyl glycol (5.51 g, 52.94 mmol) and *p*-toluenesulfonic acid (0.30 g, 1.76 mmol) were added to a 250 mL of two-neck round-bottom flask. The reaction mixture was firstly deoxygenized with argon for three times, and then 130 mL of toluene was added. The reaction mixture was heated 150 ℃ overnight under nitrogen. After cooling down to room temperature, the organic solvent was

removed under reduced pressure. The crude product was purified by silica gel column chromatography to offer 2-(3',5'-dibromo-[1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3-dioxane as a white solid (7.52 g, yield: 99.0 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 (3H), 7.58 (2H), 7.52 (2H), 5.43 (1H), 3.79 (2H), 3.66 (2H), 1.30 (3H), 0.81 (3H).

Synthesis of 5'-bromo-4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine

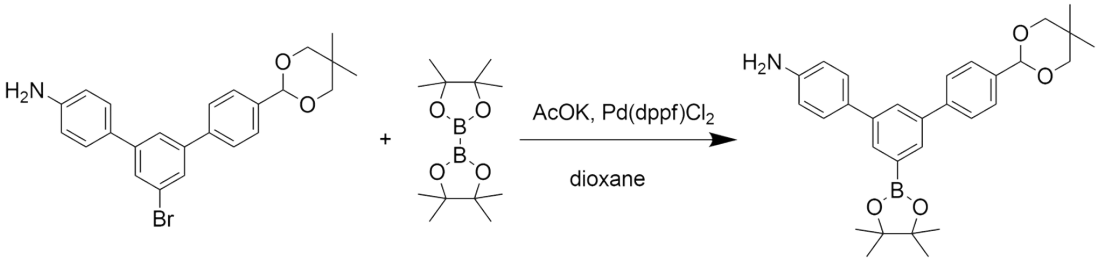
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (8.82 mmol, 1.93 g), 2-(3',5'-dibromo-[1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3-dioxane (17.65 mmol, 7.52 g), $PdCl_2$ (0.40 mmol, 0.07 g), PPh_3 (0.80 mmol, 0.22 g) and K_2CO_3 (16.0 mmol, 2.20 g) were added into one 250 mL flask containing 120 mL dioxane and 30 mL water. The mixture was degassed four times and stirred at 105 ℃ for 2 hours under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al_2O_3 column chromatography to offer 5'-bromo-4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine as a yellow solid (2.59 g, yield: 67.0 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (2H), 7.58 (5H), 7.41 (2H), 6.75 (2H), 5.41 (1H), 3.79 (2H), 3.67 (2H), 1.31 (3H), 0.81 (3H).

Synthesis of 5',5''''-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine) (BTA)



5'-bromo-4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine (6.0 mmol, 2.62 g), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (2.5 mmol, 0.93 g), $PdCl_2$ (0.20 mmol, 0.03 g), PPh_3 (0.40 mmol, 0.11 g) and K_2CO_3 (8.0 mmol, 1.10 g) were added into one 250 mL flask containing 80mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 105 ℃ overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al_2O_3 column chromatography to offer 5',5""-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine) as a yellow solid (1.90 g, yield: 89.6 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (4H), 7.90 (2H), 7.81 (2H), 7.76 (4H), 7.68 (4H), 7.55 (4H), 6.80 (4H), 5.44 (2H), 3.80 (4H), 3.68 (4H), 1.32 (6H), 0.77 (6H).

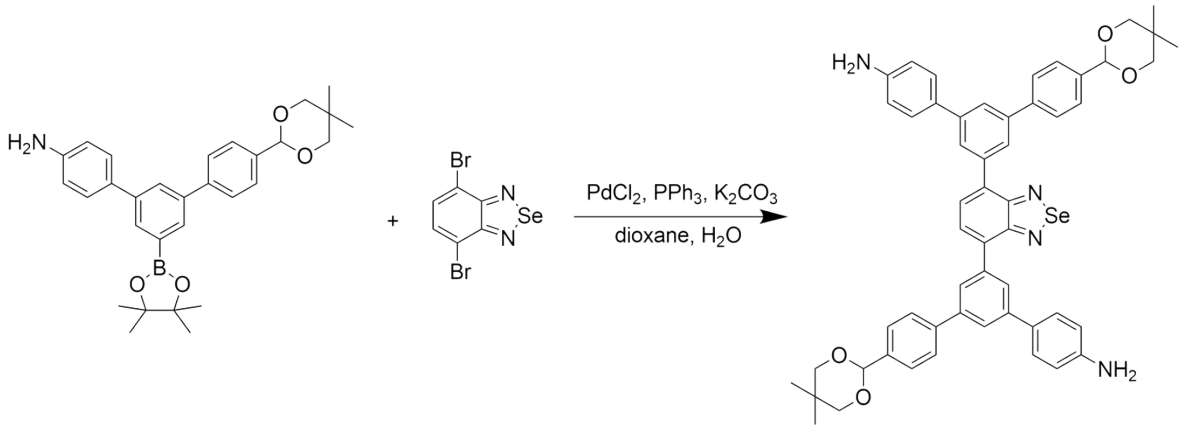
Synthesis of Synthesis of 4''-(5,5-dimethyl-1,3-dioxan-2-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4-amine



5'-bromo-4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine (8.67 mmol, 3.80

g), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (10.40 mmol, 2.64 g), Pd(dppf)Cl_2 (0.43 mmol, 0.32 g) and AcOK (26.00 mmol, 2.55 g) were added into one 250 mL flask containing 60 mL dioxane. The mixture was degassed four times and stirred at 105 ℃ overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al_2O_3 column chromatography to offer 4''-(5,5-dimethyl-1,3-dioxan-2-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4-amine as a yellow solid (3.20 g, yield: 76.05 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (2H), 7.82 (1H), 7.68 (2H), 7.56 (2H), 7.48 (2H), 6.76 (2H), 5.44 (1H), 3.79 (2H), 3.67 (2H), 1.36 (12H), 1.31 (3H), 0.81 (3H).

Synthesis of 5',5''''-(benzo[c][1,2,5]selenadiazole-4,7-diyl)bis(4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine) (BSA)



4''-(5,5-dimethyl-1,3-dioxan-2-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4-amine (3.30 mmol, 1.60 g), 4,7-dibromobenzo[*c*][1,2,5]selenadiazole (1.50 mmol, 0.51 g), $PdCl_2$ (0.20 mmol, 35.0 mg), PPh_3 (0.40 mmol, 0.11 g) and K_2CO_3 (8.0 mmol, 1.10 g) were added into one 250 mL flask containing 80 mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 105 ℃ for 42 hours under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude

product was purified by Al_2O_3 column chromatography to offer 5',5""-(benzo[*c*][1,2,5]selenadiazole-4,7-diyl)bis(4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine) as a green solid (0.56 g, yield: 41.6 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.02 (4H), 7.92 (2H), 7.82 (4H), 7.79 (2H), 7.60 (4H), 7.57 (4H), 6.67 (4H), 5.45 (2H), 3.67 (4H), 3.62 (4H), 1.18 (6H), 0.73 (6H).

Synthesis of 5',5""-(naphtho[2,3-c][1,2,5]thiadiazole-4,9-diyl)bis(4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine) (NTA)

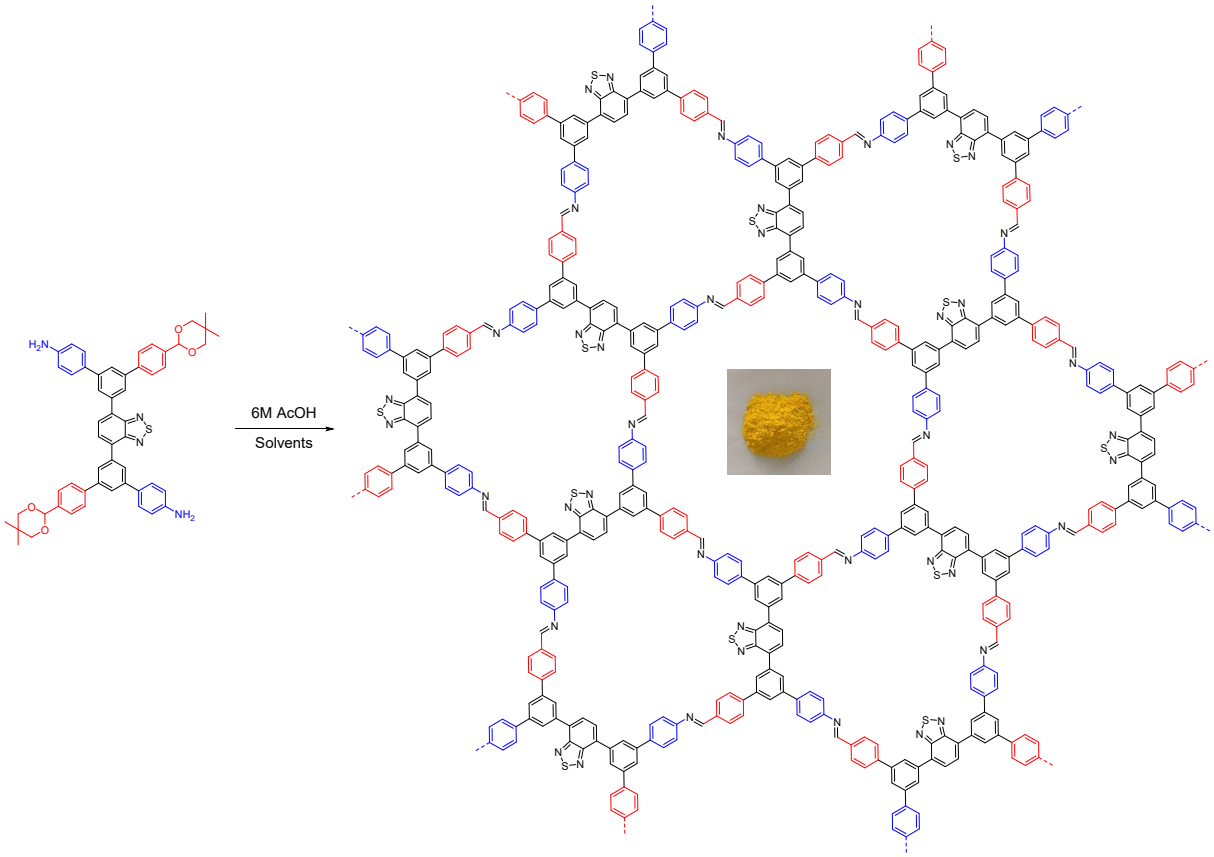
4"-(5,5-dimethyl-1,3-dioxan-2-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1"-terphenyl]-4-amine (6.00 mmol, 2.91 g), 4,9-dibromonaphtho[2,3-*c*][1,2,5]thiadiazole (2.50 mmol, 0.86 g), $PdCl_2$ (0.40 mmol, 0.07 g), PPh_3 (0.80 mmol, 0.21 g) and K_2CO_3 (16.0 mmol, 2.2 g) were added into one 250 mL flask containing 80 mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 105 ℃ for 42 hours under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al_2O_3 column chromatography to offer 5',5""-(naphtho[2,3-*c*][1,2,5]thiadiazole-4,9-diyl)bis(4"-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1"-terphenyl]-4-amine) as a tawny solid (1.93 g, yield: 85.7 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.05 (2H), 7.96 (2H), 7.81 (4H), 7.74 (4H), 7.52 (4H), 7.50 (4H), 7.46 (2H), 6.65 (4H), 5.44 (2H),

3.66 (4H), 3.62 (4H), 1.16 (6H), 0.72 (6H).

Synthesis of 5',5''''-(naphtho[2,3-c][1,2,5]selenadiazole-4,9-diyl)bis(4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine) (NSA)

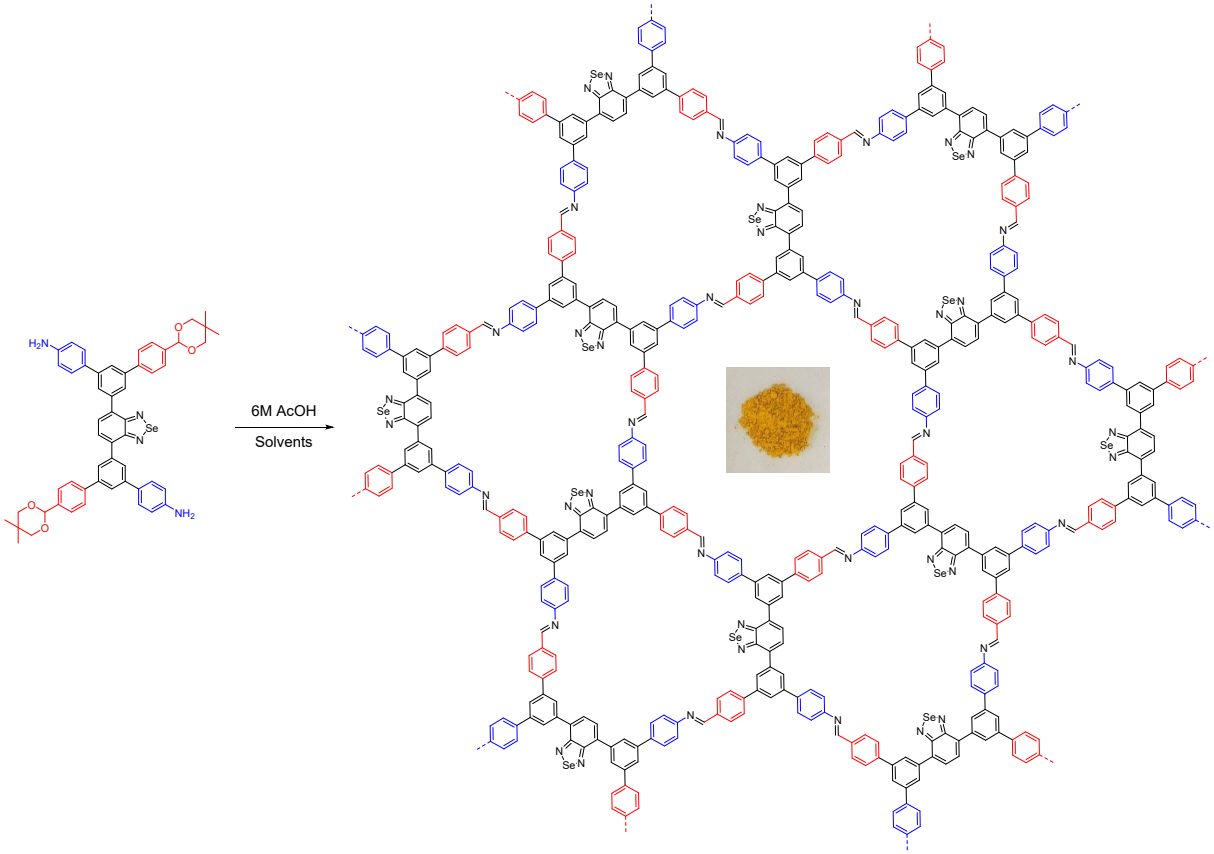
4''-(5,5-dimethyl-1,3-dioxan-2-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1':3',1''-terphenyl]-4-amine (6.00 mmol, 2.91 g), 4,9-dibromonaphtho[2,3-*c*][1,2,5]selenadiazole (2.50 mmol, 0.98 g), $PdCl_2$ (0.40 mmol, 0.07 g), PPh_3 (0.80 mmol, 0.21 g) and K_2CO_3 (16.0 mmol, 2.2 g) were added into one 250 mL flask containing 80 mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 105 ℃ for 42 hours under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al_2O_3 column chromatography to offer 5',5''''-(naphtho[2,3-*c*][1,2,5]selenadiazole-4,9-diyl)bis(4''-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1':3',1''-terphenyl]-4-amine) as a rose pink solid (1.57 g, yield: 66.2 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.92 (2H), 7.84 (2H), 7.78 (4H), 7.68 (4H), 7.51 (4H), 7.49 (4H), 7.29 (2H), 6.64 (4H), 5.43 (2H), 3.66 (4H), 3.62 (4H), 1.16 (6H), 0.68 (6H).

Synthesis of HIAM-0011



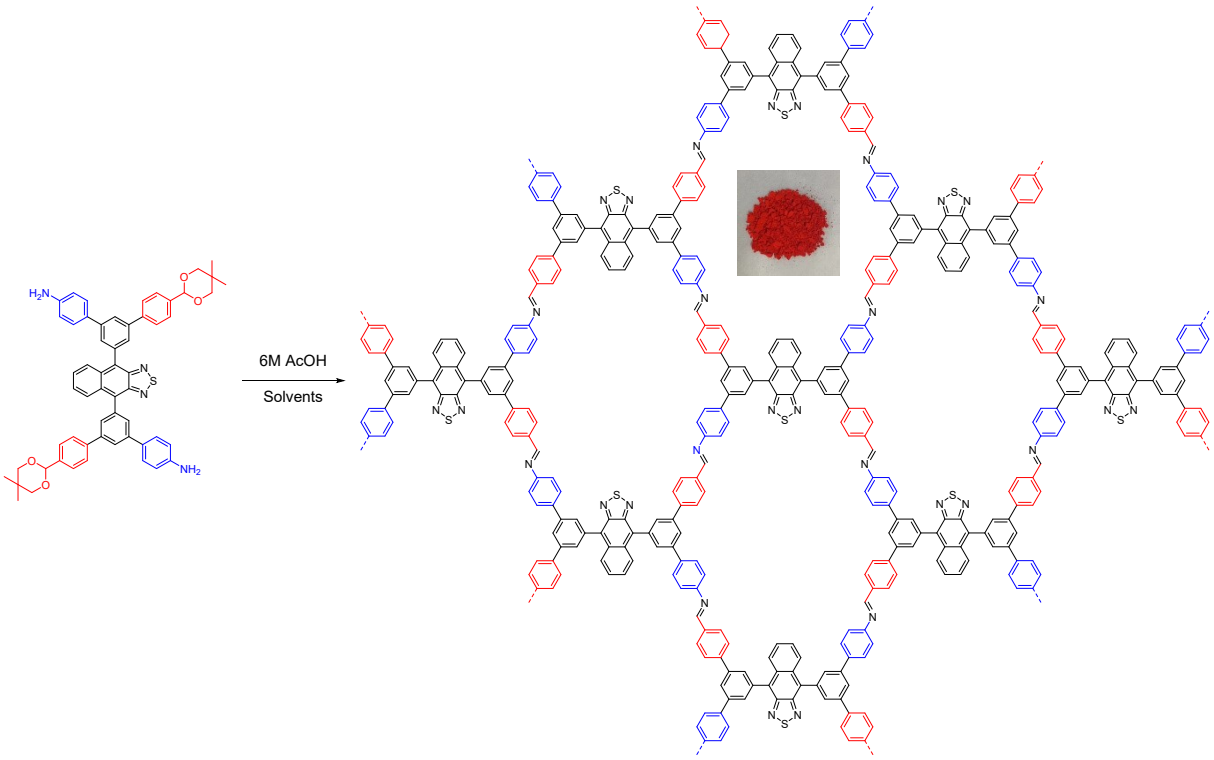
BTA (29.8 mg, 0.035 mmol) was added to a Pyrex tube (10 mL). *n*-butyl alcohol (*n*-BuOH, 1 mL), or methanol (MeOH, 1 mL) or EtOH (1 mL) or 1-pentanol (1 mL) or benzyl alcohol (BnOH, 1 mL) or tetrahydrofuran (THF, 1 mL) or mesitylene (1 mL) or *o*-dichlorobenzene (*o*-DCB, 1 mL) was added separately in eight tubes. The mixture was sonicated for 3 minutes followed by addition of 6 M acetic acid (0.3 mL). The tube was degassed through three freeze-pump-thaw cycles and then heated at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with *N,N*-dimethylformamide (DMF) and EtOH. The yellow solid was Soxhlet extracted in EtOH for 24 h and dried under 100 °C vacuum to afford HIAM-0011.

Synthesis of HIAM-0012



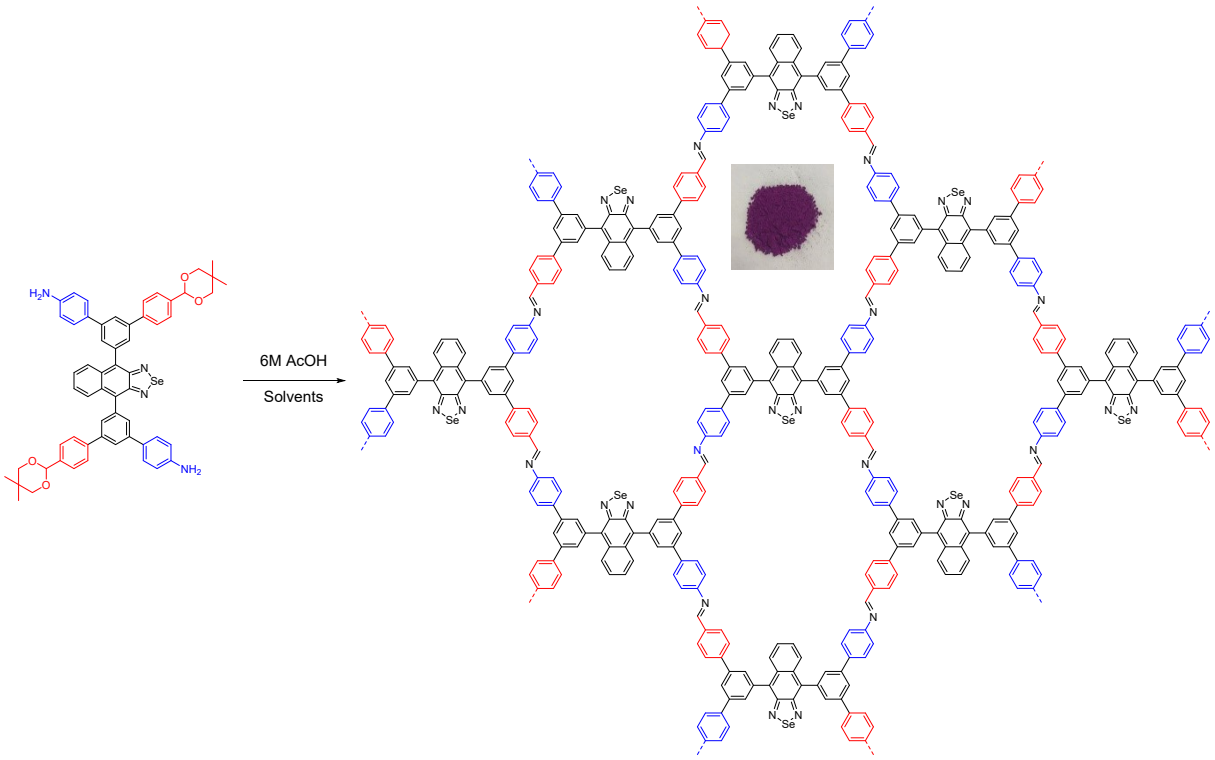
A Pyrex tube (10 mL) containing BSA (31.5 mg, 0.035 mmol) and *n*-BuOH (1 mL) was sonicated for 3 min. Subsequently, 0.3 mL of acetic acid (6 M) was added. The tube was degassed through three freeze-pump-thaw cycles and then heated at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with DMF and EtOH. The yellow solid was Soxhlet extracted in EtOH for 24 h and dried under 100 °C vacuum to afford HIAM-0012.

Synthesis of HIAM-0013



A Pyrex tube (10 mL) containing NTA (31.5 mg, 0.035 mmol) and *n*-BuOH (1 mL) was sonicated for 3 min. Subsequently, 0.3 mL of acetic acid (6 M) was added. The tube was degassed through three freeze-pump-thaw cycles and then heated at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with DMF and EtOH. The red solid was Soxhlet extracted in EtOH for 24 h and dried under 100 °C vacuum to afford HIAM-0013.

Synthesis of HIAM-0014



A Pyrex tube (10 mL) containing NSA (33.2 mg, 0.035 mmol) and *n*-BuOH (1 mL) was sonicated for 3 min. Subsequently, 0.3 mL of acetic acid (6 M) was added. The tube was degassed through three freeze-pump-thaw cycles and then heated at 120 °C for 72 h. After cooling to room temperature, the precipitate was collected by filtration and washed with DMF and EtOH. The purple solid was Soxhlet extracted in EtOH for 24 h and dried under 100 °C vacuum to afford HIAM-0014.

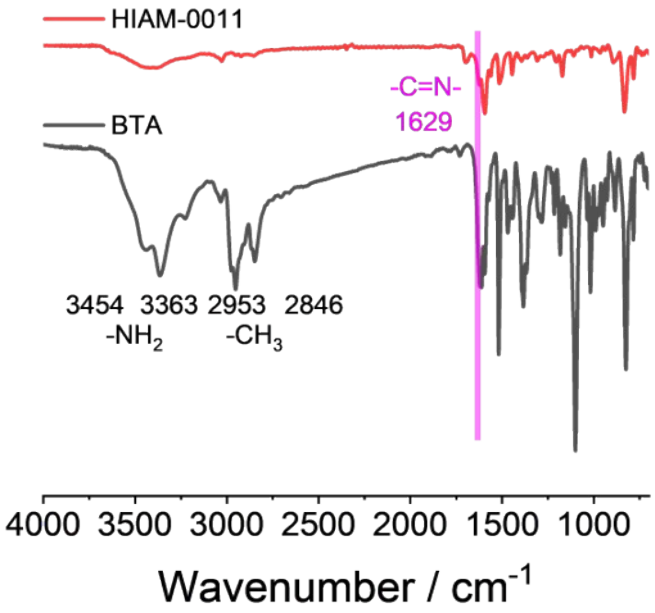


Figure S1. FT-IR spectra of HIAM-0011 synthesized in *n*-BuOH.

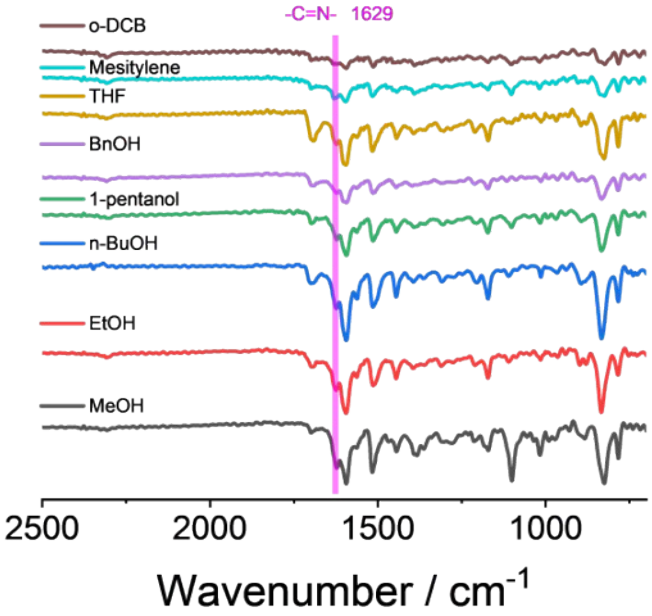


Figure S2. FT-IR spectra of HIAM-0011 synthesized using different organic solvents.

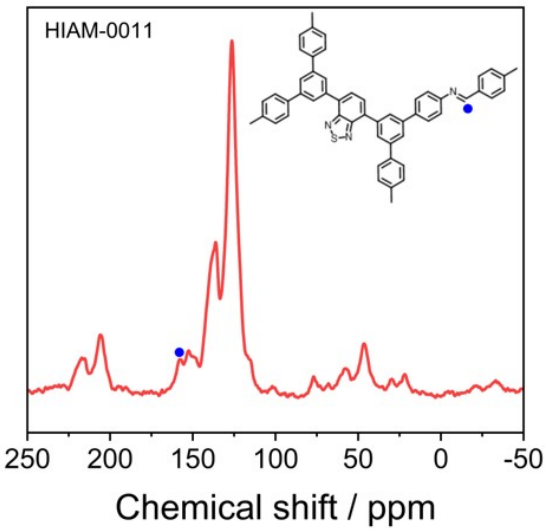


Figure S3. Solid-state ^{13}C NMR spectra of HIAM-0011.

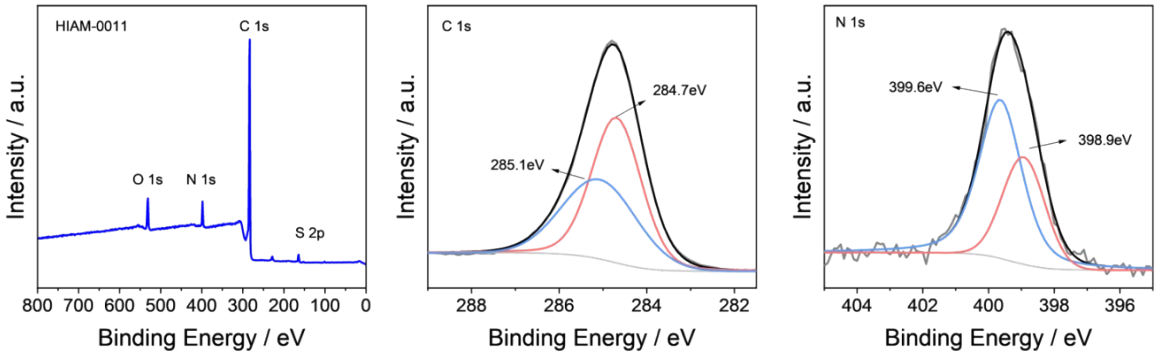


Figure S4. The XPS spectra of HIAM-0011.

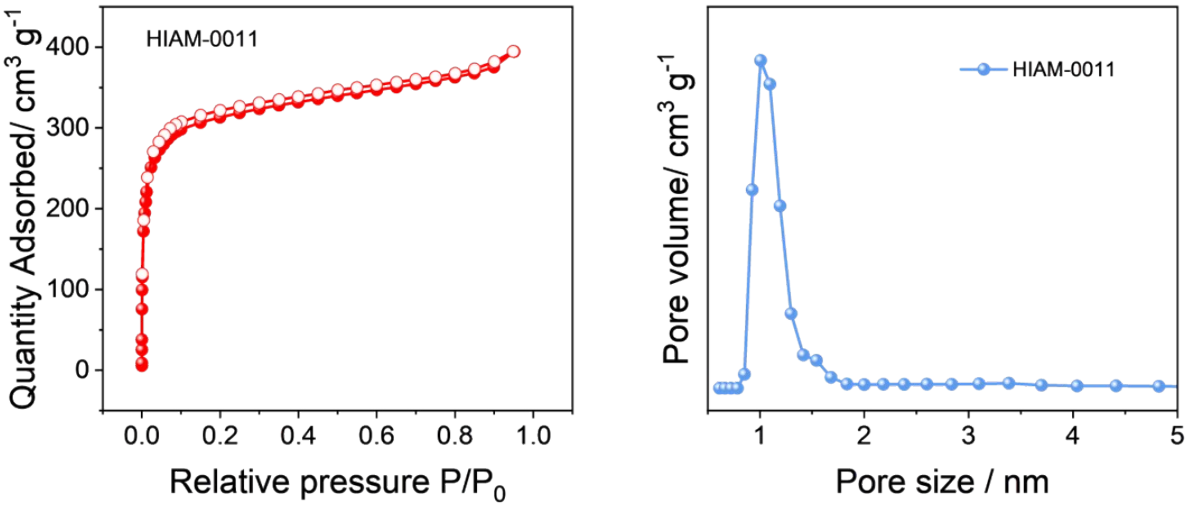


Figure S5. N_2 adsorption-desorption isotherms of HIAM-0011 at 77 K (left) and the corresponding pore size distribution (right).

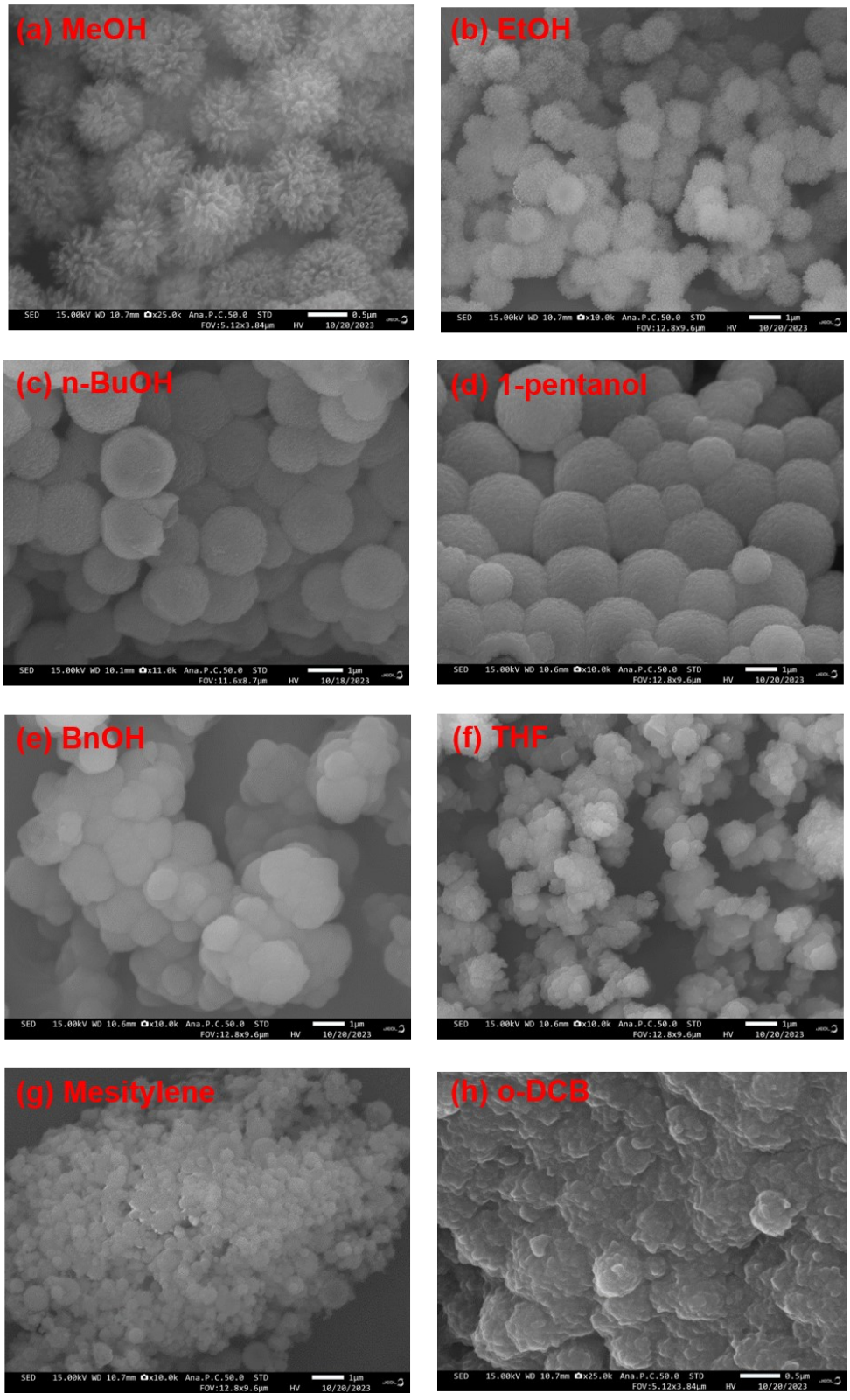


Figure S6. The SEM images of HIAM-0011 synthesized using different organic solvents.

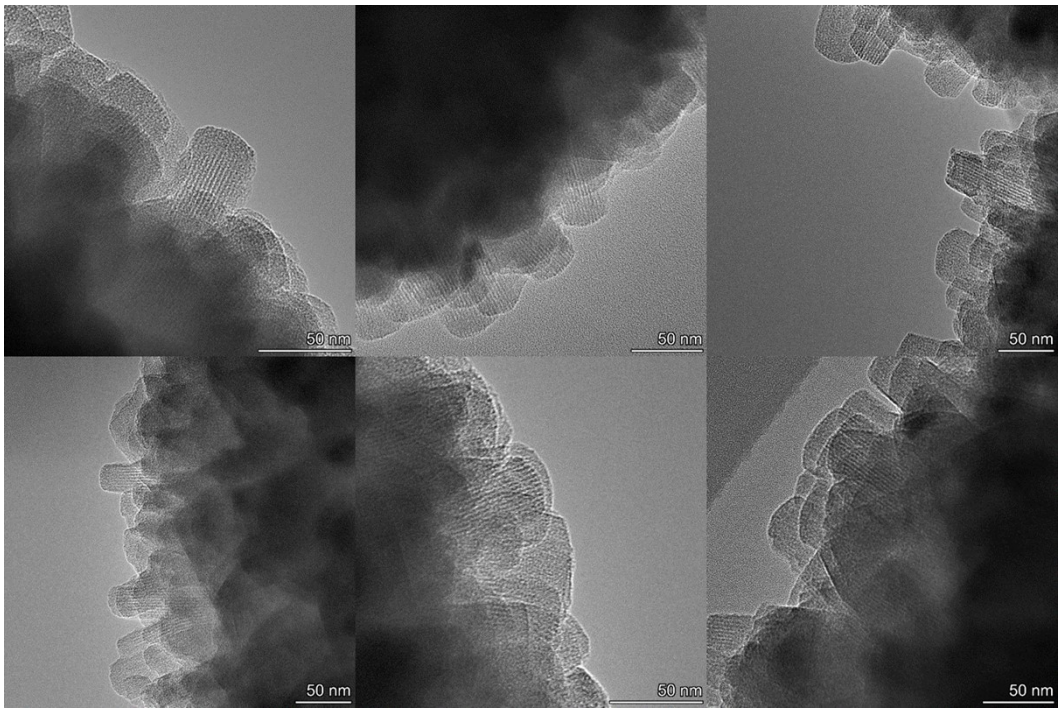


Figure S7. TEM images of HIAM-0011 synthesized in *n*-BuOH.

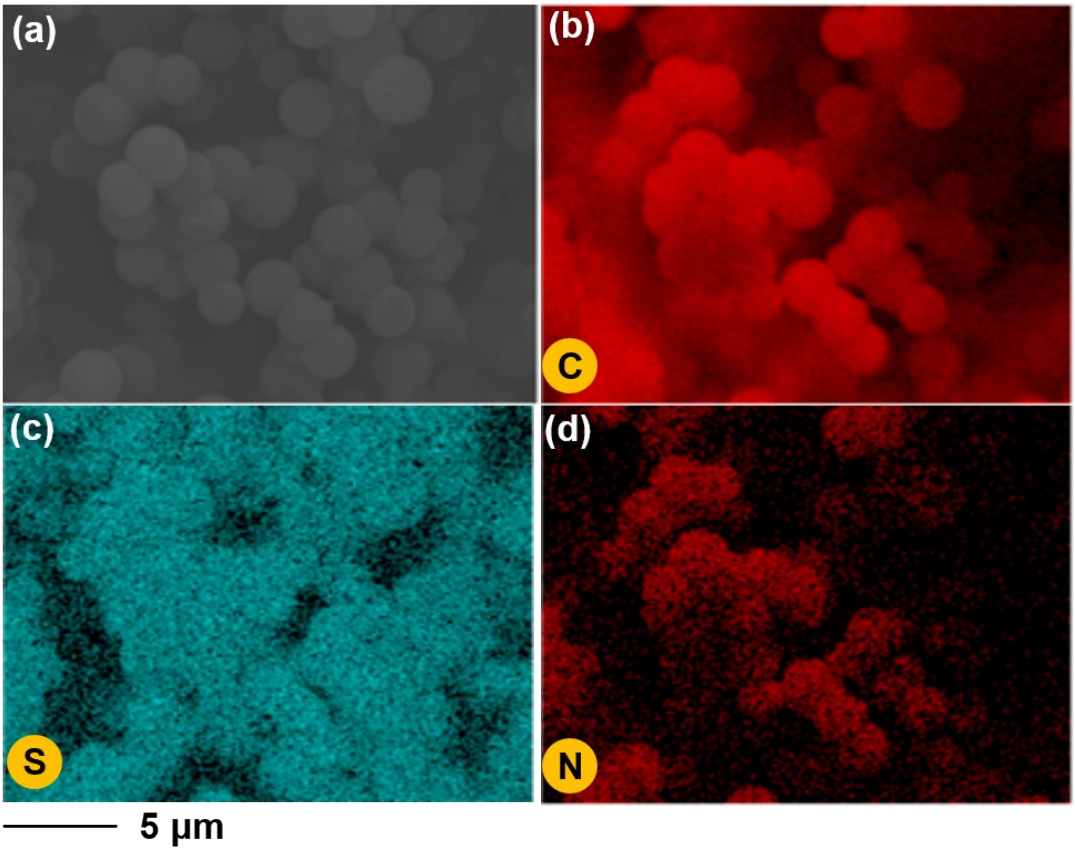


Figure S8. Energy dispersive X-ray analysis of HIAM-0011.

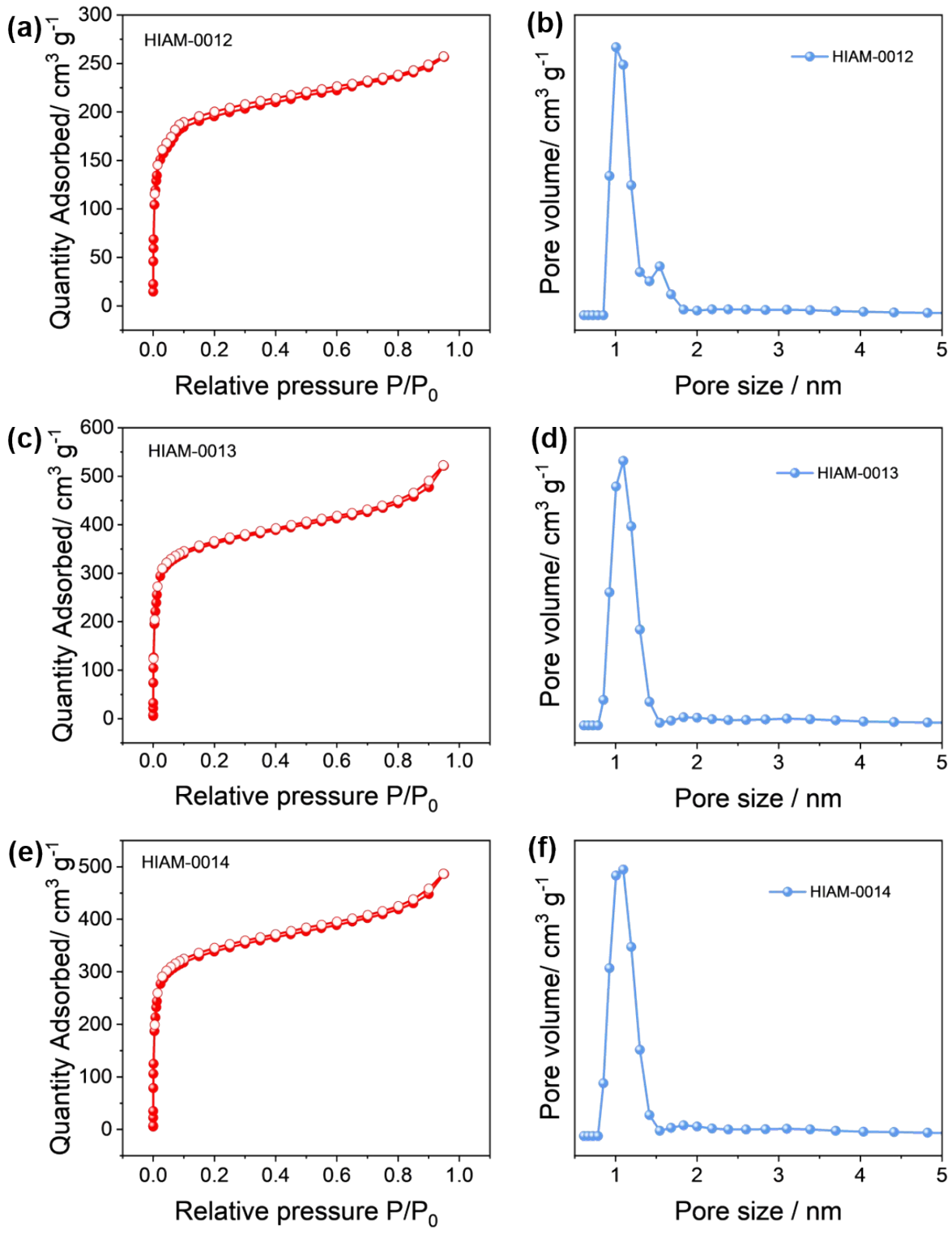


Figure S9. N_2 adsorption-desorption isotherms at 77 K and the corresponding pore size distribution of HIAM-0012 (a-b), HIAM-0013 (c-d) and HIAM-0014 (e-f).

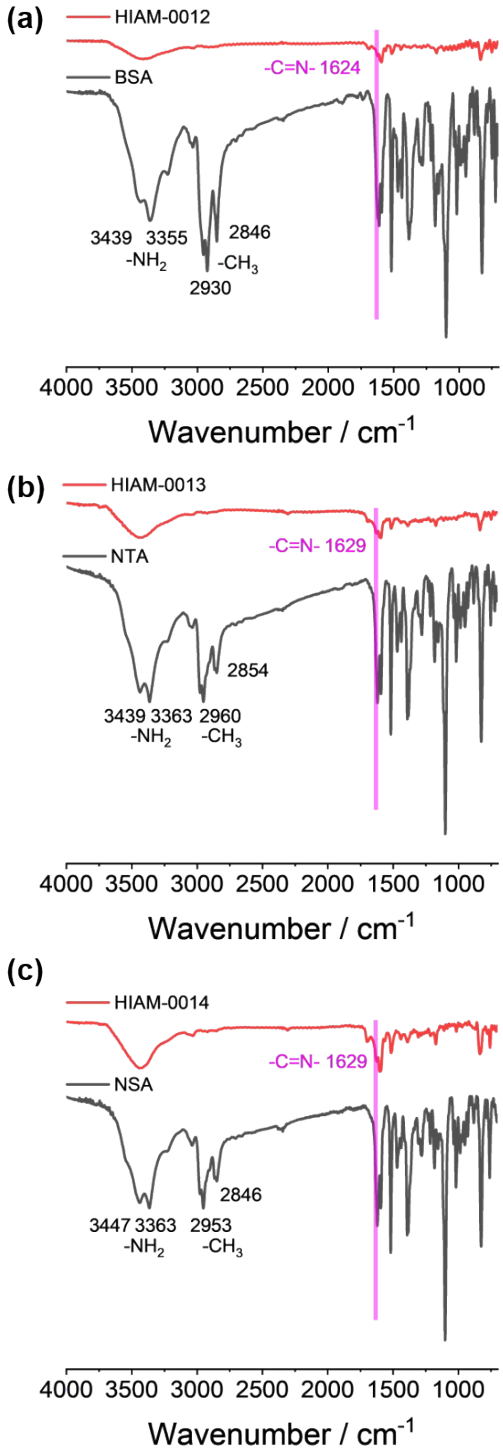


Figure S10. The FT-IR spectra of HIAM-0012 (a), HIAM-0013 (b) and HIAM-0013 (c) and the corresponding organic building units.

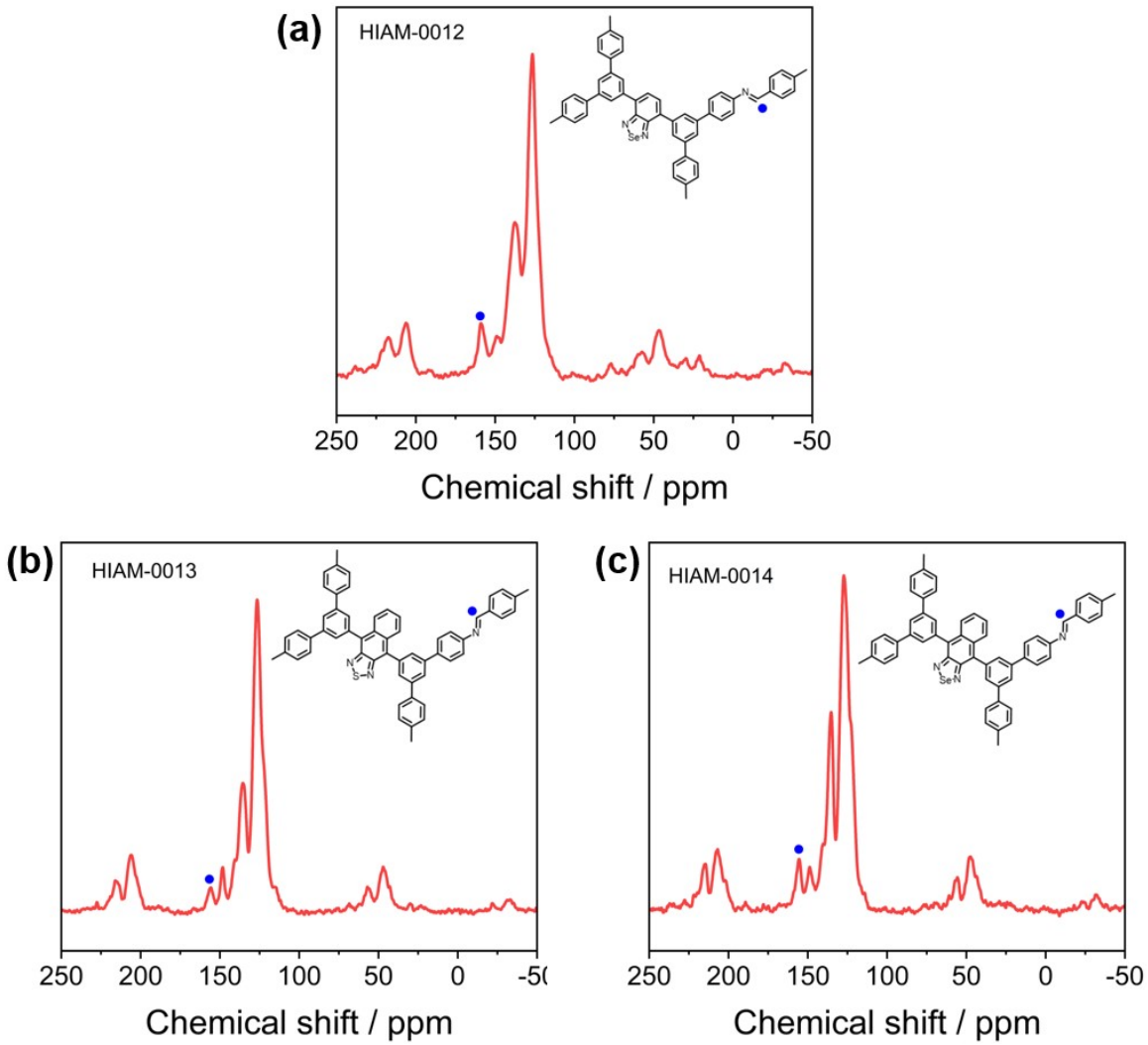


Figure S11. Solid-state ^{13}C NMR spectra of HIAM-0012 (a), HIAM-0013 (b) and HIAM-0014 (c).

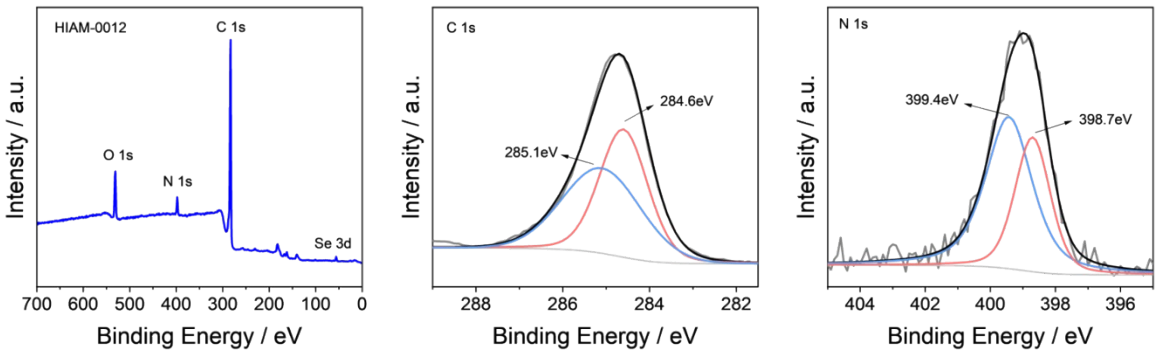


Figure S12. The XPS spectra of HIAM-0012.

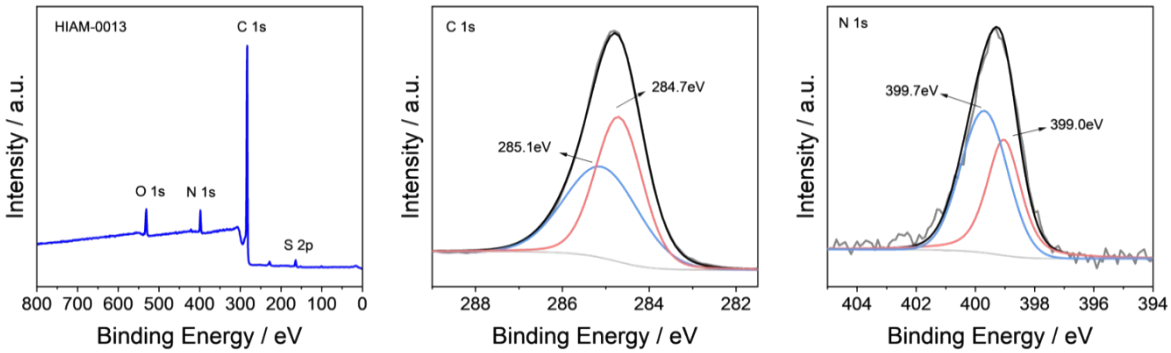


Figure S13. The XPS spectra of HIAM-0013.

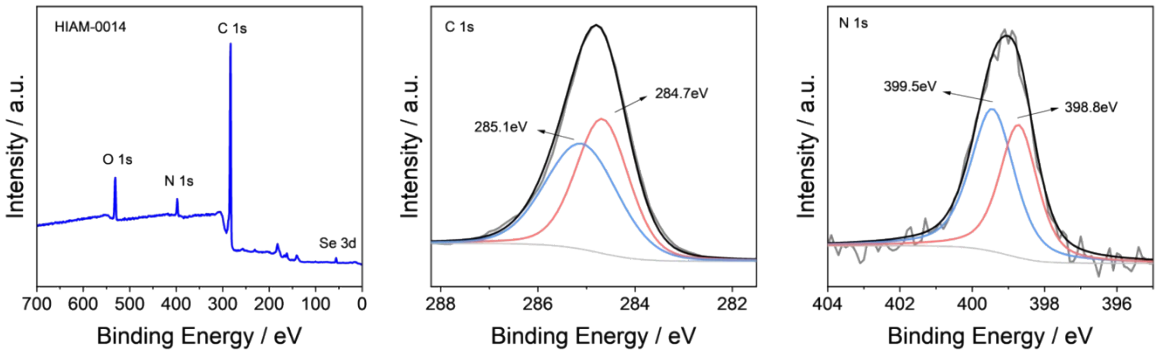


Figure S14. The XPS spectra of HIAM-0014.

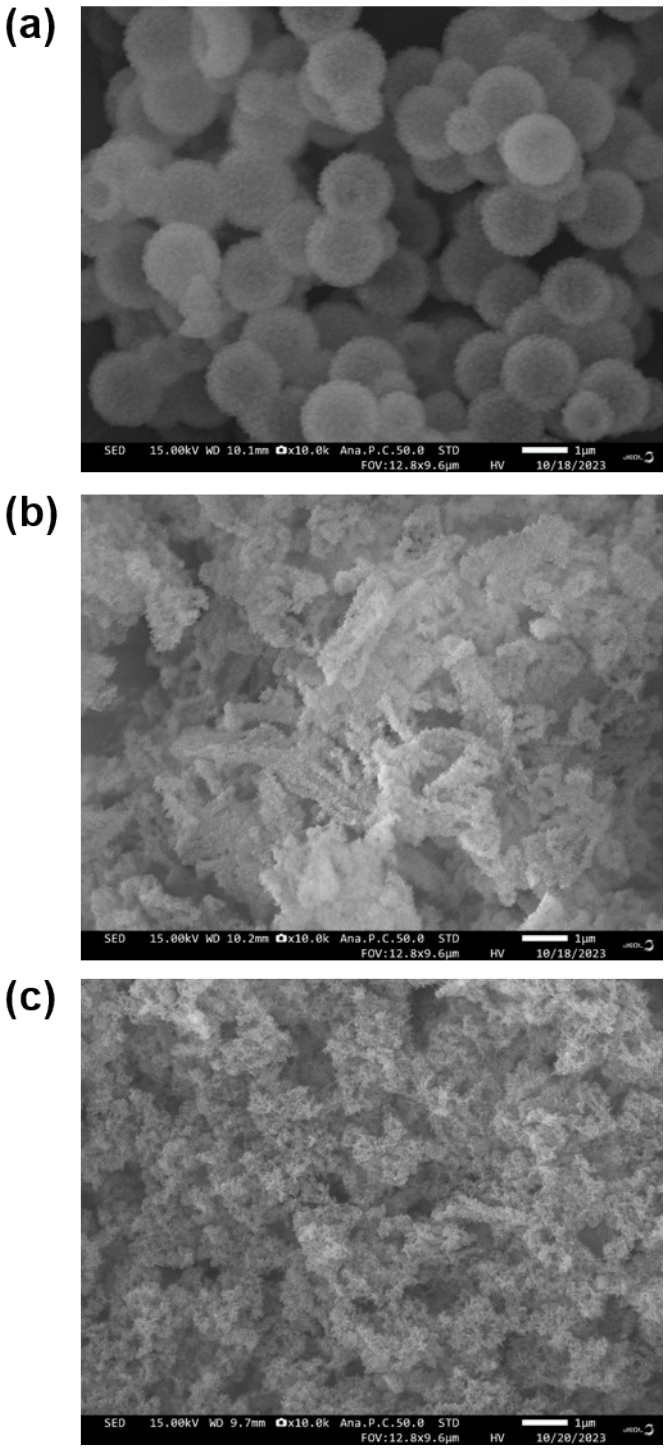


Figure S15. The SEM images of HIAM-0012 (a), HIAM-0013 (b) and HIAM-0014 (c).

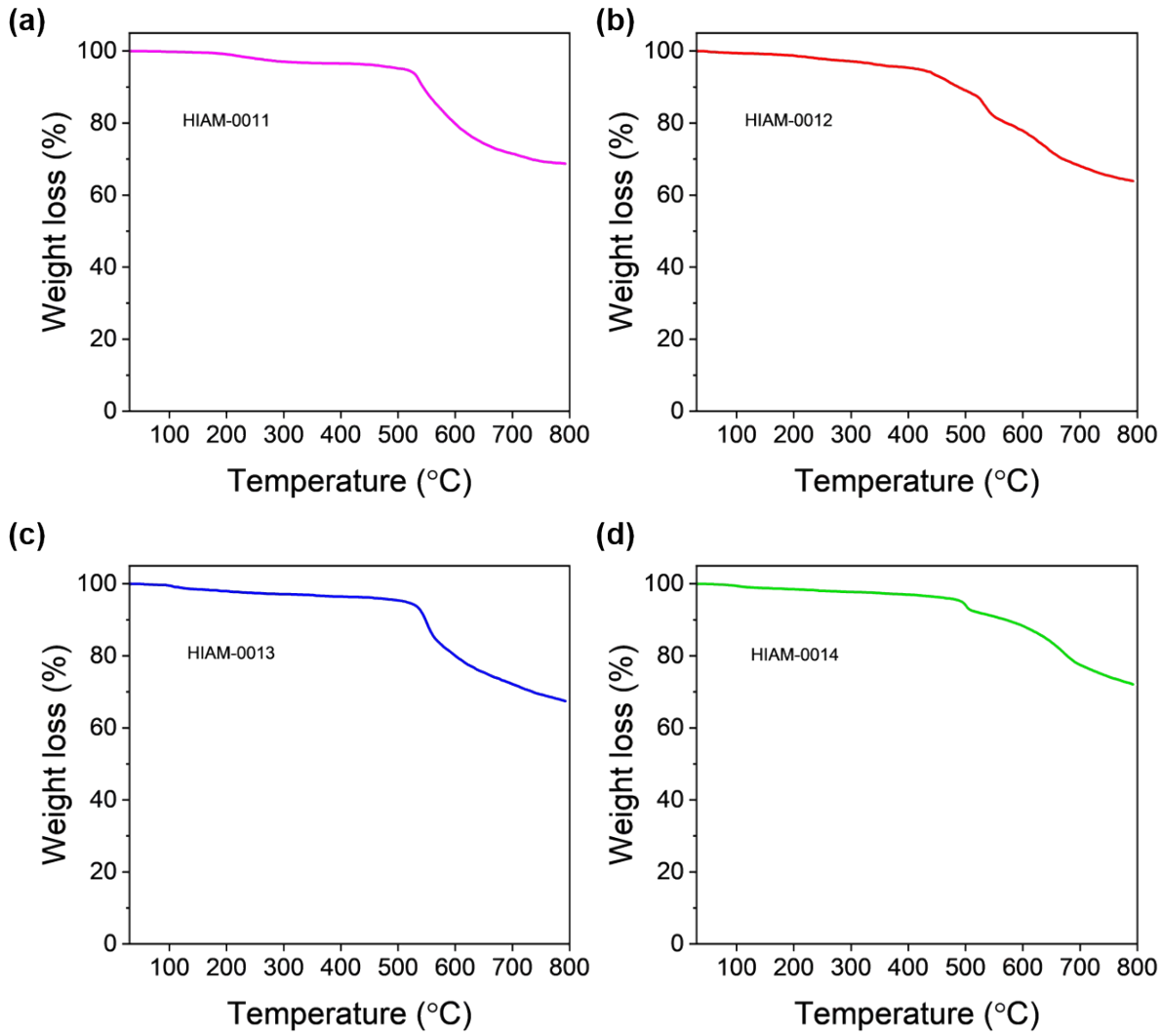


Figure S16. TGA curves of HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d).

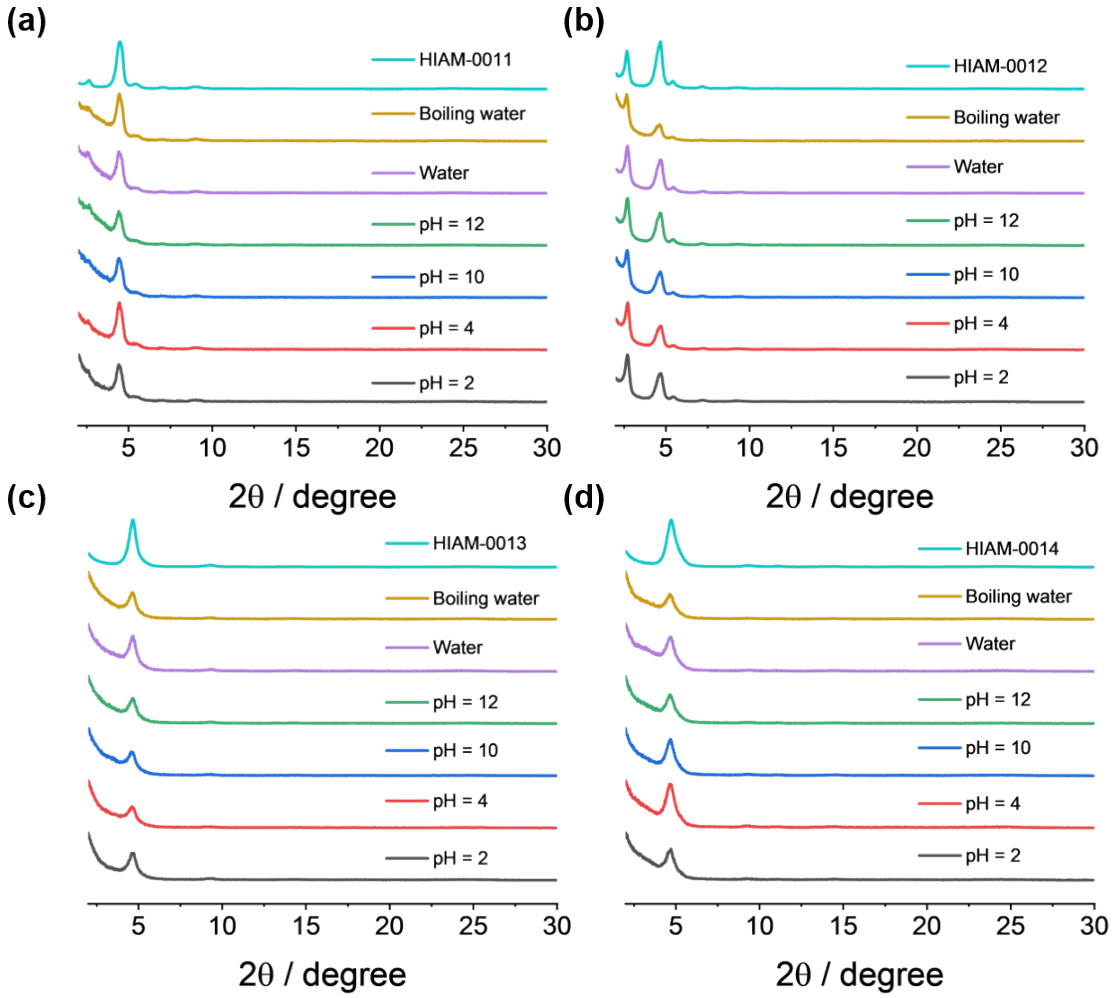


Figure S17. The PXRD patterns of HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d) after treatment under various conditions for 24 hours.

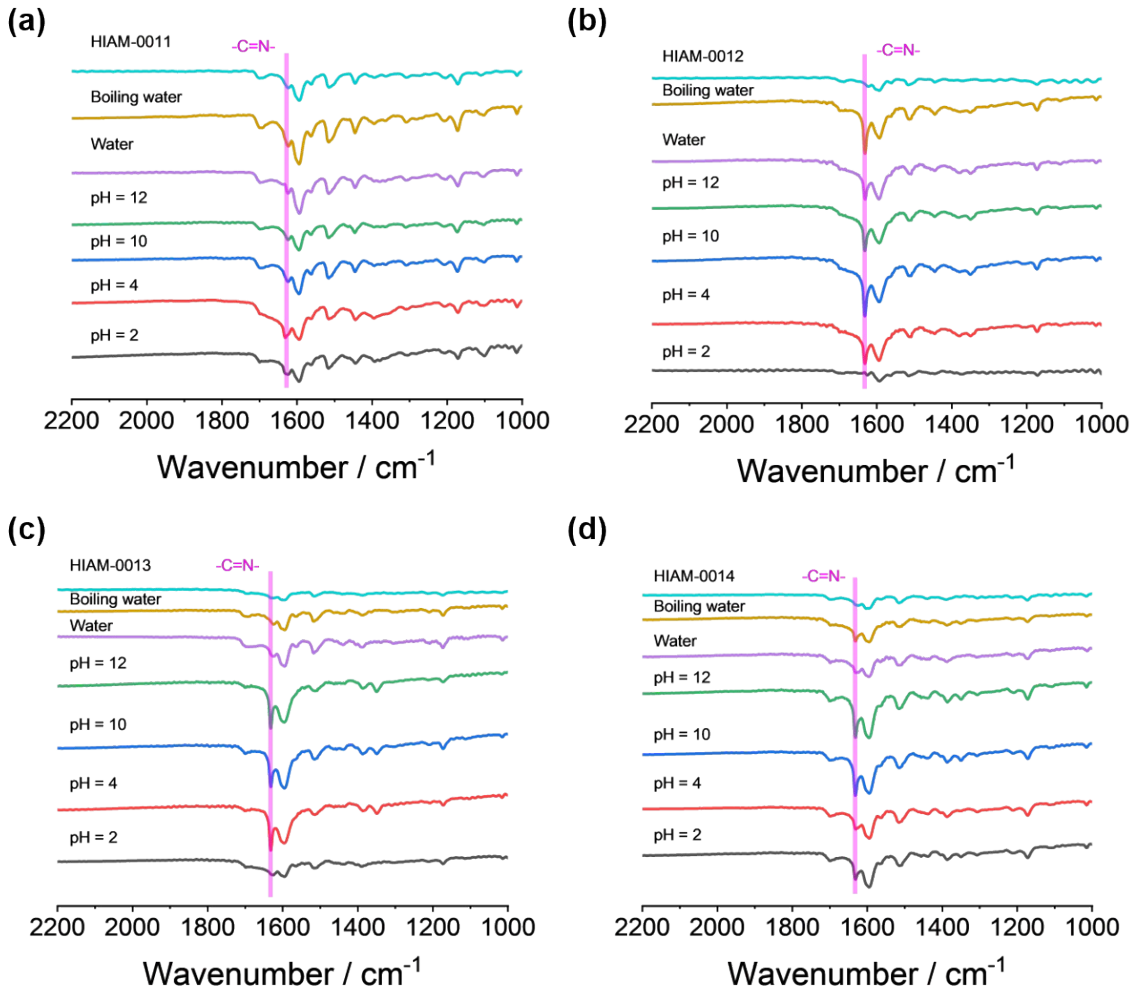


Figure S18. The FT-IR spectra of HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d) after treatment under various conditions for 24 hours.

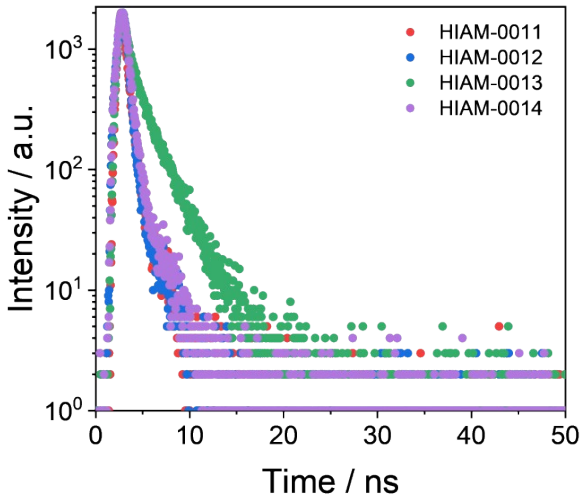


Figure S19. The transient fluorescence decay profiles of HIAM-0011, HIAM-0012, HIAM-0013 and HIAM-0014.

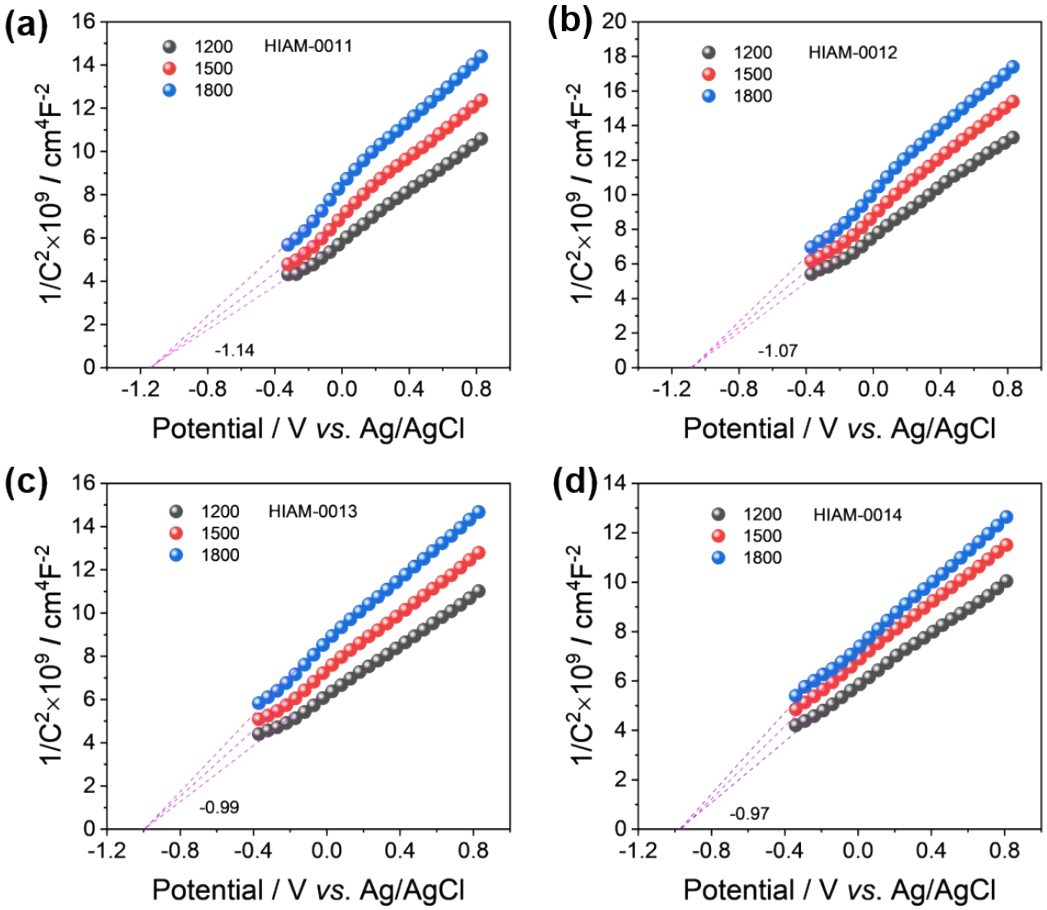


Figure S20. Mott-Schottky plots of HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d).

Figure S21. The photocurrent responses of HIAM-0011, HIAM-0012, HIAM-0013 and HIAM-0014.

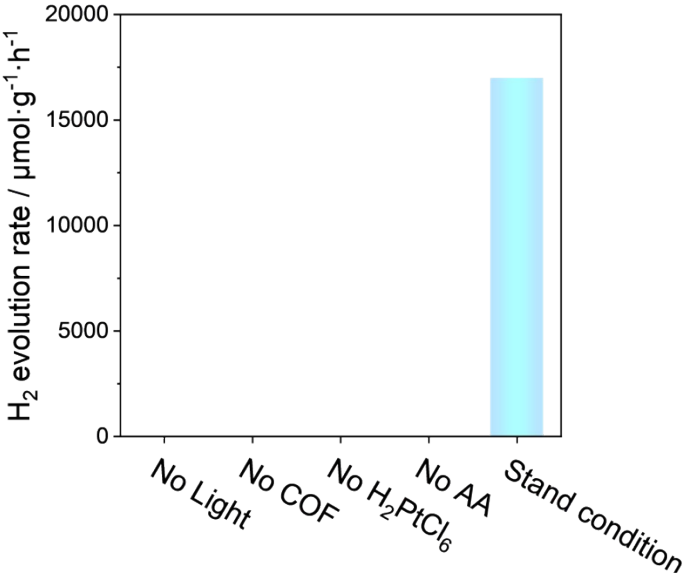


Figure S22. The control experiments of photocatalytic H_2 evolution using HIAM-0011 as the photocatalysts.

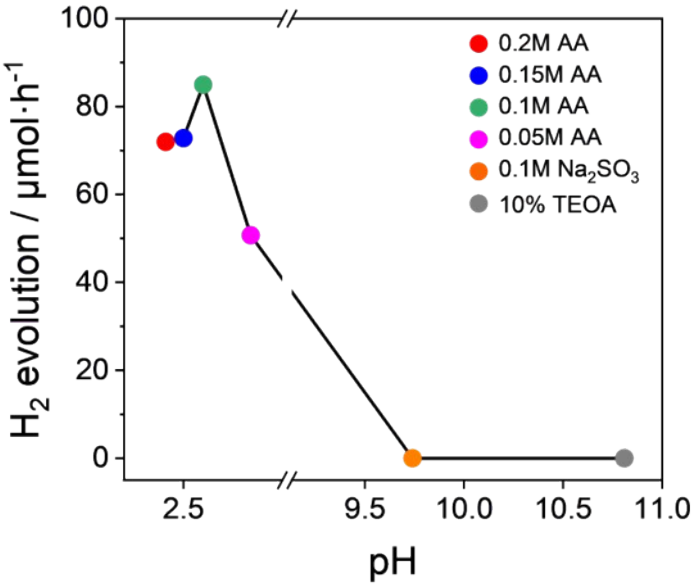


Figure S23. The pH and various sacrificial agents effect on the photocatalytic hydrogen generation of HIAM-0011.

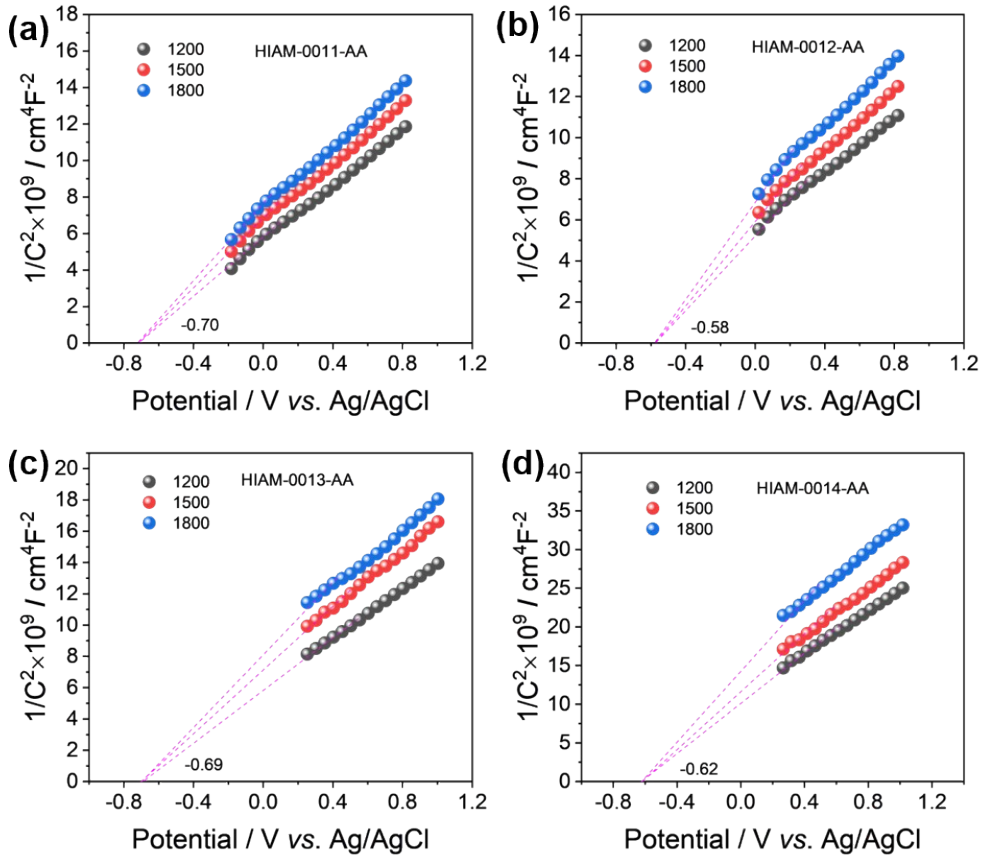


Figure S24. Mott-Schottky plots of protonated HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d) using AA.

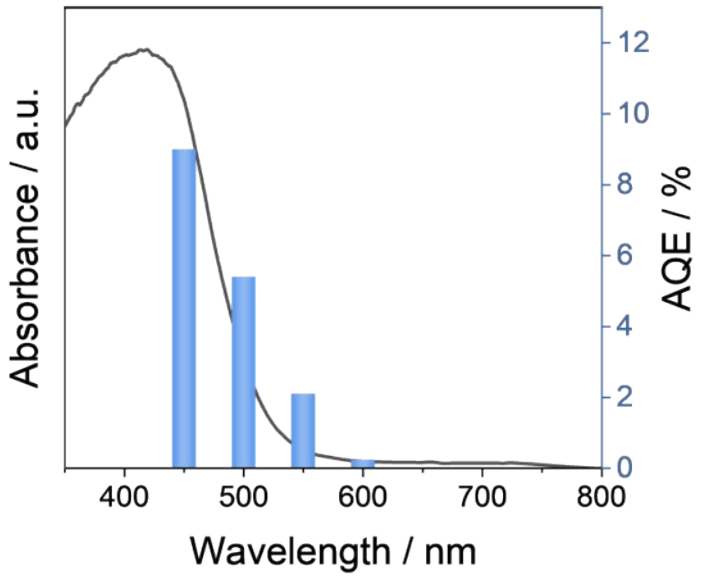


Figure S25. Wavelength dependent apparent quantum efficiency for photocatalytic hydrogen generation over HIAM-0011 under monochromatic light irradiation.

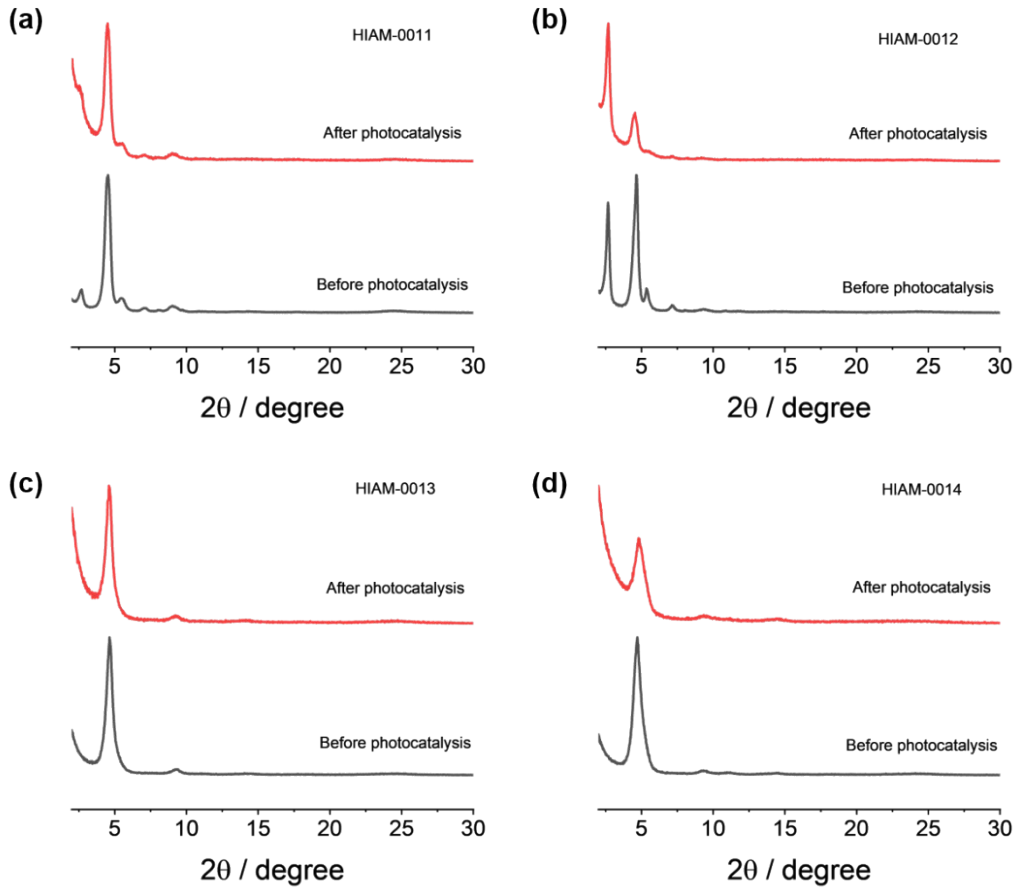


Figure S26. The PXRD patterns of HIAM-0011 (a), HIAM-0012 (b), HIAM-0013 (c) and HIAM-0014 (d) before and after photocatalytic experiments.

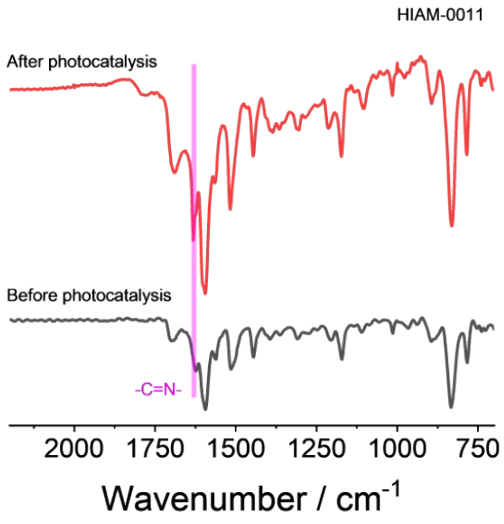


Figure S27. The FT-IR spectra of HIAM-0011 before and after photocatalytic measurement.

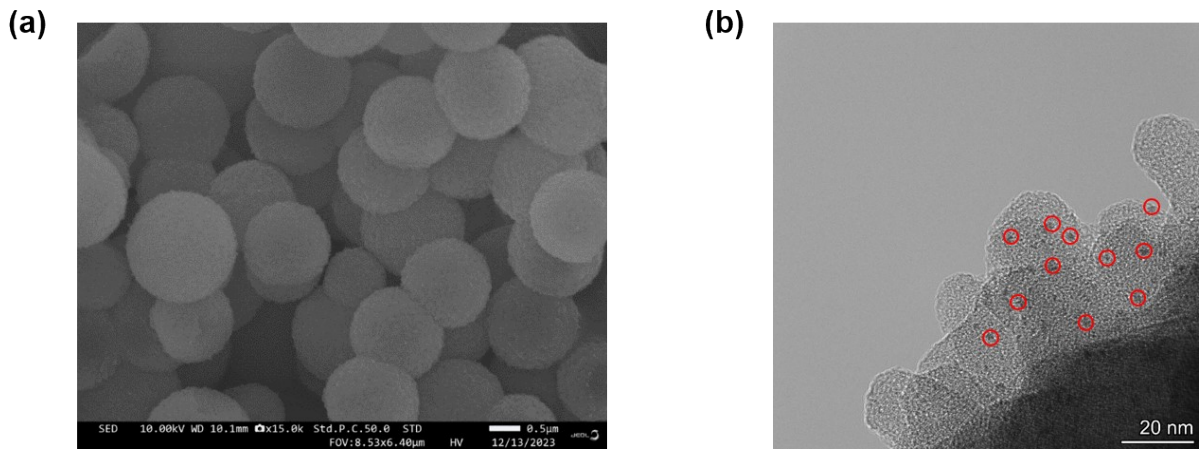


Figure S28. The SEM (a) and TEM (b) images of HIAM-0011 after photocatalytic measurement.

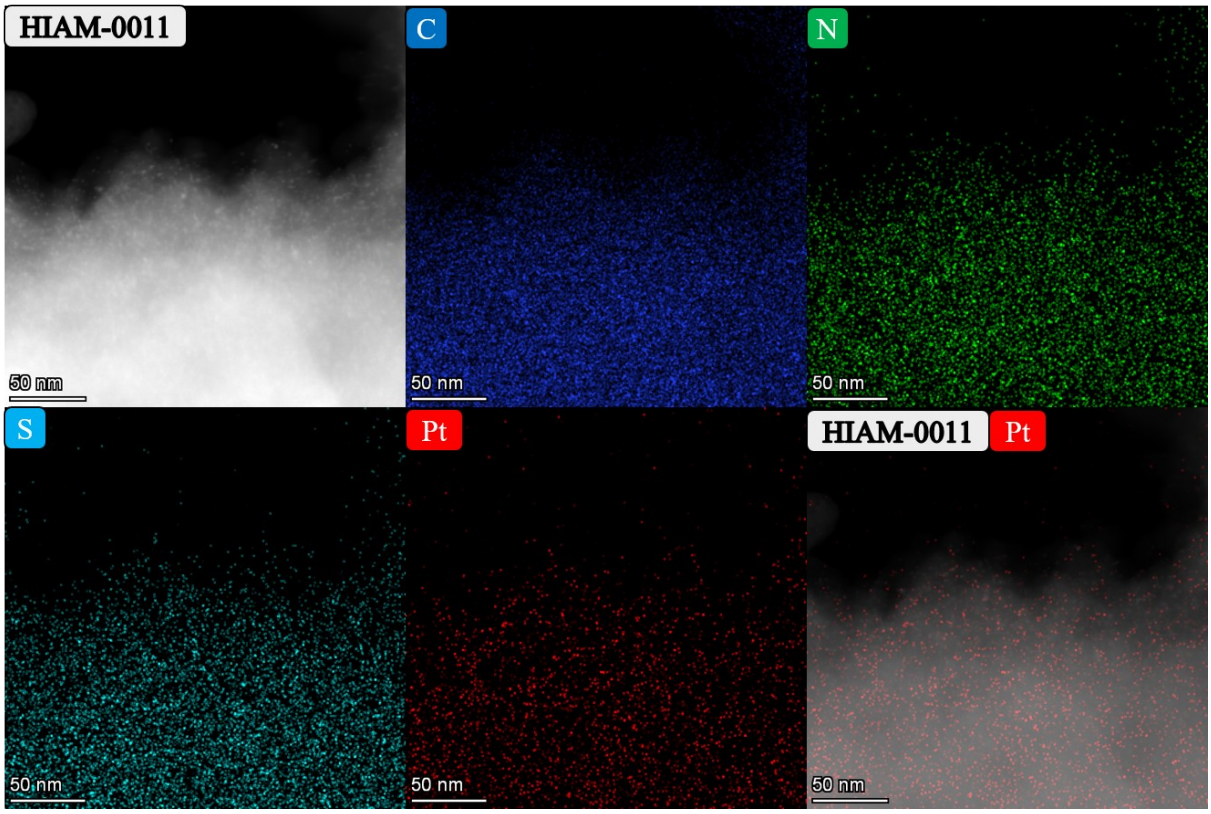


Figure S29. Energy dispersive X-ray analysis of HIAM-0011 after photocatalytic measurement.

Table S1. Atomic coordinates of AA-stacking mode of the simulated HIAM-0011.

Space group: *pm* a = 39.5903 Å, b = 3.4526 Å, and c = 39.6079 Å. α = γ = 90°, and β = 120°			
Atom	**x**	**y**	**z**
C1	0.62107	-0.00000	0.58958
C2	0.58493	-0.00000	0.55389
C3	0.55061	-0.00000	0.55632
C4	0.55077	-0.00000	0.59181
C5	0.58743	-0.00000	0.62607
C6	0.62347	-0.00000	0.62663
C7	0.51278	-0.00000	0.59309
C8	0.58234	-0.00000	0.51403
C9	0.66308	-0.00000	0.66524
C10	0.66731	-0.00000	0.70313
C11	0.70319	-0.00000	0.73720
C12	0.73941	-0.00000	0.73772
C13	0.73555	-0.00000	0.70013
C14	0.69899	-0.00000	0.66540
C15	0.77996	-0.00000	0.77523
C16	0.78423	-0.00000	0.81293
C17	0.82040	-0.00000	0.84777
C18	0.85393	-0.00000	0.84427
C19	0.85263	-0.00000	0.80803
C20	0.81517	-0.00000	0.77390
C21	0.89045	-0.00000	0.80650
C22	0.82311	-0.00000	0.88768
C23	0.92758	-0.00000	0.84113
C24	0.96226	-0.00000	0.84025
C25	0.96193	-0.00000	0.80470
C26	0.92578	-0.00000	0.77010
C27	0.89066	-0.00000	0.77080
C28	0.61599	-0.00000	0.50994
C29	0.61287	-0.00000	0.47298
C30	0.57612	-0.00000	0.43889
C31	0.54282	-0.00000	0.44234
C32	0.54567	-0.00000	0.47877

C33	0.47576	-0.00000	0.55844
C34	0.44103	-0.00000	0.55936
C35	0.44143	-0.00000	0.59502
C36	0.47742	-0.00000	0.62951
C37	0.51240	-0.00000	0.62881
C38	0.78935	-0.00000	0.89173
C39	0.79222	-0.00000	0.92840
C40	0.82875	-0.00000	0.96244
C41	0.86231	-0.00000	0.95929
C42	0.85972	-0.00000	0.92290
N43	0.99728	-0.00000	0.80253
C44	0.83324	-0.00000	1.00167
C45	0.57072	-0.00000	0.39917
N46	0.63791	-0.00000	0.71074
S47	0.65242	-0.00000	0.75852
N48	0.69904	-0.00000	0.76878
C49	0.59216	-0.00000	0.17024
C50	0.55631	-0.00000	0.17005
C51	0.55838	-0.00000	0.20673
C52	0.59388	-0.00000	0.24247
C53	0.62832	-0.00000	0.24050
C54	0.62907	-0.00000	0.20517
C55	0.59515	-0.00000	0.28177
C56	0.51681	-0.00000	0.13205
C57	0.66768	-0.00000	0.20446
C58	0.70563	-0.00000	0.23827
C59	0.73964	-0.00000	0.23650
C60	0.73994	-0.00000	0.20071
C61	0.70230	-0.00000	0.16690
C62	0.66773	-0.00000	0.16869
C63	0.77717	-0.00000	0.19750
C64	0.81507	-0.00000	0.23089
C65	0.84958	-0.00000	0.22911
C66	0.84550	-0.00000	0.19192
C67	0.80916	-0.00000	0.15713
C68	0.77533	-0.00000	0.16070
C69	0.80738	-0.00000	0.11773
C70	0.88988	-0.00000	0.26582
C71	0.84196	-0.00000	0.11533

C72	0.84101	-0.00000	0.07984
C73	0.80544	-0.00000	0.04450
C74	0.77082	-0.00000	0.04588
C75	0.77159	-0.00000	0.08172
C76	0.51344	-0.00000	0.09455
C77	0.47682	-0.00000	0.06000
C78	0.44230	-0.00000	0.06165
C79	0.44506	-0.00000	0.09817
C80	0.48118	-0.00000	0.13246
C81	0.56051	-0.00000	0.28400
C82	0.56150	-0.00000	0.31975
C83	0.59723	-0.00000	0.35520
C84	0.63167	-0.00000	0.35378
C85	0.63090	-0.00000	0.31808
C86	0.89482	-0.00000	0.30393
C87	0.93191	-0.00000	0.33730
C88	0.96540	-0.00000	0.33395
C89	0.96139	-0.00000	0.29697
C90	0.92461	-0.00000	0.26362
N91	0.80336	-0.00000	1.00704
C92	1.00490	-0.00000	0.36822
N93	0.60001	-0.00000	0.39298
C94	0.40276	-0.00000	0.02659
N95	0.71334	-0.00000	0.27535
S96	0.76122	-0.00000	0.30872
N97	0.77136	-0.00000	0.27232
C98	0.22997	-0.00000	0.61657
C99	0.22980	-0.00000	0.58074
C100	0.19314	-0.00000	0.54630
C101	0.15762	-0.00000	0.54597
C102	0.15960	-0.00000	0.58235
C103	0.19509	-0.00000	0.61854
C104	0.11866	-0.00000	0.50767
C105	0.26721	-0.00000	0.57856
C106	0.19601	-0.00000	0.65792
C107	0.16228	-0.00000	0.66201
C108	0.16421	-0.00000	0.69784
C109	0.20011	-0.00000	0.73406
C110	0.23385	-0.00000	0.73025

C111	0.23188	-0.00000	0.69382
C112	0.20350	-0.00000	0.77461
C113	0.17021	-0.00000	0.77907
C114	0.17197	-0.00000	0.81536
C115	0.20939	-0.00000	0.84881
C116	0.24423	-0.00000	0.84722
C117	0.24035	-0.00000	0.80967
C118	0.28414	-0.00000	0.88475
C119	0.13481	-0.00000	0.81822
C120	0.28738	-0.00000	0.92208
C121	0.32342	-0.00000	0.95652
C122	0.35853	-0.00000	0.95581
C123	0.35620	-0.00000	0.91938
C124	0.31989	-0.00000	0.88452
C125	0.30493	-0.00000	0.61244
C126	0.33896	-0.00000	0.60970
C127	0.33642	-0.00000	0.57313
C128	0.29971	-0.00000	0.53962
C129	0.26597	-0.00000	0.54207
C130	0.11699	-0.00000	0.47105
C131	0.08167	-0.00000	0.43600
C132	0.04611	-0.00000	0.43567
C133	0.04682	-0.00000	0.47118
C134	0.08221	-0.00000	0.50654
C135	0.09670	-0.00000	0.78459
C136	0.06298	-0.00000	0.78766
C137	0.06582	-0.00000	0.82427
C138	0.10283	-0.00000	0.85767
C139	0.13655	-0.00000	0.85487
N140	0.39659	-0.00000	0.99097
C141	0.03116	-0.00000	0.82903
N142	0.00884	-0.00000	0.40023
C143	0.37088	-0.00000	0.56812
N144	0.12516	-0.00000	0.63253
S145	0.09189	-0.00000	0.64699
N146	0.12842	-0.00000	0.69366
N147	0.40637	-0.00000	0.59760
H148	0.64726	-0.00000	0.58825
H149	0.52328	-0.00000	0.53035

H150	0.58687	-0.00000	0.65209
H151	0.76041	-0.00000	0.69604
H152	0.70027	-0.00000	0.63894
H153	0.75972	-0.00000	0.81618
H154	0.88132	-0.00000	0.87021
H155	0.81367	-0.00000	0.74632
H156	0.93174	-0.00000	0.87007
H157	0.98900	-0.00000	0.86806
H158	0.92475	-0.00000	0.74226
H159	0.86424	-0.00000	0.74281
H160	0.64518	-0.00000	0.53470
H161	0.63924	-0.00000	0.47113
H162	0.51403	-0.00000	0.41647
H163	0.51793	-0.00000	0.47743
H164	0.47196	-0.00000	0.52962
H165	0.41426	-0.00000	0.53158
H166	0.47843	-0.00000	0.65735
H167	0.53840	-0.00000	0.65707
H168	0.75998	-0.00000	0.86740
H169	0.76573	-0.00000	0.93004
H170	0.89099	-0.00000	0.98530
H171	0.88736	-0.00000	0.92397
H172	0.86276	-0.00000	1.02592
H173	0.54103	-0.00000	0.37514
H174	0.59104	-0.00000	0.14288
H175	0.53217	-0.00000	0.20766
H176	0.65440	-0.00000	0.26721
H177	0.69796	-0.00000	0.13787
H178	0.64132	-0.00000	0.14078
H179	0.81869	-0.00000	0.25888
H180	0.87113	-0.00000	0.19024
H181	0.74767	-0.00000	0.13458
H182	0.87101	-0.00000	0.14006
H183	0.86886	-0.00000	0.08115
H184	0.74296	-0.00000	0.01894
H185	0.74366	-0.00000	0.08015
H186	0.53849	-0.00000	0.09072
H187	0.47557	-0.00000	0.03207
H188	0.41886	-0.00000	0.10038

H189	0.47949	-0.00000	0.15866
H190	0.53173	-0.00000	0.25872
H191	0.53378	-0.00000	0.31873
H192	0.65957	-0.00000	0.38072
H193	0.65918	-0.00000	0.32051
H194	0.87088	-0.00000	0.30947
H195	0.93429	-0.00000	0.36576
H196	0.98700	-0.00000	0.29373
H197	0.92518	-0.00000	0.23682
H198	1.02903	-0.00000	0.36285
H199	0.37872	-0.00000	0.03205
H200	0.25749	-0.00000	0.64282
H201	0.19211	-0.00000	0.51925
H202	0.13283	-0.00000	0.58151
H203	0.26295	-0.00000	0.75500
H204	0.25972	-0.00000	0.69530
H205	0.14225	-0.00000	0.75456
H206	0.21124	-0.00000	0.87634
H207	0.26632	-0.00000	0.80801
H208	0.26274	-0.00000	0.92646
H209	0.32274	-0.00000	0.98337
H210	0.38279	-0.00000	0.91793
H211	0.32099	-0.00000	0.85793
H212	0.30925	-0.00000	0.64151
H213	0.36719	-0.00000	0.63621
H214	0.29694	-0.00000	0.51095
H215	0.23964	-0.00000	0.51416
H216	0.14224	-0.00000	0.46768
H217	0.08313	-0.00000	0.40955
H218	0.01961	-0.00000	0.47148
H219	0.07952	-0.00000	0.53223
H220	0.09139	-0.00000	0.75517
H221	0.03463	-0.00000	0.76126
H222	0.10581	-0.00000	0.88640
H223	0.16340	-0.00000	0.88238
H224	0.03670	-0.00000	0.85860
H225	0.36526	-0.00000	0.53852

Table S2. Atomic coordinates of AA-stacking mode of the simulated HIAM-0012.

Space group: *pm* a = 38.9114 Å, b = 3.4684 Å, and c = 37.9836 Å. α = γ = 90°, and β = 60°			
Atom	**x**	**y**	**z**
C1	-0.51920	0.00000	-0.21986
C2	-0.51959	0.00000	-0.18389
C3	-0.55630	0.00000	-0.14959
C4	-0.59159	0.00000	-0.14964
C5	-0.58923	0.00000	-0.18606
C6	-0.55393	0.00000	-0.22201
C7	-0.63086	0.00000	-0.11185
C8	-0.48236	0.00000	-0.18141
C9	-0.55363	0.00000	-0.26108
C10	-0.58968	0.00000	-0.26433
C11	-0.58760	0.00000	-0.30217
C12	-0.54928	0.00000	-0.33947
C13	-0.51778	0.00000	-0.33457
C14	-0.51993	0.00000	-0.29581
C15	-0.54513	0.00000	-0.38029
C16	-0.57823	0.00000	-0.38486
C17	-0.57676	0.00000	-0.42084
C18	-0.53973	0.00000	-0.45409
C19	-0.50490	0.00000	-0.45267
C20	-0.50838	0.00000	-0.41524
C21	-0.46561	0.00000	-0.49039
C22	-0.61388	0.00000	-0.42352
C23	-0.46323	0.00000	-0.52731
C24	-0.42784	0.00000	-0.56195
C25	-0.39257	0.00000	-0.56189
C26	-0.39393	0.00000	-0.52595
C27	-0.42966	0.00000	-0.49080
C28	-0.44467	0.00000	-0.21496
C29	-0.41085	0.00000	-0.21188
C30	-0.41356	0.00000	-0.17526
C31	-0.45027	0.00000	-0.14211
C32	-0.48378	0.00000	-0.14492

C33	-0.63334	0.00000	-0.07496
C34	-0.66904	0.00000	-0.04042
C35	-0.70419	0.00000	-0.04095
C36	-0.70255	0.00000	-0.07681
C37	-0.66687	0.00000	-0.11155
C38	-0.65167	0.00000	-0.38985
C39	-0.68541	0.00000	-0.39266
C40	-0.68291	0.00000	-0.42901
C41	-0.64625	0.00000	-0.46247
C42	-0.61248	0.00000	-0.45994
N43	-0.35524	0.00000	-0.59733
C44	-0.71765	0.00000	-0.43334
C45	-0.37934	0.00000	-0.16982
N46	-0.62470	0.00000	-0.23515
Se47	-0.66344	0.00000	-0.24901
N48	-0.62114	0.00000	-0.29996
C49	-0.12896	0.00000	-0.19180
C50	-0.16458	0.00000	-0.15598
C51	-0.19926	0.00000	-0.15783
C52	-0.19965	0.00000	-0.19304
C53	-0.16336	0.00000	-0.22740
C54	-0.12723	0.00000	-0.22844
C55	-0.23770	0.00000	-0.19415
C56	-0.16603	0.00000	-0.11672
C57	-0.08827	0.00000	-0.26730
C58	-0.08508	0.00000	-0.30658
C59	-0.04720	0.00000	-0.34238
C60	-0.00993	0.00000	-0.34133
C61	-0.01484	0.00000	-0.30495
C62	-0.05351	0.00000	-0.26841
C63	0.03092	0.00000	-0.37790
C64	0.03581	0.00000	-0.41576
C65	0.07213	0.00000	-0.45000
C66	0.10500	0.00000	-0.44569
C67	0.10318	0.00000	-0.40934
C68	0.06566	0.00000	-0.37571
C69	0.14067	0.00000	-0.40745
C70	0.07584	0.00000	-0.49021
C71	0.17768	0.00000	-0.44187

C72	0.21212	0.00000	-0.44091
C73	0.21185	0.00000	-0.40550
C74	0.17585	0.00000	-0.37101
C75	0.14082	0.00000	-0.37179
C76	-0.13192	0.00000	-0.11346
C77	-0.13400	0.00000	-0.07700
C78	-0.17014	0.00000	-0.04261
C79	-0.20386	0.00000	-0.04529
C80	-0.20203	0.00000	-0.08121
C81	-0.27452	0.00000	-0.15961
C82	-0.30927	0.00000	-0.16054
C83	-0.30898	0.00000	-0.19612
C84	-0.27317	0.00000	-0.23043
C85	-0.23829	0.00000	-0.22971
C86	0.04277	0.00000	-0.49521
C87	0.04657	0.00000	-0.53218
C88	0.08339	0.00000	-0.56553
C89	0.11627	0.00000	-0.56146
C90	0.11276	0.00000	-0.52477
N91	-0.75285	0.00000	-0.40351
C92	0.08863	0.00000	-0.60493
N93	-0.34388	0.00000	-0.19893
C94	-0.17468	0.00000	-0.00326
N95	-0.11432	0.00000	-0.31233
Se96	-0.10036	0.00000	-0.36499
N97	-0.04933	0.00000	-0.37376
C98	-0.93735	0.00000	0.16974
C99	-0.90163	0.00000	0.16971
C100	-0.90362	0.00000	0.20613
C101	-0.93863	0.00000	0.24163
C102	-0.97306	0.00000	0.23987
C103	-0.97405	0.00000	0.20469
C104	-0.93904	0.00000	0.28033
C105	-0.86213	0.00000	0.13237
C106	-1.01286	0.00000	0.20453
C107	-1.05212	0.00000	0.24058
C108	-1.08792	0.00000	0.23848
C109	-1.08685	0.00000	0.20013
C110	-1.05044	0.00000	0.16869

C111	-1.01391	0.00000	0.17086
C112	-1.12341	0.00000	0.19579
C113	-1.16121	0.00000	0.22867
C114	-1.19555	0.00000	0.22676
C115	-1.19134	0.00000	0.18944
C116	-1.15477	0.00000	0.15485
C117	-1.12121	0.00000	0.15891
C118	-1.15218	0.00000	0.11505
C119	-1.23556	0.00000	0.26376
C120	-1.18613	0.00000	0.11169
C121	-1.18435	0.00000	0.07575
C122	-1.14847	0.00000	0.04087
C123	-1.11451	0.00000	0.04331
C124	-1.11614	0.00000	0.07953
C125	-0.85830	0.00000	0.09483
C126	-0.82155	0.00000	0.06090
C127	-0.78756	0.00000	0.06342
C128	-0.79077	0.00000	0.09995
C129	-0.82691	0.00000	0.13354
C130	-0.90404	0.00000	0.28181
C131	-0.90415	0.00000	0.31694
C132	-0.93927	0.00000	0.35247
C133	-0.97409	0.00000	0.35191
C134	-0.97422	0.00000	0.31675
C135	-1.24000	0.00000	0.30168
C136	-1.27669	0.00000	0.33532
C137	-1.31046	0.00000	0.33264
C138	-1.30694	0.00000	0.29581
C139	-1.27045	0.00000	0.26211
N140	-1.14540	0.00000	0.00292
C141	-1.34972	0.00000	0.36740
N142	-0.94099	0.00000	0.38954
C143	-0.74809	0.00000	0.02921
N144	-1.05787	0.00000	0.27557
Se145	-1.11054	0.00000	0.31426
N146	-1.11929	0.00000	0.27198
N147	-0.74190	0.00000	-0.00616
H148	-0.49175	0.00000	-0.24606
H149	-0.55769	0.00000	-0.12237

H150	-0.61575	0.00000	-0.18537
H151	-0.48860	0.00000	-0.35887
H152	-0.49197	0.00000	-0.29769
H153	-0.60597	0.00000	-0.36067
H154	-0.53830	0.00000	-0.48132
H155	-0.48239	0.00000	-0.41357
H156	-0.48797	0.00000	-0.53141
H157	-0.42909	0.00000	-0.58846
H158	-0.36707	0.00000	-0.52512
H159	-0.42811	0.00000	-0.46449
H160	-0.44027	0.00000	-0.24402
H161	-0.38266	0.00000	-0.23815
H162	-0.45323	0.00000	-0.11343
H163	-0.51013	0.00000	-0.11727
H164	-0.60836	0.00000	-0.07118
H165	-0.66815	0.00000	-0.01371
H166	-0.72929	0.00000	-0.07789
H167	-0.66912	0.00000	-0.13743
H168	-0.65681	0.00000	-0.36058
H169	-0.71350	0.00000	-0.36624
H170	-0.64360	0.00000	-0.49101
H171	-0.58590	0.00000	-0.48746
H172	-0.71240	0.00000	-0.46273
H173	-0.38506	0.00000	-0.14023
H174	-0.10263	0.00000	-0.19089
H175	-0.22635	0.00000	-0.13170
H176	-0.16415	0.00000	-0.25322
H177	0.00936	0.00000	-0.29993
H178	-0.05142	0.00000	-0.24246
H179	0.01170	0.00000	-0.41959
H180	0.13233	0.00000	-0.47120
H181	0.06384	0.00000	-0.34800
H182	0.18211	0.00000	-0.47082
H183	0.23864	0.00000	-0.46865
H184	0.17490	0.00000	-0.34326
H185	0.11441	0.00000	-0.34400
H186	-0.10309	0.00000	-0.13846
H187	-0.10734	0.00000	-0.07580
H188	-0.23225	0.00000	-0.01919

H189	-0.22992	0.00000	-0.07942
H190	-0.27796	0.00000	-0.13097
H191	-0.33597	0.00000	-0.13292
H192	-0.27223	0.00000	-0.25818
H193	-0.21252	0.00000	-0.25792
H194	0.01329	0.00000	-0.47142
H195	0.02054	0.00000	-0.53455
H196	0.14510	0.00000	-0.58694
H197	0.14002	0.00000	-0.52520
H198	0.11810	0.00000	-0.62902
H199	-0.20420	0.00000	0.02065
H200	-0.93626	0.00000	0.14239
H201	-0.87762	0.00000	0.20707
H202	-0.99883	0.00000	0.26663
H203	-1.04535	0.00000	0.13945
H204	-0.98793	0.00000	0.14285
H205	-1.16487	0.00000	0.25649
H206	-1.21696	0.00000	0.18755
H207	-1.09344	0.00000	0.13316
H208	-1.21517	0.00000	0.13613
H209	-1.21180	0.00000	0.07635
H210	-1.08645	0.00000	0.01688
H211	-1.08856	0.00000	0.07859
H212	-0.88308	0.00000	0.09063
H213	-0.81980	0.00000	0.03279
H214	-0.76494	0.00000	0.10271
H215	-0.82524	0.00000	0.15969
H216	-0.87551	0.00000	0.25654
H217	-0.87624	0.00000	0.31540
H218	-1.00151	0.00000	0.37907
H219	-1.00261	0.00000	0.31958
H220	-1.21599	0.00000	0.30701
H221	-1.27853	0.00000	0.36349
H222	-1.33271	0.00000	0.29295
H223	-1.27104	0.00000	0.23533
H224	-1.37386	0.00000	0.36213
H225	-0.72422	0.00000	0.03490

Table S3. Atomic coordinates of AA-stacking mode of the simulated HIAM-0013.

Space group: *pm* a = 32.3412 Å, b = 3.4320 Å, and c = 27.2836 Å. α = γ = 90°, and β = 90°			
Atom	**x**	**y**	**z**
C1	0.13686	-0.00000	0.75639
C2	0.09403	-0.00000	0.75920
C3	0.07819	-0.00000	0.80575
C4	0.10372	-0.00000	0.84838
C5	0.14783	-0.00000	0.84184
C6	0.16677	-0.00000	0.79405
C7	0.08311	-0.00000	0.89851
C8	0.06666	-0.00000	0.71254
C9	0.21549	-0.00000	0.78208
C10	0.24445	-0.00000	0.82190
C11	0.28723	-0.00000	0.81834
C12	0.30961	-0.00000	0.77405
C13	0.28177	-0.00000	0.72985
C14	0.23593	-0.00000	0.73361
C15	0.35963	-0.00000	0.77713
C16	0.38504	-0.00000	0.82147
C17	0.42937	-0.00000	0.82240
C18	0.44918	-0.00000	0.77708
C19	0.42729	-0.00000	0.73276
C20	0.38422	-0.00000	0.73537
C21	0.44866	-0.00000	0.68308
C22	0.45562	-0.00000	0.86989
C23	0.49236	-0.00000	0.67937
C24	0.51131	-0.00000	0.63373
C25	0.48781	-0.00000	0.59005
C26	0.44471	-0.00000	0.59271
C27	0.42566	-0.00000	0.63785
C28	0.08407	-0.00000	0.66515
C29	0.05987	-0.00000	0.62258
C30	0.01699	-0.00000	0.62468
C31	-0.00148	-0.00000	0.67050
C32	0.02283	-0.00000	0.71377

C33	0.03921	-0.00000	0.90216
C34	0.01972	-0.00000	0.94693
C35	0.04225	-0.00000	0.99075
C36	0.08583	-0.00000	0.98903
C37	0.10589	-0.00000	0.94365
C38	0.43794	-0.00000	0.91697
C39	0.46278	-0.00000	0.95994
C40	0.50607	-0.00000	0.95752
C41	0.52399	-0.00000	0.91180
C42	0.49962	-0.00000	0.86908
C43	0.53351	-0.00000	0.00144
N44	0.01897	-0.00000	0.03500
C45	-0.00835	-0.00000	0.57923
N46	0.23336	-0.00000	0.86888
S47	0.27280	-0.00000	0.90982
N48	0.30533	-0.00000	0.86307
C49	0.29654	-0.00000	0.68038
C50	0.27243	-0.00000	0.63829
C51	0.23131	-0.00000	0.64147
C52	0.21384	-0.00000	0.68680
C53	0.71821	-0.00000	0.39767
C54	0.73747	-0.00000	0.44303
C55	0.77873	-0.00000	0.44634
C56	0.80116	-0.00000	0.40431
N57	0.50885	-0.00000	0.54418
N58	0.80211	-0.00000	0.22136
S59	0.76747	-0.00000	0.17473
N60	0.72991	-0.00000	0.21582
C61	0.49195	-0.00000	0.50030
N62	0.51834	-0.00000	0.04493
C63	0.03336	-0.00000	0.07980
N64	0.00919	-0.00000	0.53675
C65	0.99876	-0.00000	0.21868
C66	0.02323	-0.00000	0.16898
C67	1.00518	-0.00000	0.13049
C68	0.96174	-0.00000	0.12571
C69	0.93690	-0.00000	0.16751
C70	0.60420	-0.00000	0.14184
C71	0.58442	-0.00000	0.09543

C72	0.54099	-0.00000	0.09096
C73	0.51813	-0.00000	0.13321
C74	0.53747	-0.00000	0.17929
C75	0.52334	-0.00000	0.36763
C76	0.49923	-0.00000	0.40955
C77	0.51774	-0.00000	0.45645
C78	0.56076	-0.00000	0.46088
C79	0.58494	-0.00000	0.41943
C80	0.92698	-0.00000	0.44611
C81	0.94568	-0.00000	0.49226
C82	0.98860	-0.00000	0.49774
C83	0.01263	-0.00000	0.44731
C84	-0.00617	-0.00000	0.40034
C85	0.95470	-0.00000	0.21562
C86	0.94998	-0.00000	0.40236
C87	0.88542	-0.00000	0.34754
C88	0.92833	-0.00000	0.35171
C89	0.94945	-0.00000	0.30826
C90	0.92878	-0.00000	0.26204
C91	0.88418	-0.00000	0.26153
C92	0.85996	-0.00000	0.30568
C93	0.73843	-0.00000	0.35112
C94	0.78443	-0.00000	0.35459
C95	0.81018	-0.00000	0.30989
C96	0.78584	-0.00000	0.26602
C97	0.74290	-0.00000	0.26284
C98	0.71570	-0.00000	0.30310
C99	0.56722	-0.00000	0.37103
C100	0.58130	-0.00000	0.18550
C101	0.66631	-0.00000	0.29224
C102	0.64602	-0.00000	0.24445
C103	0.60205	-0.00000	0.23654
C104	0.57728	-0.00000	0.27815
C105	0.59406	-0.00000	0.32538
C106	0.63717	-0.00000	0.32963
H107	0.14548	-0.00000	0.72322
H108	0.04566	-0.00000	0.80782
H109	0.16556	-0.00000	0.87490
H110	0.37217	-0.00000	0.85630

H111	0.48179	-0.00000	0.77553
H112	0.37183	-0.00000	0.70292
H113	0.51304	-0.00000	0.71088
H114	0.54475	-0.00000	0.63245
H115	0.42493	-0.00000	0.56027
H116	0.39253	-0.00000	0.63478
H117	0.11642	-0.00000	0.65816
H118	0.07514	-0.00000	0.58769
H119	-0.03486	-0.00000	0.67289
H120	0.00616	-0.00000	0.74739
H121	0.01780	-0.00000	0.87156
H122	-0.01378	-0.00000	0.94744
H123	0.10477	-0.00000	1.02221
H124	0.13922	-0.00000	0.94500
H125	0.40507	-0.00000	0.92211
H126	0.44799	-0.00000	0.99509
H127	0.55735	-0.00000	0.90891
H128	0.51723	-0.00000	0.83634
H129	0.56654	-0.00000	-0.00353
H130	-0.04150	-0.00000	0.58252
H131	0.32516	-0.00000	0.66506
H132	0.28580	-0.00000	0.60209
H133	0.21267	-0.00000	0.60767
H134	0.18323	-0.00000	0.67548
H135	0.68804	-0.00000	0.40830
H136	0.72014	-0.00000	0.47669
H137	0.79349	-0.00000	0.48266
H138	0.83030	-0.00000	0.42034
H139	0.45881	-0.00000	0.49463
H140	0.06636	-0.00000	0.08722
H141	1.01662	-0.00000	0.25229
H142	0.05660	-0.00000	0.17389
H143	0.94689	-0.00000	0.08969
H144	0.90390	-0.00000	0.16103
H145	0.63747	-0.00000	0.14200
H146	0.60359	-0.00000	0.06363
H147	0.48465	-0.00000	0.13042
H148	0.51623	-0.00000	0.20881
H149	0.50638	-0.00000	0.33321

H150	0.46584	-0.00000	0.40522
H151	0.57605	-0.00000	0.49668
H152	0.61754	-0.00000	0.42780
H153	0.89404	-0.00000	0.44755
H154	0.92563	-0.00000	0.52322
H155	0.04604	-0.00000	0.45090
H156	0.01439	-0.00000	0.36994
H157	0.87292	-0.00000	0.37873
H158	0.98210	-0.00000	0.31144
H159	0.87021	-0.00000	0.22612
H160	0.66271	-0.00000	0.21209
H161	0.54468	-0.00000	0.27446
H162	0.64580	-0.00000	0.36366

Table S4. Atomic coordinates of AA-stacking mode of the simulated HIAM-0014.

Space group: *pm* a = 32.3636 Å, b = 3.4552 Å, and c = 27.3428 Å. α = γ = 90°, and β = 90°			
Atom	**x**	**y**	**z**
C1	0.13589	-0.00000	0.74555
C2	0.09292	-0.00000	0.74867
C3	0.07644	-0.00000	0.79531
C4	0.10152	-0.00000	0.83752
C5	0.14546	-0.00000	0.83065
C6	0.16523	-0.00000	0.78327
C7	0.08102	-0.00000	0.88793
C8	0.06603	-0.00000	0.70235
C9	0.21434	-0.00000	0.77294
C10	0.24286	-0.00000	0.81609
C11	0.28807	-0.00000	0.81270
C12	0.31138	-0.00000	0.76566
C13	0.28477	-0.00000	0.72402
C14	0.23592	-0.00000	0.72769
C15	0.36126	-0.00000	0.76854
C16	0.38629	-0.00000	0.81253
C17	0.43063	-0.00000	0.81287
C18	0.45074	-0.00000	0.76727
C19	0.42902	-0.00000	0.72345
C20	0.38603	-0.00000	0.72680
C21	0.45024	-0.00000	0.67340
C22	0.45654	-0.00000	0.85995
C23	0.49384	-0.00000	0.66835
C24	0.51246	-0.00000	0.62212
C25	0.48859	-0.00000	0.57935
C26	0.44565	-0.00000	0.58346
C27	0.42702	-0.00000	0.62903
C28	0.08382	-0.00000	0.65480
C29	0.05987	-0.00000	0.61260
C30	0.01696	-0.00000	0.61530
C31	0.99805	-0.00000	0.66490
C32	0.02222	-0.00000	0.70414
C33	0.03725	-0.00000	0.89282

C34	0.01806	-0.00000	0.93820
C35	0.04098	-0.00000	0.98116
C36	0.08440	-0.00000	0.97801
C37	0.10403	-0.00000	0.93223
C38	0.43858	-0.00000	0.90722
C39	0.46313	-0.00000	0.94979
C40	0.50642	-0.00000	0.94678
C41	0.52458	-0.00000	0.90082
C42	0.50050	-0.00000	0.85852
C43	0.53367	-0.00000	0.99040
N44	0.01837	-0.00000	0.02606
C45	0.99151	-0.00000	0.57397
N46	0.22973	-0.00000	0.86046
Se47	0.27090	-0.00000	0.90864
N48	0.30617	-0.00000	0.85474
C49	0.29988	-0.00000	0.67111
C50	0.27658	-0.00000	0.63155
C51	0.23337	-0.00000	0.63479
C52	0.21485	-0.00000	0.67750
C53	0.71524	-0.00000	0.38442
C54	0.73398	-0.00000	0.42722
C55	0.77720	-0.00000	0.43068
C56	0.80029	-0.00000	0.39123
N57	0.50905	-0.00000	0.53280
N58	0.80566	-0.00000	0.20761
Se59	0.77013	-0.00000	0.15354
N60	0.72922	-0.00000	0.20153
C61	0.49162	-0.00000	0.48972
C62	0.03352	-0.00000	0.07005
N63	0.00919	-0.00000	0.52754
C64	0.00036	-0.00000	0.20153
C65	0.02440	-0.00000	0.15950
C66	0.00622	-0.00000	0.11333
C67	0.96272	-0.00000	0.11344
C68	0.93820	-0.00000	0.15577
C69	0.60387	-0.00000	0.12915
C70	0.58431	-0.00000	0.08312
C71	0.54090	-0.00000	0.07939
C72	0.51792	-0.00000	0.12203

C73	0.53704	-0.00000	0.16769
C74	0.52219	-0.00000	0.35636
C75	0.49822	-0.00000	0.39889
C76	0.51693	-0.00000	0.44513
C77	0.55985	-0.00000	0.44834
C78	0.58381	-0.00000	0.40640
C79	0.92705	-0.00000	0.43389
C80	0.94566	-0.00000	0.47966
C81	0.98859	-0.00000	0.48430
C82	0.01266	-0.00000	0.43823
C83	0.99385	-0.00000	0.39536
C84	0.95620	-0.00000	0.20325
C85	0.95026	-0.00000	0.38981
C86	0.88603	-0.00000	0.33579
C87	0.92900	-0.00000	0.33953
C88	0.95062	-0.00000	0.29590
C89	0.93039	-0.00000	0.25011
C90	0.88603	-0.00000	0.25007
C91	0.86116	-0.00000	0.29391
C92	0.73607	-0.00000	0.33436
C93	0.78493	-0.00000	0.33822
C94	0.81131	-0.00000	0.29666
C95	0.78776	-0.00000	0.24955
C96	0.74255	-0.00000	0.24598
C97	0.71425	-0.00000	0.28903
C98	0.56601	-0.00000	0.35864
C99	0.58080	-0.00000	0.17314
C100	0.66508	-0.00000	0.27857
C101	0.64517	-0.00000	0.23109
C102	0.60126	-0.00000	0.22380
C103	0.57626	-0.00000	0.26575
C104	0.59283	-0.00000	0.31258
C105	0.63583	-0.00000	0.31610
H106	0.14474	-0.00000	0.71219
H107	0.04387	-0.00000	0.79798
H108	0.16247	-0.00000	0.86340
H109	0.37314	-0.00000	0.84749
H110	0.48337	-0.00000	0.76509
H111	0.37334	-0.00000	0.69511

H112	0.51457	-0.00000	0.69924
H113	0.54584	-0.00000	0.61963
H114	0.42559	-0.00000	0.55185
H115	0.39400	-0.00000	0.62685
H116	0.11629	-0.00000	0.64753
H117	0.07533	-0.00000	0.57756
H118	0.96468	-0.00000	0.66780
H119	0.00528	-0.00000	0.73789
H120	0.01591	-0.00000	0.86271
H121	0.98442	-0.00000	0.94347
H122	0.10363	-0.00000	0.01004
H123	0.13729	-0.00000	0.93295
H124	0.40569	-0.00000	0.91278
H125	0.44812	-0.00000	0.98509
H126	0.55793	-0.00000	0.89742
H127	0.51825	-0.00000	0.82553
H128	0.56669	-0.00000	0.98484
H129	0.95837	-0.00000	0.57797
H130	0.32865	-0.00000	0.65516
H131	0.28975	-0.00000	0.59493
H132	0.21609	-0.00000	0.60046
H133	0.18450	-0.00000	0.66596
H134	0.68493	-0.00000	0.39575
H135	0.71687	-0.00000	0.46147
H136	0.79056	-0.00000	0.46737
H137	0.82912	-0.00000	0.40739
H138	0.45848	-0.00000	0.48529
H139	0.06654	-0.00000	0.07607
H140	0.01815	-0.00000	0.23470
H141	0.05775	-0.00000	0.16329
H142	0.94768	-0.00000	0.07798
H143	0.90529	-0.00000	0.14993
H144	0.63712	-0.00000	0.12880
H145	0.60359	-0.00000	0.05103
H146	0.48448	-0.00000	0.11987
H147	0.51570	-0.00000	0.19754
H148	0.50525	-0.00000	0.32242
H149	0.46486	-0.00000	0.39557
H150	0.57529	-0.00000	0.48359

H151	0.61631	-0.00000	0.41402
H152	0.89405	-0.00000	0.43573
H153	0.92558	-0.00000	0.51102
H154	0.04604	-0.00000	0.44112
H155	0.01475	-0.00000	0.36110
H156	0.87336	-0.00000	0.36727
H157	0.98327	-0.00000	0.29842
H158	0.87276	-0.00000	0.21498
H159	0.66208	-0.00000	0.19852
H160	0.54368	-0.00000	0.26268
H161	0.64470	-0.00000	0.34961
N162	0.51842	-0.00000	0.03382

Table S5. The summary of benzothiadiazol-based COFs for photocatalytic hydrogen generation performance.

Photocatalyst	Illumination	Sacrificial agent	Co-catalyst	H_2 Evolution Rate ($mmol \cdot g^{-1} \cdot h^{-1}$)	Reference
CTF-BT/Th-1	λ≥420 nm	TEOA	3 wt% Pt	6.6	[1]
BT-TAPT-COF	λ≥420 nm	AA	8 wt% Pt	0.949	[2]
Py-ClTP-BT-COF	λ＞420 nm	AA	5 wt% Pt	8.875	[3]
Py-FTP-BT-COF	λ＞420 nm	AA	5 wt% Pt	2.875	
Py-HTP-BT-COF	λ＞420 nm	AA	5 wt% Pt	1.078	
COF-F	AM 1.5	AA	3 wt% Pt	10.581	[4]
COF-Cl	AM 1.5	AA	3 wt% Pt	5.838	
COF-H	AM 1.5	AA	3 wt% Pt	5.034	
BTCOF150	λ≥400 nm	TEOA	1 wt% Pt	0.75	[5]
NKCOF-108	λ＞420 nm	AA	5 wt% Pt	11.6	[6]
30%PEG@BT-COF	λ＞420 nm	AA	3.7 wt% Pt	11.14	[7]
USTB-7	λ≥420 nm	AA	3 wt% Pt	4.3	[8]
USTB-8	λ≥420 nm	AA	3 wt% Pt	13.7	
TeTz-COF1	λ＞420 nm	AA	4 wt% Pt	2.103	[9]
HPT-COF	λ≥420 nm	AA	3 wt% Pt	3.8	[10]
BT-COF	λ≥420 nm	AA	3 wt% Pt	0.68	
HIAM-0001	λ＞420 nm	AA	5 wt% Pt	1.41	[11]
		TEOA	12 wt% Pt	1.217	
HIAM-0011	λ＞420 nm	AA	1 wt% Pt	16.98	This work

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