Supporting Information

Impact of Imine Bond Orientations on Photocatalytic Hydrogen Generation

of Benzothiadiazole-based Covalent Organic Frameworks Constructed using

"Two-in-One" Monomers

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Chemicals

3,5-dibromobenzaldehyde, neopentyl glycol, *p*-toluenesulfonic acid, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde, 3,5-dibromoaniline 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 photoluminescent and UV-vis absorption spectra were recorded on FLS1000 spectrofluorometer (Edinburgh Instruments) and Shimadzu UV-3600 spectrophotometer, respectively. Fourier transform infrared (FT-IR) spectra were recorded using a PerkinElmer spectrometer. 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) and Transmission electron microscope (TEM) images were taken using a JEOL JSM-IT800 (SHL) and Thermo Scientific Talos F200S, respectively. 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-0026/HIAM-0026 ν 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 Na₂SO₄ aqueous solution was used as the electrolyte. Mott-Schottky measurement was carried out at frequency of 1000, 1500 and 2000 Hz with amplitude of 5 mV.

Stability testing of COFs

Samples of HIAM-0026/HIAM-0026v (~ 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 sealed in 5 mL glass vials and stored at room temperature or 100 °C for 24 hours. The samples were then washed with ethanol and dried under 100 °C vacuum. The resultant COFs were used for PXRD and IR analysis.

Photocatalytic hydrogen evolution

3 mg HIAM-0026/HIAM-0026v was well dispersed in 50 mL deionized water containing 0.1 M ascorbic acid (AA) as the sacrificial agent. Then 0.018 M chloroplatinic acid (H₂PtCl₆) aqueous solution (3 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.

Apparent quantum efficiency (AQY) measurements were performed under monochromatic irradiation generated from a 300 W Xe lamp equipped with bandpass filters (central

wavelength: 450, 500 and 550 nm; full width at half maximum: 10 nm). Monochromatic photon fluxes at each wavelength were measured using an optical photodiode power meter (CEL-NP2000 Intense Light Power Meter). The corresponding intensities were 4.614, 9.536 and 5.906 mW cm⁻², respectively. The AQY was calculated using the following equation:

$$\eta_{AQY} = \frac{N_{\rm e}}{N_{\rm p}} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where, N_e is the amount of generated electrons, N_p is the incident photons, M is the amount of H₂ molecules (mol), N_A is Avogadro constant (6.022×10²³ mol⁻¹), h is the Planck constant (6.626×10⁻³⁴ J·s), c is the speed of light (3×108 m·s⁻¹), S is the irradiation area (cm²), P is the intensity of irradiation light (W·cm⁻²), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Synthesis of 2-(3,5-dibromophenyl)-5,5-dimethyl-1,3-dioxane



3,5-dibromobenzaldehyde (10.56 g, 40.00 mmol), neopentyl glycol (12.50 g, 120.00 mmol) and *p*-toluenesulfonic acid (0.68 g, 4.00 mmol) were added to a 500 mL of two-neck round-bottom flask. The reaction mixture was firstly deoxygenized with nitrogen for three times, and then 300 mL of toluene was added. The reaction mixture was heated 150 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure to offer 2-(3,5-dibromophenyl)-5,5-dimethyl-1,3-dioxane as a white solid (14.00 g, yield: 99.0 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.61 (1H), 7.56 (2H), 5.29 (1H), 3.73 (2H), 3.61(2H), 1.23 (3H), 0.77 (3H).

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



2-(3,5-dibromophenyl)-5,5-dimethyl-1,3-dioxane (40.00 mmol, 14.00 g), 4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (20.00 mmol, 4.38 g), PdCl₂ (1.00 mmol, 0.17 g),

PPh₃ (2.00 mmol, 0.52 g) and K₂CO₃ (40.00 mmol, 5.53 g) were added into one 500 mL flask containing 160 mL dioxane and 40 mL water. The mixture was degassed four times and stirred at 110 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al₂O₃ column chromatography to offer 3'-bromo-5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4-amine as a yellow solid (3.78 g, yield: 52.1 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.63 (1H), 7.56 (2H), 7.38 (1H), 7.36 (1H), 6.71 (2H), 5.37(1H), 3.78 (2H), 3.64 (2H), 1.28 (3H), 0.79 (3H). Synthesis of 5',5'''-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4-amine) (BTBBA)



3'-bromo-5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4-amine (10.43 mmol, 3.78 g), 4,7bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (3.48 mmol, 1.35 g), PdCl₂ (0.34 mmol, 0.06 g), PPh₃ (0.69 mmol, 0.18 g) and K₂CO₃ (10.43 mmol, 1.44 g) were added into one 250 mL flask containing 80mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 110 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was

purified by Al₂O₃ column chromatography to offer 5',5"''-(benzo[c][1,2,5]thiadiazole-4,7diyl)bis(3'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4-amine) as an orange color solid (2.00 g, yield: 82.2 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.19 (2H), 8.03 (2H), 7.89 (2H), 7.82 (2H), 7.58(4H), 6.82 (4H), 5.61 (2H), 3.87 (4H), 3.77 (4H), 1.38 (6H), 0.88 (6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm):154.28, 146.12, 141.74, 139.41, 138.03,132.30, 132.20, 128.76, 128.64, 128.45, 125.16, 124.41, 115.53, 101.82, 75.18, 30.46, 25.00, 23.31, 22.09.

Synthesis of 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4.64 g, 20 mmol), neopentyl glycol (6.25 g, 60.00 mmol) and *p*-toluenesulfonic acid (0.34 g, 2.00 mmol) were added to a 500 mL of two-neck round-bottom flask. The reaction mixture was firstly deoxygenized with nitrogen for three times, and then 300 mL of toluene was added. The reaction mixture was heated 150 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure to offer 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a white solid (6.36 g, yield: 99.0 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.78 (2H), 7.46 (2H), 5.38 (1H), 3.75 (2H), 3.63(2H), 1.27 (3H), 0.99 (6H), 0.88 (6H), 0.78 (3H).

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



2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25.00 mmol, 7.96 g), 3,5-dibromoaniline (100.00 mmol, 25.09 g), PdCl₂ (1.25 mmol, 0.22 g), PPh₃ (2.50 mmol, 0.65 g) and K₂CO₃ (50.00 mmol, 6.91 g) were added into one 500 mL flask containing 200 mL dioxane and 50 mL water. The mixture was degassed four times and stirred at 110 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al₂O₃ column chromatography to offer 3'-bromo-5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4-amine as a yellow solid (2.10 g, yield: 23.1 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.54 (2H), 7.50 (2H), 7.07 (1H), 7.80 (1H), 6.75(1H), 5.38 (1H), 3.78 (2H), 3.66 (2H), 1.29 (3H), 0.80 (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'-biphenyl]-3-amine) (BTBBAv)**



5-bromo-4'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-3-amine (12.70 mmol, 4.60 g), 4,7bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (8.47 mmol, 3.29 g), PdCl₂ (0.42 mmol, 0.07 g), PPh₃ (0.84 mmol, 0.22 g) and K₂CO₃ (16.93 mmol, 2.34 g) were added into one 250 mL flask containing 80mL dioxane and 20 mL water. The mixture was degassed four times and stirred at 110 °C overnight under nitrogen. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by Al₂O₃ column chromatography to offer 5,5"-(benzo[c][1,2,5]thiadiazole-4,7diyl)bis(4'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-3-amine) as an orange color solid (1.80 g, yield: 30.43 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.76 (2H), 7.64 (4H), 7.56 (4H), 7.49 (2H), 7.26(2H), 6.96 (2H), 5.43 (2H), 3.78 (4H), 3.66 (4H), 1.30 (6H), 0.77 (6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm):154.16, 147.00, 142.54, 141.92, 139.01, 137.73, 133.52, 128.18, 127.32, 126.61, 119.03, 115.23, 114.14, 101.67, 75.11, 30.35, 24.93, 23.16, 22.00



Figure S1. ¹H NMR spectrum of 2-(3,5-dibromophenyl)-5,5-dimethyl-1,3-dioxane.



Figure S2. ¹H NMR spectrum of 3'-bromo-5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-4amine.





Figure S4. ¹³C NMR spectrum of BTBBA.



Figure S5. ¹H NMR spectrum of 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-4,4,5,5tetramethyl-1,3,2-dioxaborolane.





Figure S6. ¹H NMR spectrum of 5-bromo-4'-(5,5-dimethyl-1,3-dioxan-2-yl)-[1,1'-biphenyl]-3amine.







Figure S8. ¹³C NMR spectrum of BTBBAv.

Synthesis of HIAM-0026



A Pyrex tube (10 mL) containing BTBBA (31.4 mg, 0.045 mmol) and *n*-butyl alcohol (*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 *N*,*N*-dimethylformamide (DMF) and ethanol (EtOH). The yellow solid was Soxhlet extracted in EtOH for 24 h and dried under 100 °C vacuum to afford HIAM-0026 (12.5 mg, yield: 56.6%).

Synthesis of HIAM-0026v



A Pyrex tube (10 mL) containing BTBBAv (31.4 mg, 0.045 mmol) and *n*-BuOH (1 mL) was sonicated for 3 min. Subsequently, 0.8 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-0026v (18.7 mg, yield: 85.0%).



Figure S9. FT-IR spectra of HIAM-0026 (a) and HIAM-0026v (b) and the corresponding organic building units.



Figure S10. SEM images of HIAM-0026 and HIAM-0026v.



Figure S11. TEM images of HIAM-0026 and HIAM-0026v.



Figure S12. Energy dispersive X-ray analysis of HIAM-0026 (a) and HIAM-0026v (b).



Figure S13. The PXRD patterns of HIAM-0026 (a) and HIAM-0026v after treatment under various conditions for 24 hours.



Figure S14. The FT-IR spectra of HIAM-0026 (a) and HIAM-0026*v* after treatment under various conditions for 24 hours.



Figure S15. TGA curves of HIAM-0026 (a) and HIAM-0026v (b).



Figure S16. The photoluminescence spectra of HIAM-0026 and HIAM-0026v.



Figure S17. The images of the experimental setup used for the photocatalytic hydrogen generation.





Figure S19. The photocatalyst mass (a), the amount of co-catalyst (b) and concentration of AA (c) effect on the photocatalytic hydrogen performance of HIAM-0026.



Figure S20. The photocatalytic hydrogen production performance of HIAM-0026 with various sacrificial donors.



Figure S21. The control experiments of photocatalytic H_2 evolution using HIAM-0026 as the photocatalysts.



Figure S22. The wavelength-dependent AQY of photocatalytic H_2 evolution for HIAM-0026.



Figure S23. The PXRD patterns of HIAM-0026 before and after photocatalytic measurement.



Figure S24. The FT-IR spectra of HIAM-0026 before and after photocatalytic measurement.



Figure S25. The SEM (a) and TEM (b) images of HIAM-0026 after photocatalytic measurement.



Figure S26. The HAADF-STEM and EDX analysis of HIAM-0026 after photocatalytic measurement.

	a = 17	Space group: <i>pm</i> a = 17.6928 Å, b = 3.3510 Å, and c = 16.6652 Å. α = γ = 90°, and β = 116.7130°			
	Atom	X	У	Z	
C1	0.47148	-0.00000	0.44363		
C2	0.43696	-0.00000	0.34852		
C3	0.34776	-0.00000	0.30183		
C4	0.29703	-0.00000	0.34556		
C5	0.33078	-0.00000	0.43999		
C6	0.42082	-0.00000	0.48749		
C7	0.48899	-0.00000	0.29655		
C8	0.27122	-0.00000	0.48351		
С9	0.57903	-0.00000	0.33931		
C10	0.62688	-0.00000	0.29105		
C11	0.58272	-0.00000	0.19825		
C12	0.4958	-0.00000	0.15386		
C13	0.4486	-0.00000	0.20134		
C14	0.18265	-0.00000	0.43133		
C15	0.12868	-0.00000	0.47138		
C16	0.16078	-0.00000	0.56427		
C17	0.24723	-0.00000	0.6195		
C18	0.30074	-0.00000	0.57738		
C19	0.72195	-0.00000	0.33505		
C20	0.28134	-0.00000	0.72002		
C21	0.03771	-0.00000	0.41597		
C22	0.45966	-0.00000	0.05665		
C23	0.77066	-0.00000	0.42948		
C24	0.85858	-0.00000	0.46788		
C25	0.8998	-0.00000	0.41373		
C26	0.85315	-0.00000	0.32081		
C27	0.76642	-0.00000	0.28233		
C28	0.22757	-0.00000	0.76298		
C29	0.2597	-0.00000	0.85625		
C30	0.34629	-0.00000	0.91054		
C31	0.40269	-0.00000	0.86625		
C32	0.36919	-0.00000	0.77479		
N33	0.98935	-0.00000	0.45598		
N34	0.37617	-0.00000	1.00099		
N35	0.46596	-0.00000	0.57738		
S36	0.57662	-0.00000	0.61474		

Table S1. Atomic coordinates of AA-stacking mode of the simulated HIAM-0026.

N37	0.55456	-0.00000	0.50026
H38	0.31299	-0.00000	0.23001
H39	0.2305	-0.00000	0.30123
H40	0.61379	-0.00000	0.40945
H41	0.61416	-0.00000	0.15666
H42	0.38134	-0.00000	0.16118
H43	0.15244	-0.00000	0.35928
H44	0.11658	-0.00000	0.59188
H45	0.3653	-0.00000	0.61855
H46	0.01357	-0.00000	0.34393
H47	0.50532	-0.00000	1.03111
H48	0.74353	-0.00000	0.47572
H49	0.89491	-0.00000	0.54031
H50	0.88205	-0.00000	0.27602
H51	0.73828	-0.00000	0.21049
H52	0.15971	-0.00000	0.72703
H53	0.21653	-0.00000	0.88614
H54	0.47068	-0.00000	0.9002
H55	0.4162	-0.00000	0.75087

Space group: <i>pm</i> a = 16.7604 Å, b = 3.4336 Å, and c = 17.6106 Å. α = γ = 90°, and β =115.2181°				
Atom	X	У	Z	
C1	0.46804	-0.00000	0.42068	
C2	0.42437	-0.00000	0.33134	
C3	0.33152	-0.00000	0.29732	
C4	0.28575	-0.00000	0.34732	
C5	0.3287	-0.00000	0.43611	
C6	0.42237	-0.00000	0.47062	
C7	0.47066	-0.00000	0.27299	
C8	0.27482	-0.00000	0.48786	
С9	0.56377	-0.00000	0.30419	
C10	0.60799	-0.00000	0.2523	
C11	0.55634	-0.00000	0.16636	
C12	0.46434	-0.00000	0.13093	
C13	0.42215	-0.00000	0.18417	
C14	0.18218	-0.00000	0.44851	
C15	0.13164	-0.00000	0.49457	
C16	0.17248	-0.00000	0.58135	
C17	0.26438	-0.00000	0.62473	
C18	0.31341	-0.00000	0.57639	
C19	0.70752	-0.00000	0.28649	
C20	0.30927	-0.00000	0.71939	
N21	0.03758	-0.00000	0.45588	
N22	0.41254	-0.00000	0.04103	
C23	0.76222	-0.00000	0.37388	
C24	0.85354	-0.00000	0.4043	
C25	0.89309	-0.00000	0.34867	
C26	0.84124	-0.00000	0.2629	
C27	0.75044	-0.00000	0.23206	
C28	0.26101	-0.00000	0.76905	
C29	0.30408	-0.00000	0.85673	
C30	0.39596	-0.00000	0.89647	
C31	0.44413	-0.00000	0.84871	
C32	0.40226	-0.00000	0.76244	
C33	0.98822	-0.00000	0.37813	
C34	0.44676	-0.00000	0.9871	
N35	0.47597	-0.00000	0.55311	
S36	0.58926	-0.00000	0.5755	

Table S2. Atomic coordinates of AA-stacking mode of the simulated HIAM-0026v.

N37	0.55594	-0.00000	0.46584
H38	0.29036	-0.00000	0.23104
H39	0.21548	-0.00000	0.31211
H40	0.60388	-0.00000	0.36855
H41	0.58846	-0.00000	0.12685
H42	0.35139	-0.00000	0.15318
H43	0.14806	-0.00000	0.3822
H44	0.1298	-0.00000	0.61285
H45	0.38168	-0.00000	0.60876
H46	0.73758	-0.00000	0.42111
H47	0.89305	-0.00000	0.47154
H48	0.8711	-0.00000	0.21908
H49	0.71777	-0.00000	0.16482
H50	0.19014	-0.00000	0.74246
H51	0.26576	-0.00000	0.89309
H52	0.51565	-0.00000	0.8783
H53	0.44663	-0.00000	0.73301
H54	0.01284	-0.00000	0.32966
H55	0.51642	-0.00000	1.00573

COFs	illumination	sacrificial agent	co-catalyst	AQY (%)	H ₂ Evolution Rate $(mmol \cdot g^{-1} \cdot h^{-1})$	Ref
CTF- BT/Th-1	λ≥420 nm	TEOA	3 wt% Pt	7.3 (420 nm)	6.6	1
BT-TAPT- COF	λ≥420 nm	AA	8 wt% Pt	0.19 (410 nm)	0.949	2
Py-ClTP- BT-COF	λ>420 nm	AA	5 wt% Pt	8.45 (420 nm)	8.875	
Py-FTP- BT-COF	$\lambda > 420 \text{ nm}$	AA	5 wt% Pt		2.875	3
Py-HTP- BT-COF	λ>420 nm	AA	5 wt% Pt		1.078	
COF-F	AM 1.5	AA	3 wt% Pt	0.29 (500 nm)	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	0.4 (420 nm)	0.75	5
NKCOF- 108	$\lambda > 420 \text{ nm}$	AA	5 wt% Pt	5.92 (520 nm)	11.6	6
30%PEG@ BT-COF	$\lambda > 420 \text{ nm}$	AA	3.7 wt% Pt	11.2 (520 nm)	11.14	7
USTB-7	λ≥420 nm	AA	3 wt% Pt		4.3	•
USTB-8	λ≥420 nm	AA	3 wt% Pt		13.7	. 0
TeTz-COF1	$\lambda > 420 \text{ nm}$	AA	4 wt% Pt	3.5 (475 nm)	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-	2 > 420	AA	5 wt% Pt		1.41	11
0001	$\lambda > 420 \text{ nm}$	TEOA	12 wt% Pt		1.217	
Py-N-DBT- COF	$\lambda > 420 \text{ nm}$	AA	5 wt% Pt		0.82	12
Py-C-DBT- COF	$\lambda > 420 \text{ nm}$	AA	5 wt% Pt	8.65 (450 nm)	21.37	12
HIAM- 0011	$\lambda > 420 \text{ nm}$	AA	1 wt% Pt	9 (450 nm)	16.98	13
HIAM- 0026	λ >420 nm	AA	3 wt% Pt	1.96 (450 nm)	14.09	This work

Table S3. The summary of benzothiadiazole-based COFs for photocatalytic hydrogen generation performance.

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