Electronic Supplementary Information

Lateral functionalization of a one-dimensional covalent organic framework for efficient photocatalytic hydrogen evolution from water

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Section A. General Information.

Chemicals and materials

All the reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise mentioned. 1,2-Dichlorobenzene (*o*-DCB), *n*-butanol (*n*-BuOH), 1,4-dioxane (Diox), mesitylene (Mes), tetrahydrofuran (THF), and *N*, *N*-dimethylacetamide (DMAc), methanol (MeOH), *N*, *N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), acetonitrile (ACN), dimethyl sulfoxide (DMSO), 1,3-dimethyl-2-imidazolidinone (DMI), ethanol (EtOH), hexamethylphosphoramide (HMPA), *N*-methylformamide (NMF), and tetramethylene sulfone (TMSF) were purchased from Energy Chemical. Dichloro (1,5-cyclooctadiene) platinum (II) ($Pt(COD)Cl_2$), L-ascorbic acid (AA), triethanolamine (TEOA), 2-hydroxypropanoic acid (LA), and acetic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water was purchased from Shanghai Titan Scientific Co., Ltd. 4,4',4",4"'-(Pyrene-1,3,6,8-tetrayl) tetra aniline (Pyr-NH_2) and 5'-([2,2':6',2"-terpyridin]-4'-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (Tpy-CHO) were synthesized by Suzuki-Miyaura reaction, and most of the raw materials used were purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd.

Instruments

Powder X-ray diffraction (PXRD) measurements were carried out with an X'Pert PROX system using monochromated Cu/Kα (λ = 0.1542 nm). The sample was spread on the square recess of a XRD sample holder as a thin layer. Fourier transform infrared (FT-IR) spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets. Solid state ^{13}C cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy was carried out on an Agilent DD2 600 Solid NMR System with 3.2 mm zirconia rotors. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 instrument. Nitrogen adsorption-desorption isotherm measurements were carried out using a Quantachrome autosorb iQ automatic volumetric instrument. Before gas

adsorption measurements, the as-prepared samples (~50 mg) were activated by being immersed in anhydrous dioxane for 12 hours. The solvent was decanted and the samples were dried under dynamic vacuum at 150 ℃ for 3 hours. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the nonlocal density functional theory (NLDFT), the pore size distributions were derived from the sorption curves. The Hartmann-Hahn conditions of the CP experiment were obtained at 8 kHz MAS spinning speed with a contact time of 1 ms. Recycle delay times are 2 seconds. X-ray photoelectron spectroscopy was performed using a Shimadzu-Kratos AXIS Ultra electron spectrometer (Al Kα X-ray source, 1486 eV) with a multi-detector analyzer. The spectra were collected at 15 kV, 10 mA and 9-10 Pa residual pressure. Thermogravimetric analyses (TGA) were performed on a Waters TGA Q500 or a NETZSCH STA 449 F3 Thermal Analyzer. Samples were well dried prior to thermogravimetric analysis. Tests were carried out under an N_2 atmosphere at a ramp rate of 10 °C/min. The tests range from room temperature to 900 °C. Elemental analysis (EA) data collected by Elementary Vario EL II. The X-ray Photoelectron Spectroscopy (XPS) tests data collected by Thermo Scientific K-Alpha.

Structural simulations and powder X-ray diffraction analysis

The Pawley refinement of the experimental PXRD patterns was conducted with the Reflux module in the Materials Studio 7.0 (Accelrys Inc.). Before the simulations, the structure was firstly optimized in Gaussian 09 package by semiempirical calculations at PM3 level. The simulations of the possible structures were carried out in Accelrys Materials Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. P1 space group was chosen for the primitive models in the initial simulations.

Theoretical calculations

The electrostatic potential surfaces of Tpy-COF, Pt-Tpy-COF, and H_2O model

systems were analyzed using density functional theory (DFT) calculations with the Dmol3 software in Materials Studio software 7.0. The exchange-correlation energy was calculated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional, a TS custom method for DFT-D correction was used to accurately describe van der Walls interactions.

Photocatalytic hydrogen evolution reaction measurements

The COFs were ground in a mortar and pestle before testing. Then 5 mg of photocatalyst was dispersed into 12 mL aqueous ascorbic acid solution (0.1 M) and added to the photoreactor. The resulting suspension was ultrasonicated for 30 minutes to obtain a well-dispersed suspension. No additional co-catalyst was added except for the control experiments. The mixture was evacuated several times to completely remove air before irradiation ($\lambda > 400$ nm) under a 300 W Xe lamp and water-cooling filter. The temperature of the reaction solution was kept at room temperature by flow of cooling water. The generated gases were analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) with argon as the carrier gas. All photocatalytic experiments were performed in a quartz reaction vessel with a volume of 20 mL.

Cycling experiments

After each photocatalysis, the powder was collected and filtered, and exhaustively washed with EtOH. The resulting solid was dried, and then subjected to Soxhlet extractions with THF and acetone for 24 hours respectively. The solid powder was then dried under vacuum conditions at 120 °C for 4 hours.

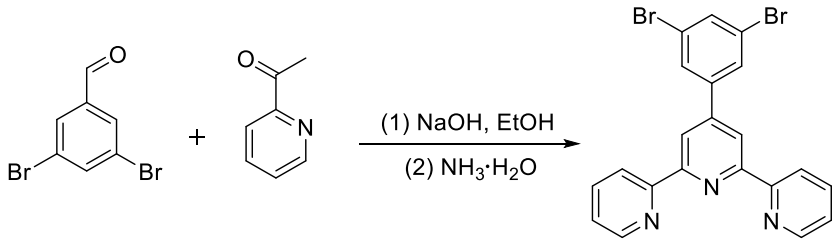
Electrochemical measurements

Indium-tin oxide (ITO) glasses were firstly cleaned by sonication in ethanol and acetone for 30 minutes and dried under nitrogen flow. 5 mg of COF powder was mixed with 450 μL ethanol and ultra-sonicated for 30 minutes to get a slurry. Then 50 μL 5%

Nafion was added into the slurry for another 30 minutes ultra-sonication. The slurry was spreading onto ITO glass. After air drying, the boundary of the electrode was covered with an effective area of 1 cm^2. A conventional three electrodes cell was used with a platinum sheet (1 cm^2) as the counter electrode and an Ag/AgCl electrode (saturated KCl aqueous solution) as reference electrode. The electrolyte was a 0.1 M Na_2SO_4 aqueous solution (pH = 6.8) and was purged with nitrogen gas for 1 hour prior to the measurements. The working electrodes were immersed in the electrolyte for 60 seconds before any measurements were taken. The photocurrent measurements were conducted with a CHI660d workstation, with the working electrodes irradiated from the front side. The visible light was generated by a 300 W xenon lamp (PLS-SXE300+, Beijing Perfectlight Technology Co., Ltd) with a 400 nm cut-off filter, and was chopped manually. For Mott-Schottky experiments, the perturbation signal was 5 mV with the frequency from 500-1500 Hz. The electrochemical impedance spectra (EIS) were performed in dark at open-circuit voltage with AC amplitude of 5 mV in the frequencies range of 0.01 Hz to 10^5 Hz. The applied potentials vs. Ag/AgCl are converted to RHE potentials using the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.0591\text{pH} + E_{\theta Ag/AgCl}$ ($E_{\theta Ag/AgCl}$ = 0.199 V)

Section B. Synthetic Procedures.

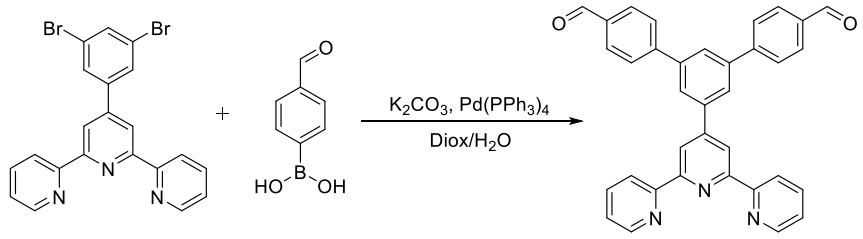
Synthesis of 4'-(3,5-Dibromophenyl)-2,2':6',2''-pyridine [1, 2]



3,5-dibromobenzaldehyde (4.49 g, 17.0 mmol) was added to anhydrous ethanol (600 mL) and stirred to dissolve in a clean vial (1000 mL). Then 2-acetylpyridine (4.12 g, 34.0 mmol) was added dropwise to the vial. After dropping, sodium hydroxide (4.76 g, 119.0 mmol) was added to the reaction solution in batches, and the system was stirred overnight at room temperature. $NH_3 \cdot H_2O$ (1.49 g, 42.5 mmol) was added to the vial

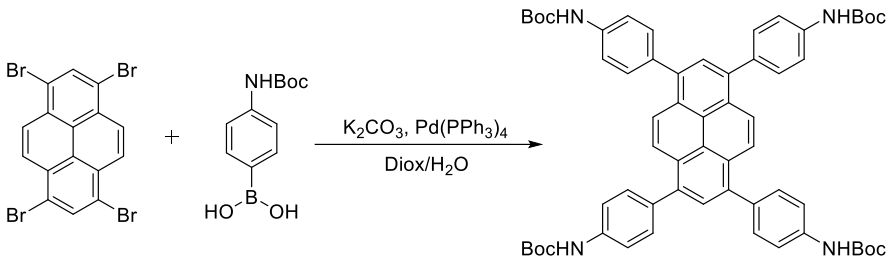
and the reaction was heated to 65 °C for 24 hours. After completion of the reaction, the system was cooled to room temperature, the mixture was filtered and the solid was washed three times with ethanol and distilled water, respectively, and then dried in an infrared oven to give the target product as a white solid (3.53 g, yield 44.4%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79-8.73 (m, 2H), 8.63 (d, J = 9.9 Hz, 4H), 8.08 (s, 2H), 8.06-7.96 (m, 3H), 7.59-7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.27, 155.76, 149.21, 147.72, 142.20, 137.29, 134.53, 129.29, 124.32, 123.71, 121.63, 118.89. MS(EI): m/z 466.0 $[M+1]^+$. HRMS(EI): Calcd. for $C_{21}H_{13}Br_2N_3$ $[M+1]^+$: 465.9476, Found: 465.9538.

Synthesis of Tpy-CHO



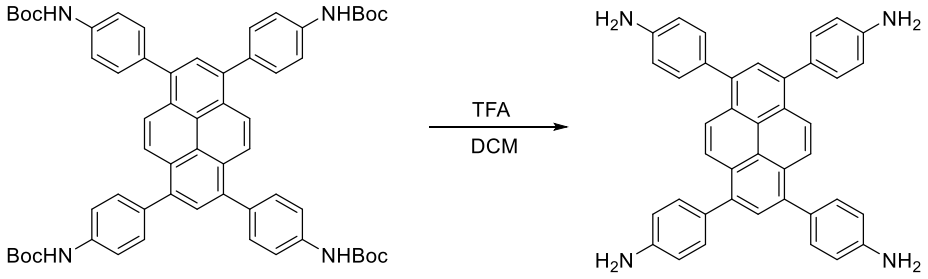
A mixture of 4'-(3,5-dibromophenyl)-2,2':6',2''-pyridine (1.50 g, 3.22 mmol), 4-formylphenylboronic acid (1.20 g, 8.06 mmol), tetrakis(triphenylphosphine)palladium (0.19 g, 0.16 mmol), 1,4-dioxane (120 mL), and distilled water (10 mL) were degased by three freeze-extraction-thaw-backfill cycles of nitrogen under a nitrogen atmosphere and then placed under stirring at 105 °C for 72 hours. After cooling to room temperature, the reaction mixture was filtered through a Brinell funnel. The resulting filter cake was washed successively with distilled water (500 mL), methanol (100 mL), acetone (100 mL), and dichloromethane (100 mL), and then dried in an infrared oven to give Tpy-CHO as a white solid (1.08 g, yield 64.7%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 2H), 8.77 (s, 4H), 8.63 (d, J = 7.9 Hz, 2H), 8.19-8.12 (m, 7H), 8.02 (d, J = 8.0 Hz, 6H), 7.55-7.50 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.81, 155.62, 154.99, 149.30, 148.93, 145.05, 140.65, 139.49, 137.39, 135.44, 130.08, 127.98, 126.90, 125.76, 124.50, 121.02, 118.56. MS(EI): m/z 518.2 $[M+1]^+$. HRMS(EI): Calcd. for $C_{35}H_{23}N_3O_2$ $[M+1]^+$: 518.1790, Found: 518.1857.

Synthesis of Pyr-NHBoc [3]



A mixture of 1,3,6,8-Tetrabromopyrene (1.04 g, 2.00 mmol), 4-(*N*-Boc-amino) benzeneboronic acid (1.91 g, 8.05 mmol), potassium carbonate (2.23 g, 16.10 mmol), tetrakis(triphenylphosphine)palladium (0.12 g, 0. 10 mmol), 1,4-dioxane (120 mL) and distilled water (10 mL) was degassed by three freeze-extraction-thaw-backfill nitrogen cycles under nitrogen atmosphere and then stirred at 105 °C for 72 hours. After cooling to room temperature, the reaction solution was filtered through a Büchner funnel. The filter cake obtained was washed alternately with distilled water (100 mL) and methanol (100 mL), respectively. The resulting solid was recrystallized with ethyl acetate and then dried in an infrared oven to give a pale yellow solid (1.53 g, yield 79.3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 4H), 8.14 (s, 4H), 7.90 (s, 2H), 7.68 (d, J = 8.5 Hz, 8H), 7.58 (d, J = 8.6 Hz, 8H), 1.52 (s, 36H).

Synthesis of Pyr-NH$_2$ [4]



Pyr-NHBoc (1.53 g, 1.58 mmol) was transferred to a 100 mL three-necked flask and dichloromethane (20 mL) was added to dissolve it under stirring conditions. A mixture of trifluoroacetic acid/dichloromethane (1/4, v/v) (10.0 mL) was then added slowly (0.5 hours to complete). The mixture was and stirred at room temperature for 2 hours. The Saturated aqueous $NaHCO_3$ solution was added to adjust the pH of the reaction mixture to 8~10, and extracted with dichloromethane (200 mL × 3). The

organic phase was collected and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was dried in a vacuum oven at 80 °C for 3 hours to give Pyr-NH_2 as a bright yellow solid (0.81 g, yield 89.9%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 4H), 7.78 (s, 2H), 7.34 (d, J = 8.3 Hz, 8H), 6.77 (d, J = 8.4 Hz, 8H), 5.31 (s, 8H).

Section C. Supporting Figures.

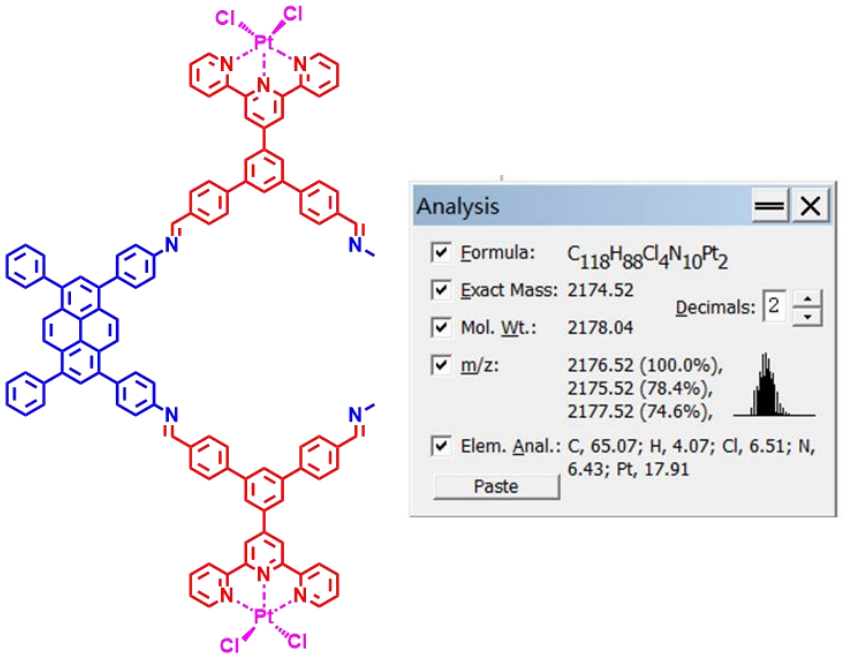


Fig. S1. Unit structure of Pt-Tpy-COF.

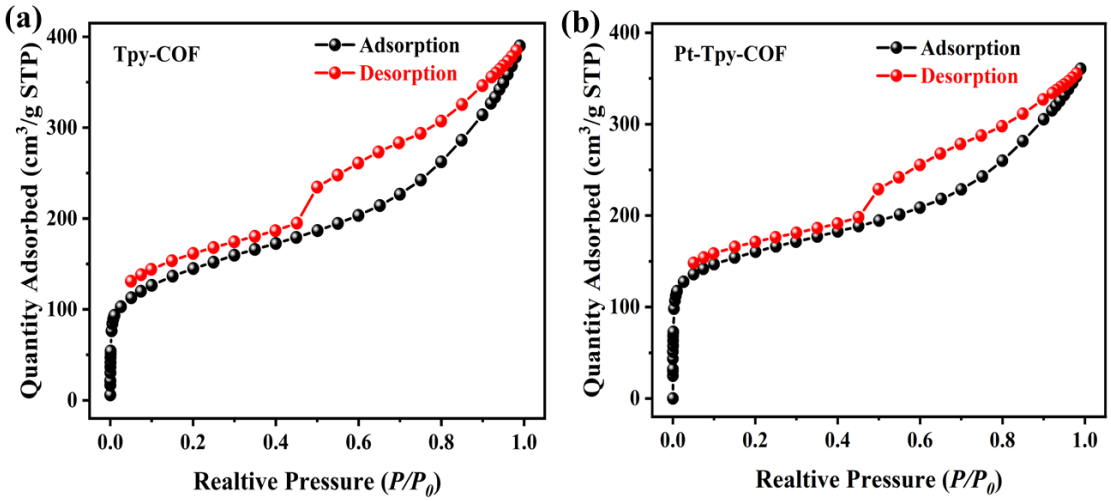


Fig. S2. Nitrogen adsorption and desorption isotherms of (a) Tpy-COF and (b) Pt-Tpy-COF.

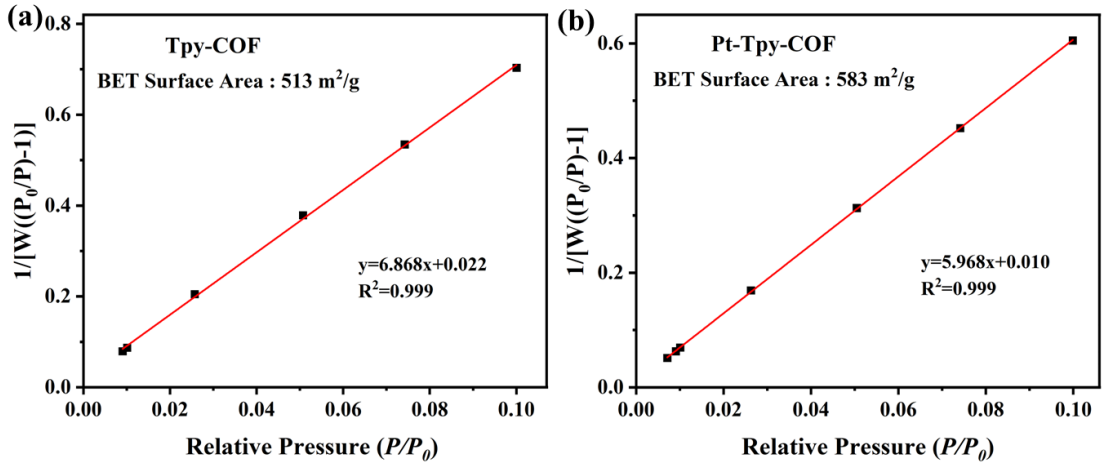


Fig. S3. BET plots of (a) Tpy-COF and (b) Pt-Tpy-COF calculated from N_2 adsorption data (P/P_0 = 0.01-0.10) at 77K.

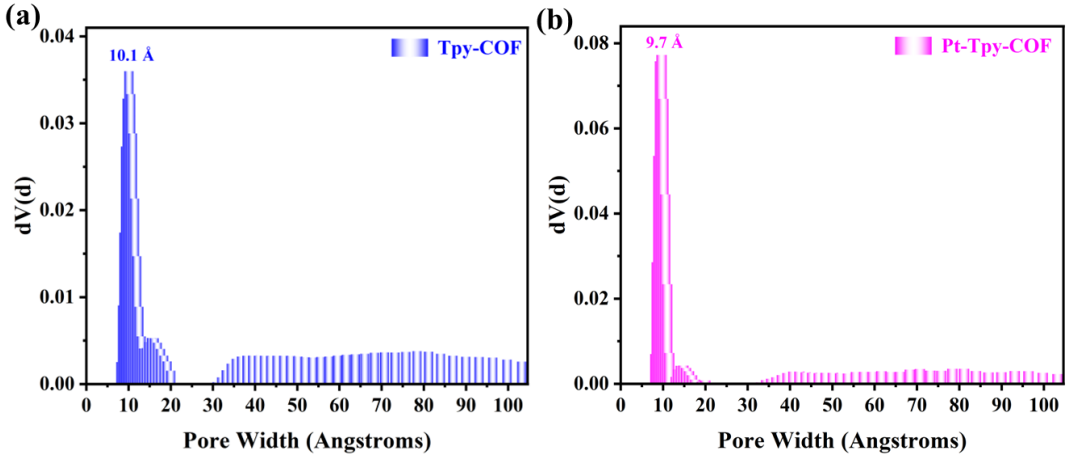


Fig. S4. Pore size distribution profiles of (a) Tpy-COF and (b) Pt-Tpy-COF.

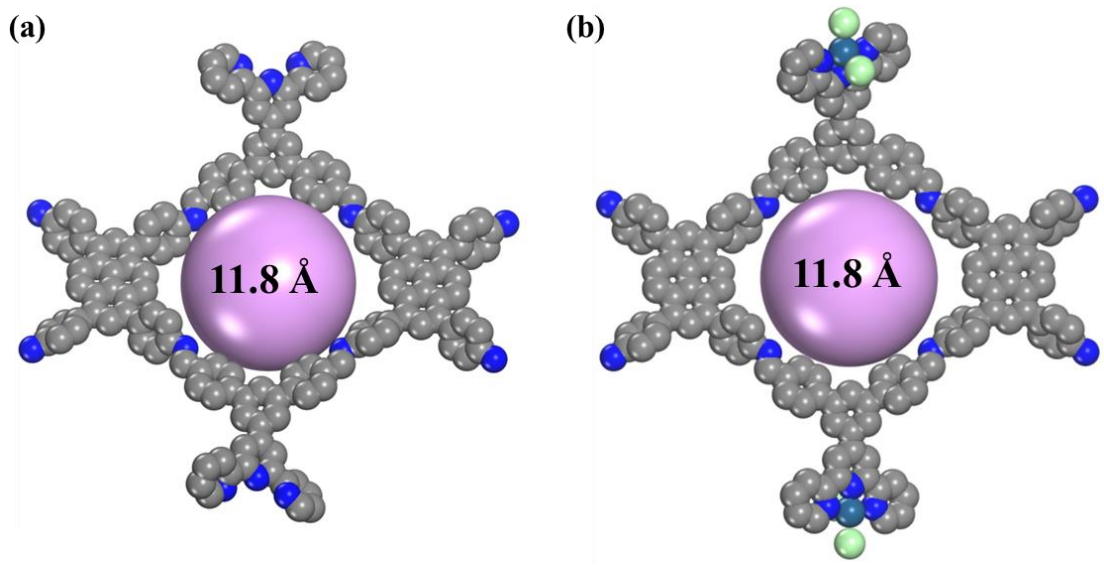


Fig. S5. Theoretical pore size of (a) Tpy-COF and (b) Pt-Tpy-COF.

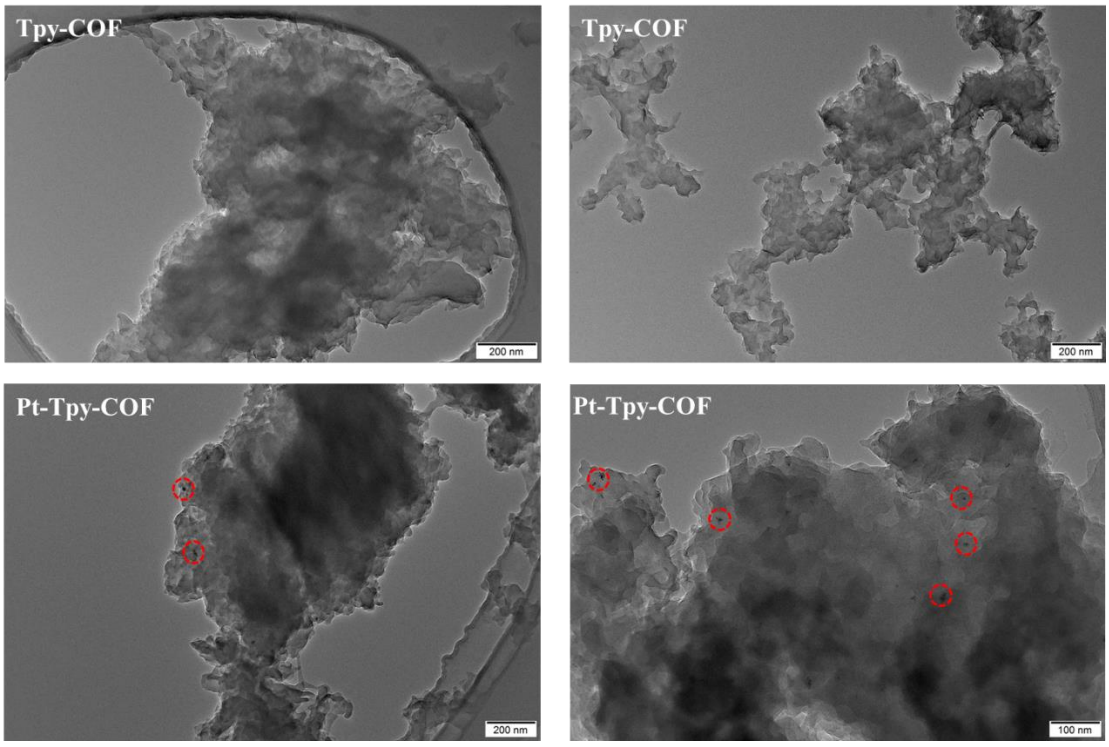


Fig. S6. TEM images of Tpy-COF and Pt-Tpy-COF.

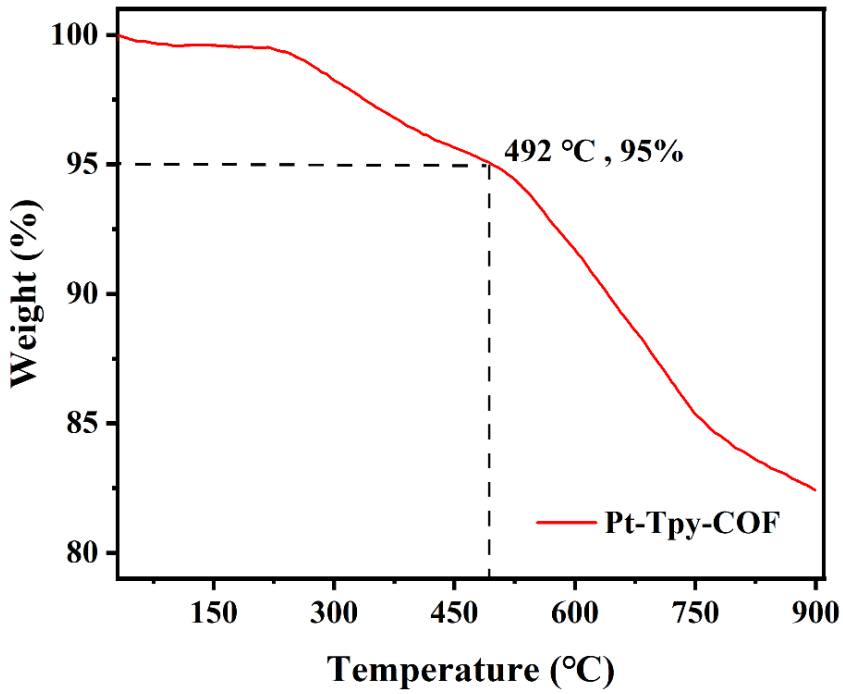


Fig. S7. TGA profile of Pt-Tpy-COF.

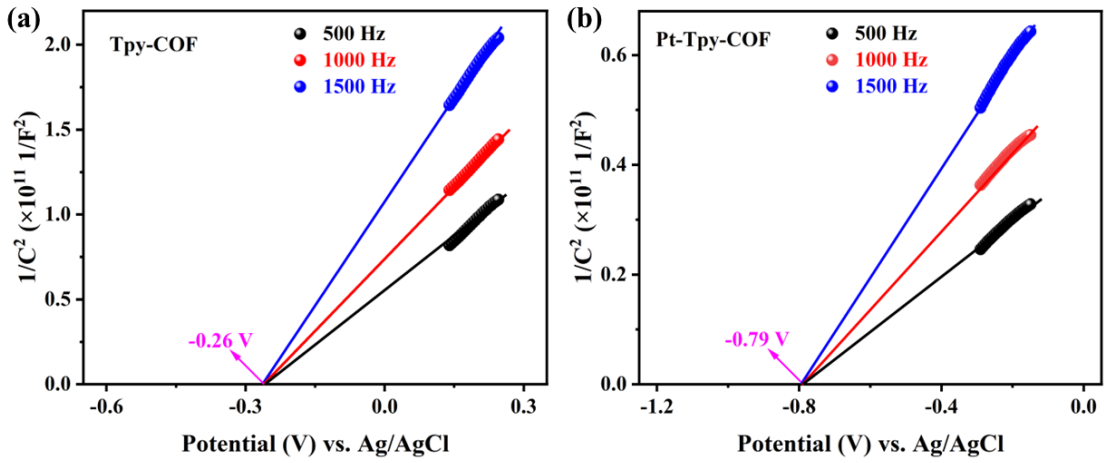


Fig. S8. Mott-Schottky plots of (a) Tpy-COF and (b) Pt-Tpy-COF.

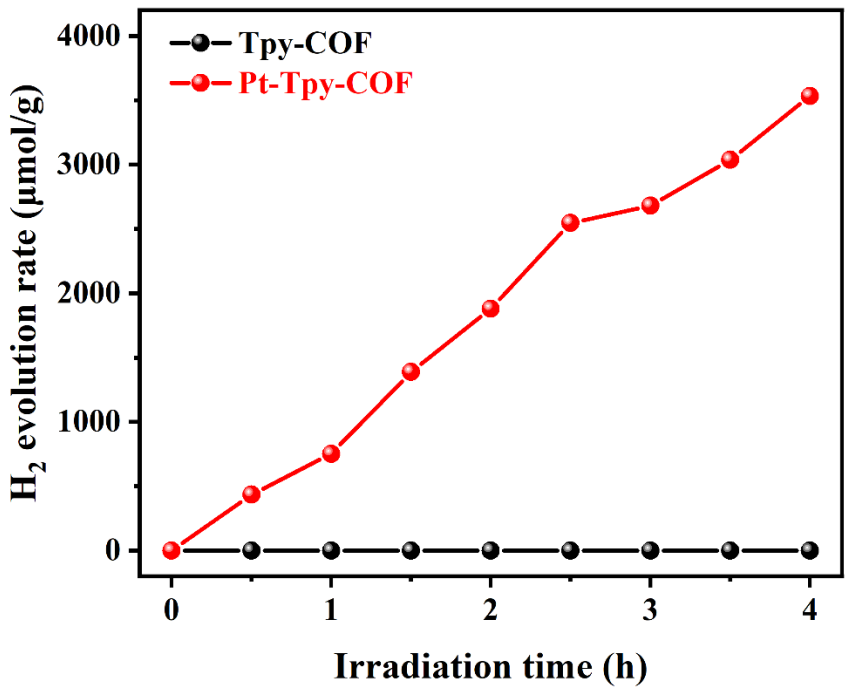


Fig. S9. Time course for hydrogen evolution under visible light (λ > 400 nm) catalyzed by Tpy-COF and Pt-Tpy-COF in the presence of ascorbic acid (AA).

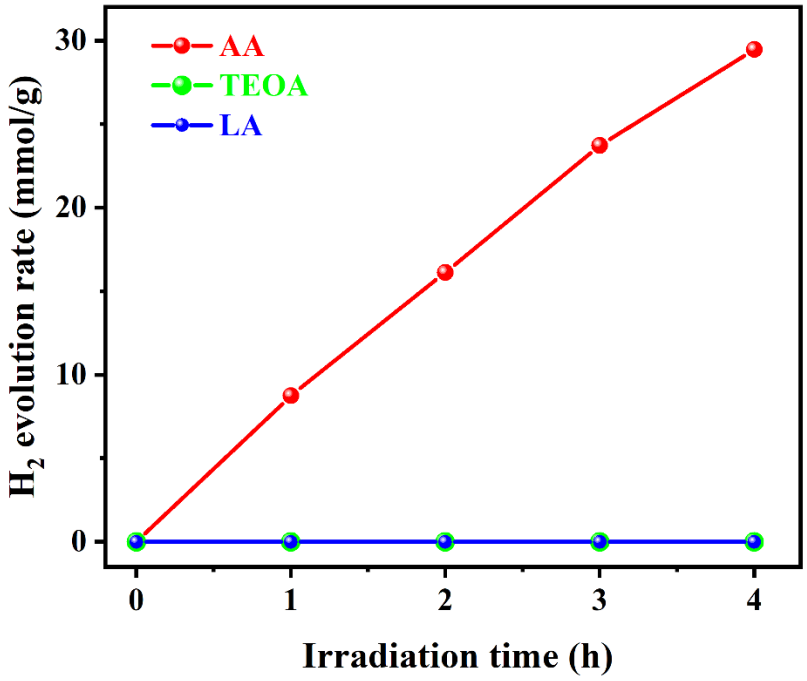


Fig. S10. Time-dependent hydrogen evolution catalyzed by Pt-Tpy-COF with different sacrificial electron donor species.

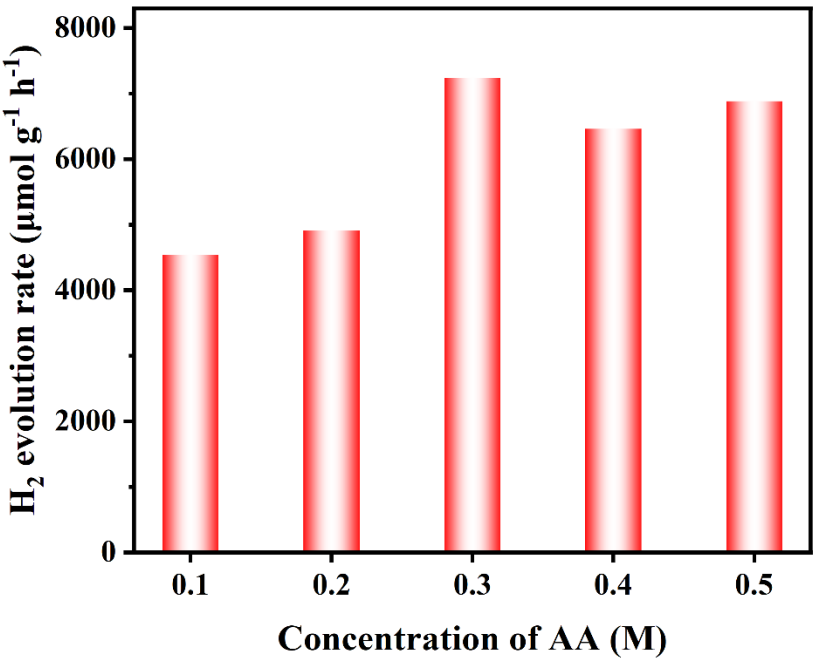


Fig. S11. Comparison of hydrogen evolution rates catalyzed by Pt-Tpy-COF with different concentrations of AA under the mixed solution system of water and NMP.

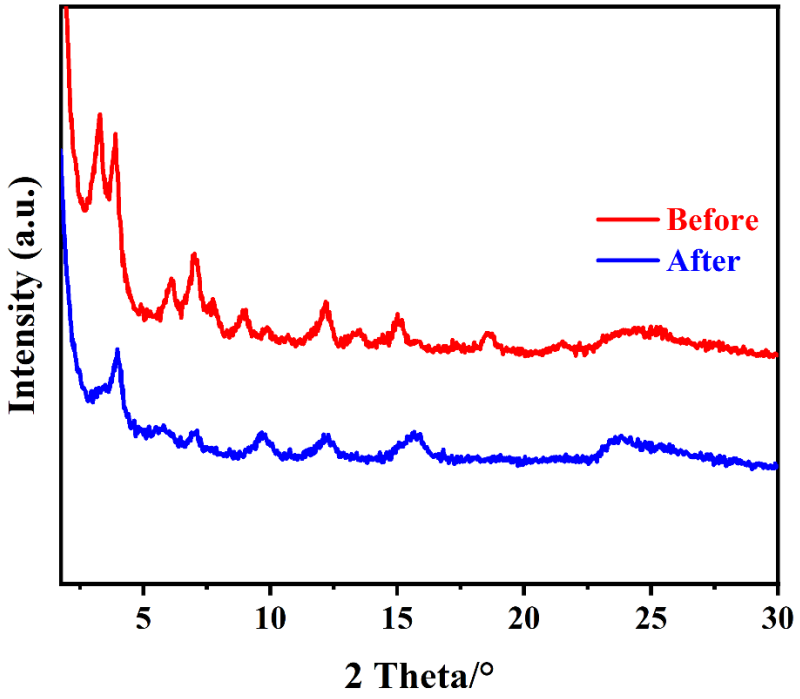


Fig. S12. PXRD patterns of Pt-Tpy-COF before and after photocatalytic hydrogen evolution.

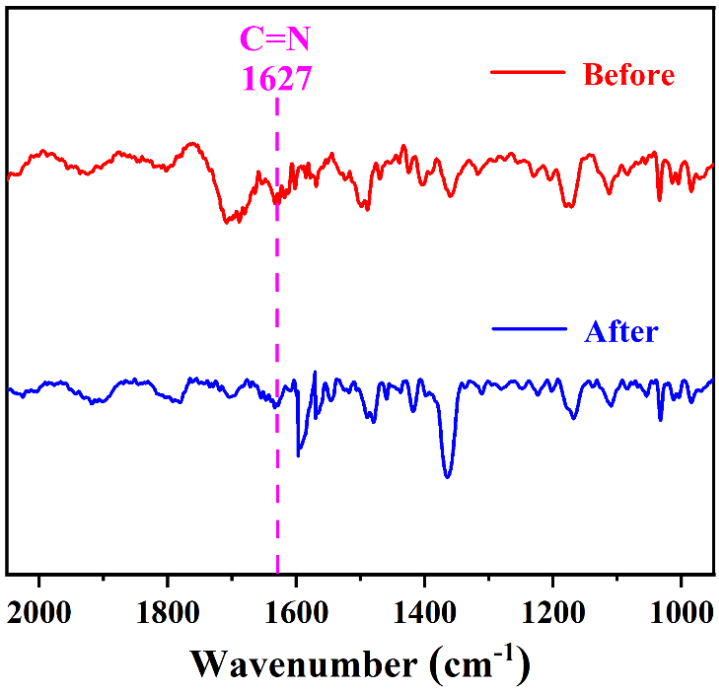


Fig. S13. The FT-IR spectra of Pt-Tpy-COF before and after photocatalytic hydrogen evolution.

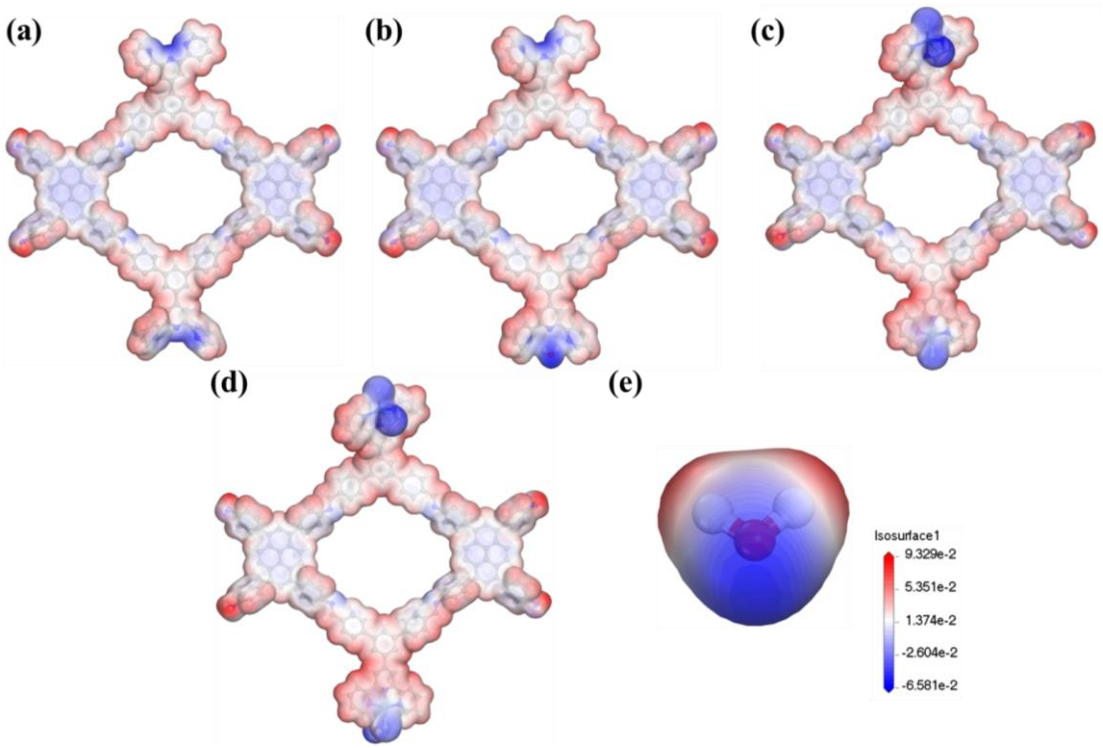


Fig. S14. Electrostatic potential surfaces of the model systems for (a) Tpy-COF, (b) Tpy-COF@H_2O, (c) Pt-Tpy-COF, (d) Pt-Tpy-COF@H_2O and (e) H_2O.

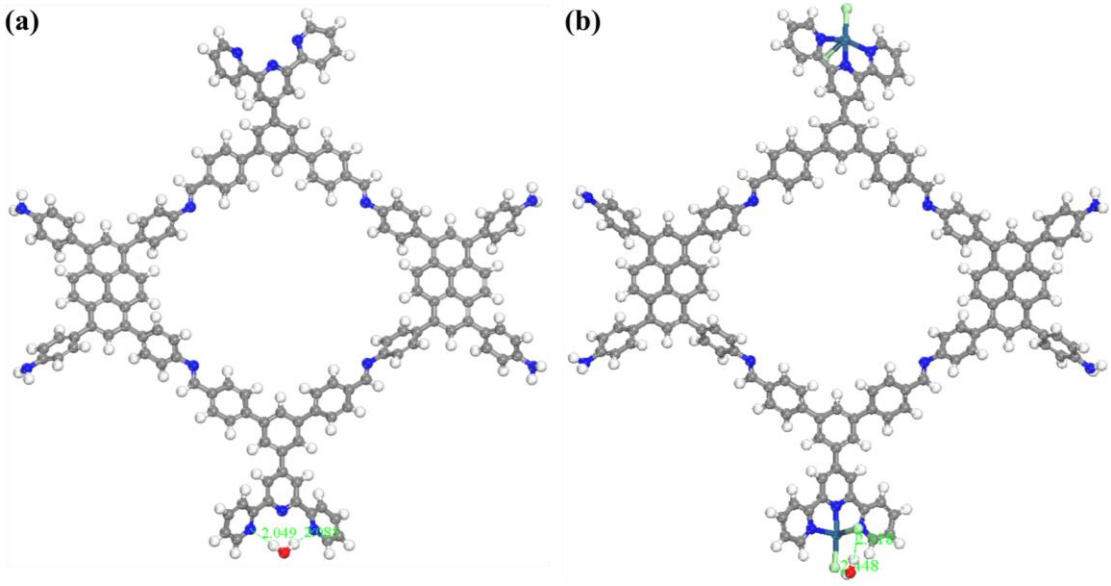


Fig. S15. Adsorption positions of water molecules on (a) Tpy-COF and (b) Pt-Tpy-COF. The blue, gray, white, red, pale green, and deep green spheres represent N, C, H, O, Cl, and Pt atoms, respectively.

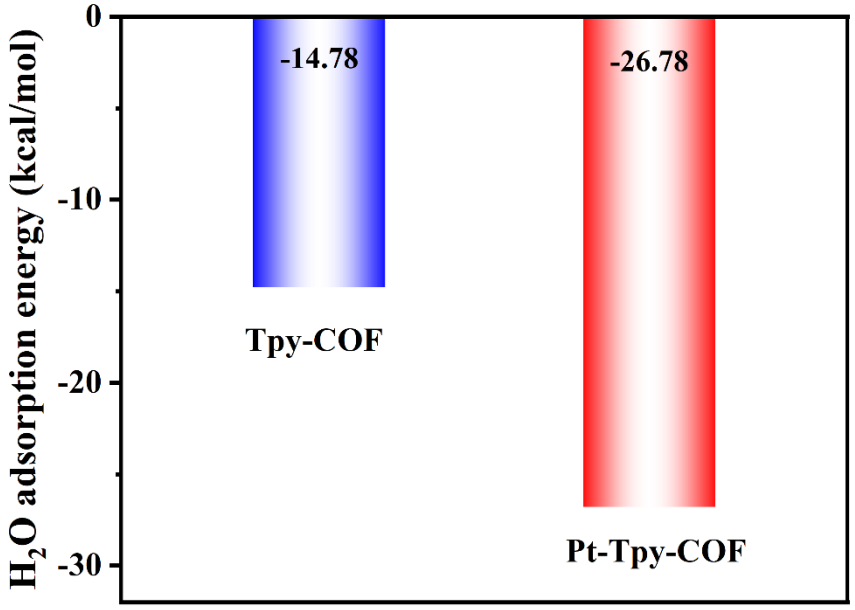


Fig. S16. Adsorption energies for water molecules on Tpy-COF and Pt-Tpy-COF, respectively.

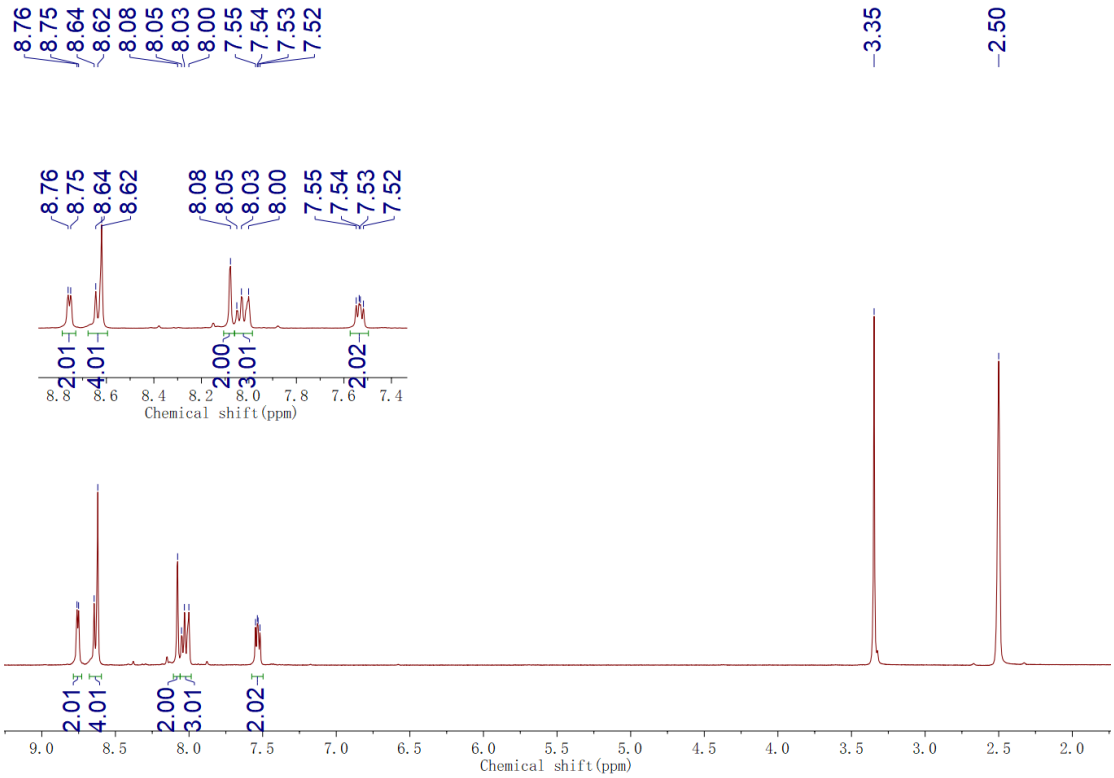


Fig. S17. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 4'-(3,5-dibromophenyl)-2,2':6',2''-terpyridine.

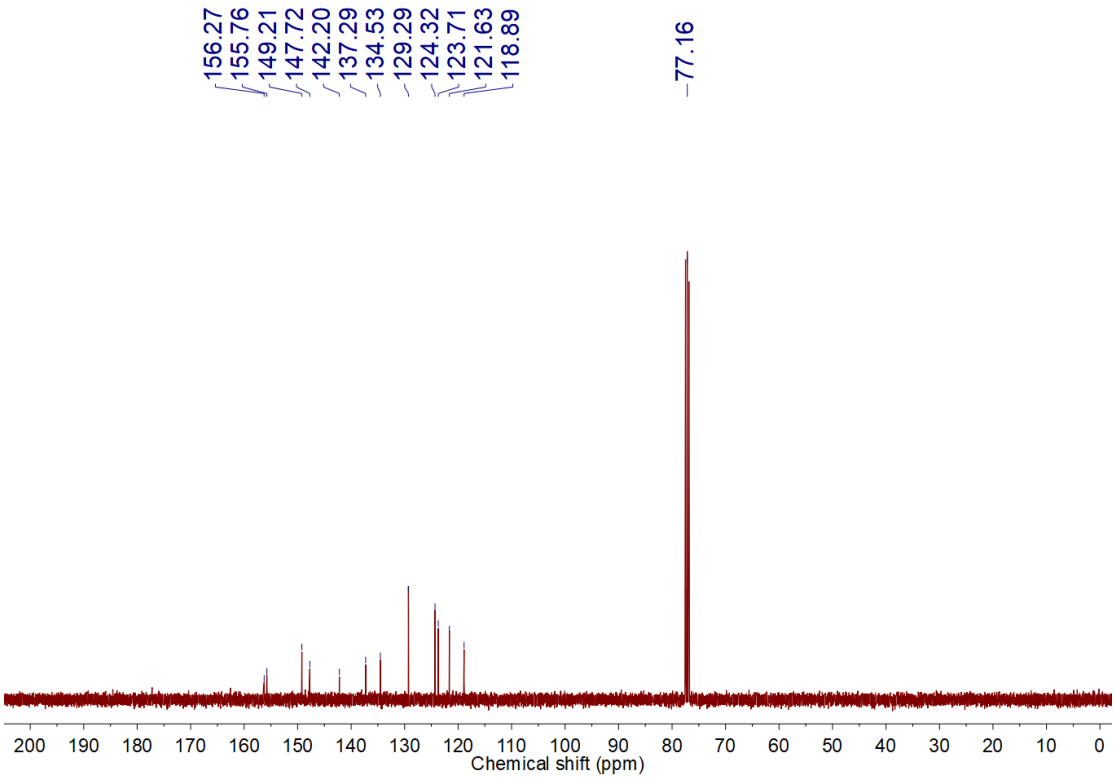


Fig. S18. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4'-(3,5-dibromophenyl)-2,2':6',2''-terpyridine.

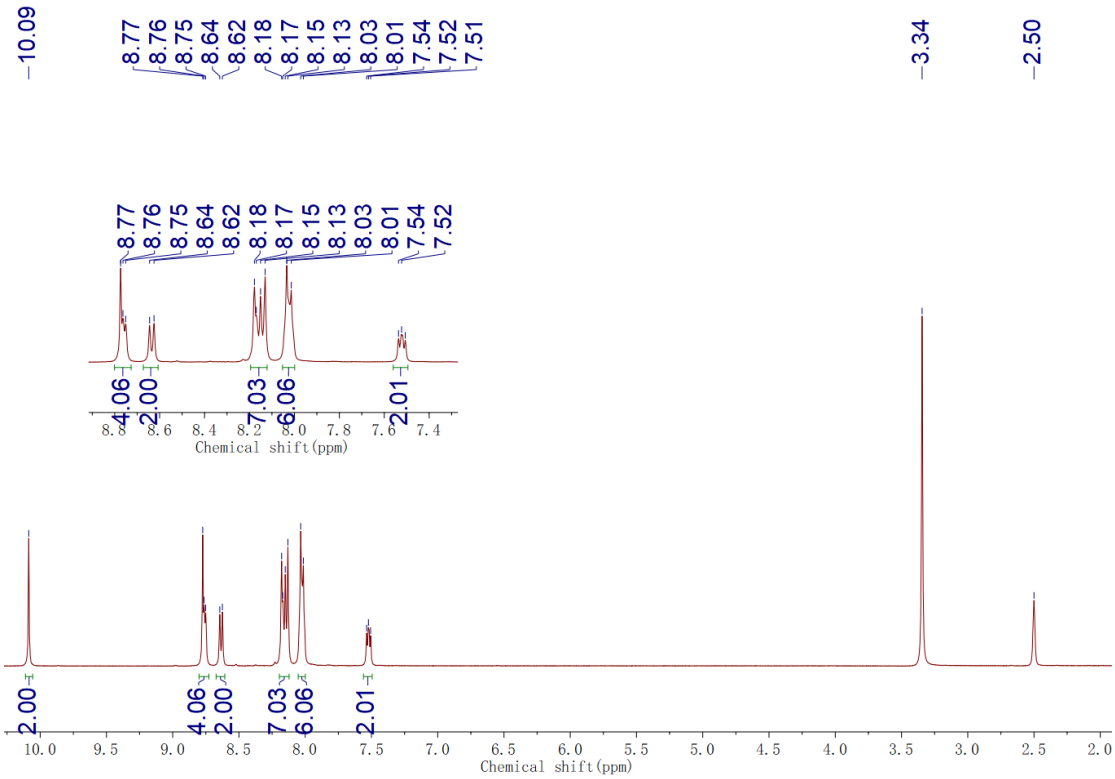


Fig. S19. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of Tpy-CHO.

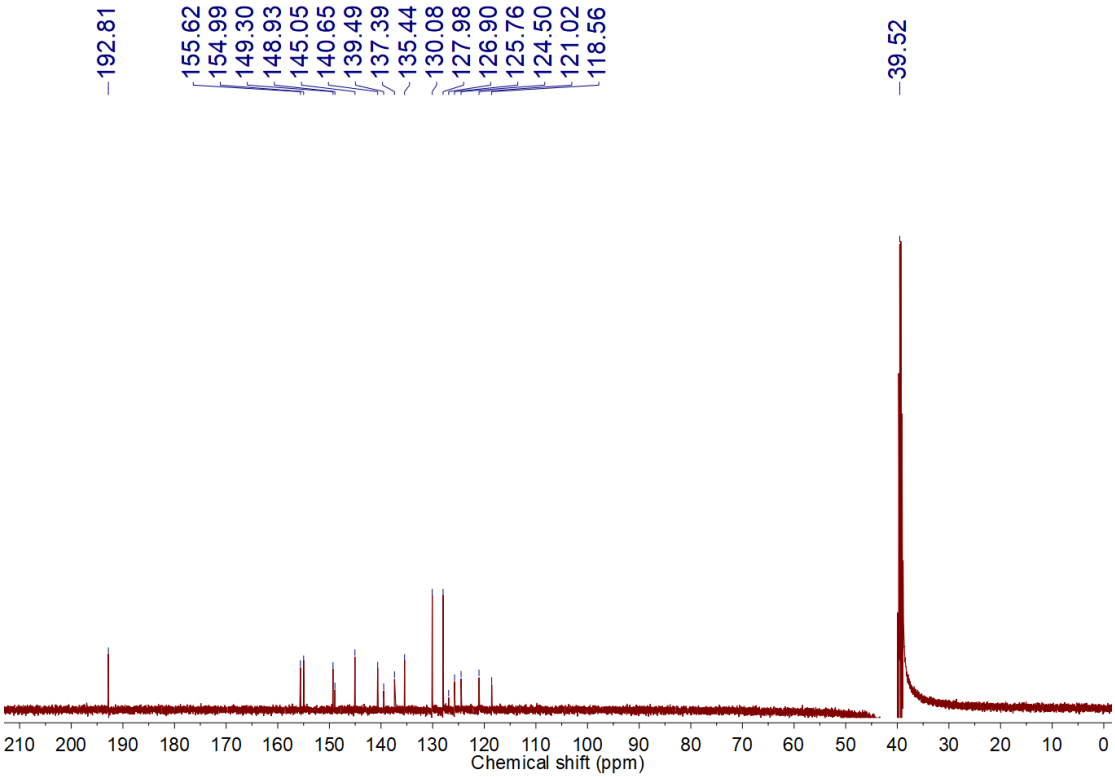


Fig. S20. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of Tpy-CHO.

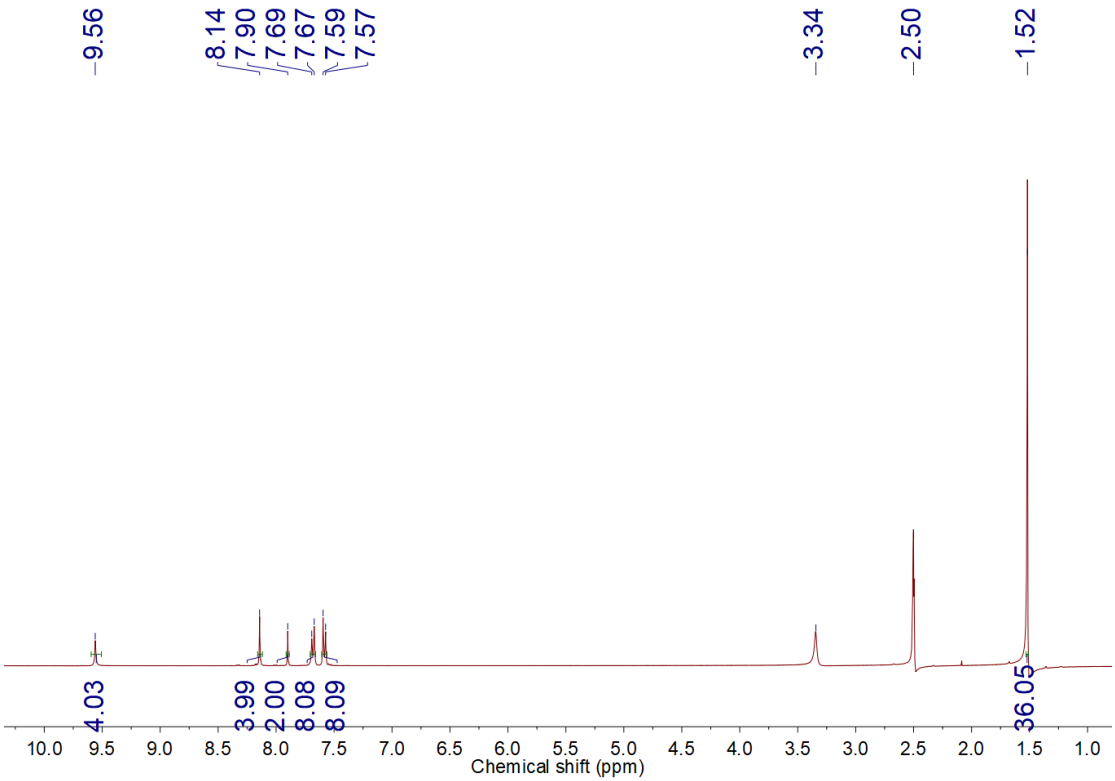


Fig. S21. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of Pyr-NHBoc.

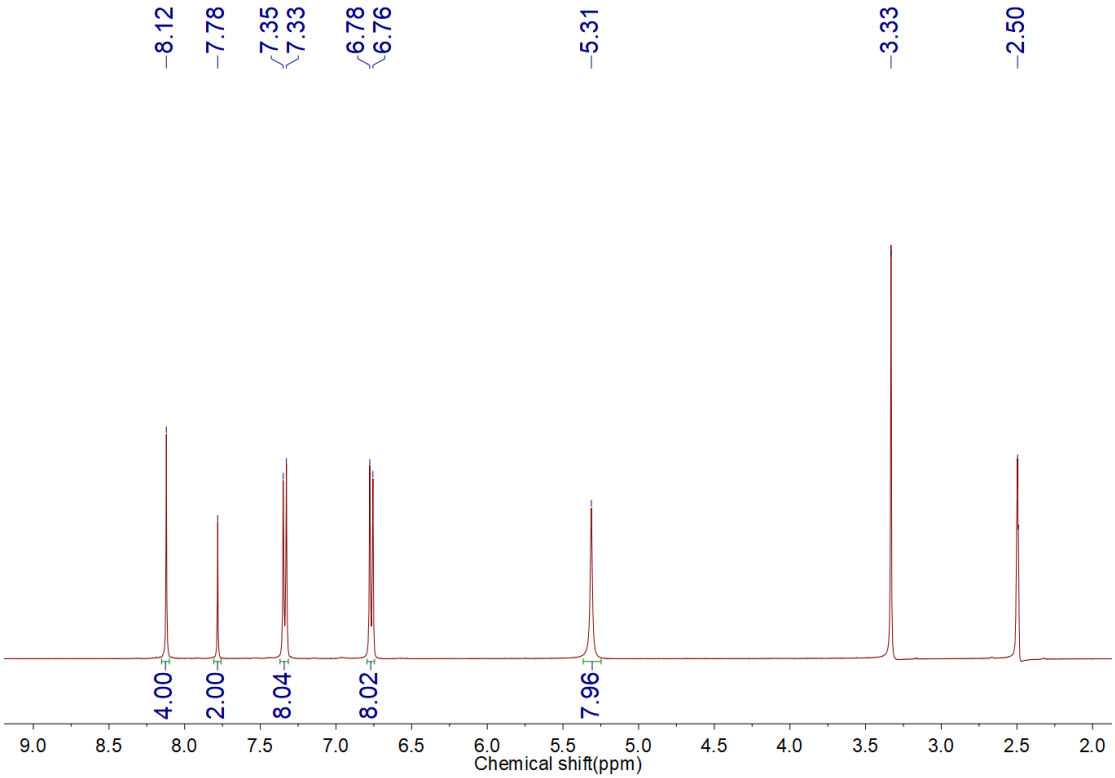


Fig. S22. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of Pyr-NH_2.

Table S1. Elemental Analysis of Pt-Tpy-COF.

Entry		Pt (%)
Pt-Tpy-COF	Theoretical	17.91
	Experimental	8.44

Table S2. Comparison of the photocatalytic hydrogen evolution properties of other COF photocatalysts.

COFs	**SED**	**Co-catalyst**	**HER (mmol g^{-1} h^{-1})**	**Light**	**Ref.**
BTT-PDA	AA	H_2PtCl_6	2.04	$\lambda > 420$ nm	5
BTT-BPhDA			3.27		
BTT-AnthDA			4.23		
BTT-NDA			5.22		
COF-H	AA	H_2PtCl_6	5.03	AM 1.5	6
COF-F			10.58		
COF-Cl			5.84		
PyPz-COF	AA	H_2PtCl_6	7.54	$\lambda > 420$ nm	7
PyTp-COF			1.71		
Zn-Por-TT COF	AA	K_2PtCl_6	8.2	$\lambda > 400$ nm	8
PETZ-COF	AA	H_2PtCl_6	7.32	$\lambda > 420$ nm	9
BTT-BpyDAN-COF	TEOA	H_2PtCl_6	10.1	$\lambda \geq 420$ nm	10
BTT-PDAN-COF			3.9		
COF-OH-0	AA	H_2PtCl_6	0.11	$\lambda \geq 420$ nm	11
COF-OH-2			2.91		
COF-OH-3			9.89		
DABT-Py-COF	AA	H_2PtCl_6	5.458	AM 1.5	12
TTh-COF	AA	H_2PtCl_6	22.22	$780 \geq \lambda \geq 420$ nm	13
Th-COF			15.58		
Ph-COF			3.48		
Zi-VCOF-1	AA	H_2PtCl_6	13.547	$\lambda > 420$ nm	14
Zi-VCOF-2			5.057		
BTTh-TZ-COF	AA	H_2PtCl_6	5.22	$\lambda > 420$ nm	15
TThB-TZ-COF			1.03		
TeTpb-COF	AA	H_2PtCl_6	21.6	$\lambda > 420$ nm	16
TeTf-COF			2.4		
TeTt-COF			0.2		
Pt-Tpy-COF	AA	—	7.8	$\lambda > 400$ nm	**This work**

SED: sacrificial electron donor; **HER**: hydrogen evolution rate; **AA**: ascorbic acid; **TEOA**: triethanolamine; **AM 1.5**: air mass 1.5.

Table S3. Fractional atomic coordinates for the unit cell of Tpy-COF with AA stacking.

P1									
a = 29.83 Å, b = 24.11 Å, c = 4.14 Å, $\alpha = \beta = 90°$, $\gamma = 114.48°$									
Element	Number	x	y	z	Element	Number	x	y	z
C	1	2.3759	-2.50578	-0.04454	N	95	1.82487	-3.18362	-0.33075
C	2	2.4285	-2.47851	-0.04057	N	96	1.83787	-3.30621	-1.1884
C	3	2.45529	-2.4137	-0.02786	C	97	1.81041	-3.35388	-1.37861
C	4	2.42878	-2.3762	-0.01822	C	98	1.8317	-3.39134	-1.50505
C	5	2.37627	-2.40224	-0.03296	C	99	1.88079	-3.37895	-1.42947
C	6	2.35171	-2.46633	-0.02857	C	100	1.90797	-3.3289	-1.23144
C	7	2.45623	-2.5137	-0.05345	C	101	1.87087	-3.14169	-0.40873
C	8	2.50725	-2.48751	-0.02515	C	102	1.88603	-3.29082	-1.11099
C	9	2.53475	-2.42388	-0.03976	C	103	1.95458	-3.13277	-0.54067
C	10	2.50833	-2.38625	-0.03495	C	104	1.90291	-3.16155	-0.57472
C	11	2.53511	-2.3214	-0.04779	N	105	1.88426	-3.21241	-0.76205
C	12	2.50722	-2.28635	-0.04483	C	106	1.91092	-3.23807	-0.92102
C	13	2.45642	-2.31263	-0.00069	C	107	1.9627	-3.20886	-0.8883
C	14	2.58712	-2.39784	-0.06445	C	108	2.13808	-2.97293	-0.54187
C	15	2.61178	-2.33381	-0.05871	C	109	2.13927	-3.17665	-0.46437
C	16	2.58771	-2.29416	-0.06641	C	110	1.9851	-3.15631	-0.69514
C	17	2.34543	-2.56931	-0.07944	C	111	2.1387	-3.07472	-0.52594
C	18	2.34687	-2.36874	-0.07422	C	112	2.1138	-3.03688	-0.58121
C	19	2.61627	-2.43131	-0.11571	C	113	2.06321	-3.06513	-0.65957
C	20	2.61837	-2.23073	-0.10745	C	114	2.03658	-3.12891	-0.64677
C	21	2.60161	-2.48014	-0.33939	C	115	2.06235	-3.16479	-0.57111
C	22	2.62933	-2.51438	-0.38797	C	116	2.11389	-3.13909	-0.52087
C	23	2.67479	-2.49802	-0.23214	N	117	2.25722	-2.75607	-0.24424
C	24	2.69109	-2.44822	-0.01674	N	118	2.7004	-2.53079	-0.31346
C	25	2.66201	-2.41599	0.04315	N	119	2.26209	-2.26896	-0.22987

C	26	2.65837	-2.21257	-0.32783	N	120	2.70679	-2.04483	-0.29492
C	27	2.68939	-2.15117	-0.38076	H	121	2.31406	-2.4855	-0.02319
C	28	2.6805	-2.10455	-0.22828	H	122	2.44044	-2.55955	-0.08526
C	29	2.64134	-2.12117	-0.00748	H	123	2.52373	-2.51679	0.00095
C	30	2.61215	-2.1831	0.06083	H	124	2.52265	-2.24052	-0.07613
C	31	2.36124	-2.31884	-0.29142	H	125	2.44011	-2.28349	0.03841
C	32	2.33373	-2.28404	-0.3276	H	126	2.64945	-2.31491	-0.0587
C	33	2.28828	-2.3018	-0.1705	H	127	2.57052	-2.49107	-0.47482
C	34	2.27168	-2.35297	0.03452	H	128	2.61703	-2.55021	-0.54618
C	35	2.30113	-2.38501	0.08726	H	129	2.72385	-2.43527	0.10088
C	36	2.30493	-2.58832	-0.29547	H	130	2.6745	-2.38147	0.20925
C	37	2.27426	-2.65001	-0.34271	H	131	2.66506	-2.24403	-0.46156
C	38	2.28392	-2.69595	-0.18853	H	132	2.71721	-2.14104	-0.54302
C	39	2.32369	-2.67826	0.02808	H	133	2.63474	-2.08795	0.10947
C	40	2.35265	-2.61605	0.09084	H	134	2.58666	-2.19289	0.24148
C	41	2.84012	-2.76887	-0.77474	H	135	2.39203	-2.30738	-0.43089
C	42	2.8855	-2.74176	-0.94043	H	136	2.34592	-2.24707	-0.47816
C	43	2.91033	-2.67795	-0.9816	H	137	2.23869	-2.3661	0.15089
C	44	2.88607	-2.64183	-0.87455	H	138	2.28883	-2.42016	0.24952
C	45	2.83971	-2.66719	-0.72054	H	139	2.29761	-2.55732	-0.42909
C	46	2.81792	-2.73064	-0.66703	H	140	2.2459	-2.66081	-0.50051
C	47	2.95864	-2.65089	-1.11205	H	141	2.33087	-2.71091	0.14649
C	48	2.81825	-2.83186	-0.70293	H	142	2.37892	-2.60525	0.26715
C	49	2.81621	-2.63059	-0.60888	H	143	2.90103	-2.76919	-1.03051
C	50	2.99394	-2.67363	-1.03213	H	144	2.90288	-2.59568	-0.90299
C	51	3.04251	-2.64602	-1.15302	H	145	2.78572	-2.74912	-0.53891
N	52	3.05384	-2.59653	-1.34641	H	146	2.98459	-2.70934	-0.87548
C	53	3.02284	-2.57073	-1.43344	H	147	2.94964	-2.58169	-1.37238
C	54	2.97422	-2.59892	-1.31316	H	148	3.03494	-2.7585	-0.95061

C	55	3.07963	-2.66584	-1.07638	H	149	3.10258	-2.78395	-0.8133
C	56	3.04087	-2.51839	-1.63424	H	150	3.18654	-2.70791	-0.87474
C	57	3.07001	-2.72568	-0.97047	H	151	3.20148	-2.6054	-1.05627
C	58	3.10928	-2.74105	-0.89262	H	152	3.14393	-2.44035	-2.0378
C	59	3.15783	-2.69706	-0.92538	H	153	3.09872	-2.37986	-2.19223
C	60	3.16648	-2.63827	-1.03202	H	154	3.01615	-2.40741	-1.98351
N	61	3.12765	-2.6252	-1.10326	H	155	2.97947	-2.49405	-1.63542
N	62	3.08742	-2.49944	-1.75583	H	156	2.87973	-2.56072	-0.40221
C	63	3.10919	-2.45087	-1.95337	H	157	2.8391	-2.50429	-0.16984
C	64	3.0832	-2.41623	-2.04164	H	158	2.70444	-2.62737	-0.57255
C	65	3.03541	-2.43247	-1.92204	H	159	2.74499	-2.68635	-0.79062
C	66	3.01415	-2.48352	-1.71913	H	160	2.74444	-2.84673	-0.81284
C	67	2.84273	-2.57609	-0.43686	H	161	2.70733	-2.95092	-0.64417
C	68	2.81881	-2.54232	-0.30223	H	162	2.84786	-2.94366	-0.42438
C	69	2.76779	-2.56055	-0.3482	H	163	2.88478	-2.8389	-0.57355
C	70	2.74133	-2.61357	-0.53137	H	164	2.77373	-3.04203	-0.44129
C	71	2.7652	-2.6482	-0.65896	H	165	2.76395	-2.4933	-0.04602
C	72	2.76666	-2.86614	-0.72552	H	166	2.18964	-2.75883	-0.37767
C	73	2.74476	-2.92743	-0.62795	H	167	2.19454	-3.33763	-0.33652
C	74	2.77402	-2.95658	-0.51319	H	168	2.09426	-3.25033	-0.76734
C	75	2.82566	-2.92348	-0.50256	H	169	2.13543	-3.31396	-0.66716
C	76	2.84737	-2.86187	-0.59353	H	170	2.2372	-3.17955	-0.06663
C	77	2.75291	-3.01777	-0.41757	H	171	2.19398	-3.11697	-0.14378
C	78	2.74517	-2.52514	-0.21492	H	172	2.20569	-2.95978	-0.7698
C	79	2.21023	-2.78333	-0.35145	H	173	2.24745	-2.85291	-0.6541
C	80	2.2138	-3.29164	-0.30508	H	174	2.11883	-2.85707	-0.20897
C	81	2.12348	-3.23481	-0.61152	H	175	2.07848	-2.96376	-0.29895
C	82	2.14802	-3.2725	-0.55587	H	176	1.91791	-3.04695	-0.36404
C	83	2.19002	-3.25301	-0.35666	H	177	1.8616	-3.02204	-0.04014

C	84	2.20684	-3.1948	-0.21335	H	178	1.78137	-3.10103	0.09446
C	85	2.18144	-3.15774	-0.26265	H	179	1.75876	-3.20502	-0.09699
C	86	2.18723	-2.93908	-0.64535	H	180	1.77479	-3.36179	-1.42992
C	87	2.21177	-2.87634	-0.5798	H	181	1.81179	-3.42702	-1.65093
C	88	2.18712	-2.84567	-0.41788	H	182	1.89671	-3.40603	-1.51942
C	89	2.13763	-2.8784	-0.32461	H	183	1.94341	-3.32119	-1.17758
C	90	2.11377	-2.94124	-0.38176	H	184	1.97016	-3.09579	-0.39262
C	91	1.8845	-3.0807	-0.30561	H	185	1.98465	-3.22506	-1.00798
C	92	1.85175	-3.06574	-0.11902	H	186	2.17573	-3.05467	-0.48426
C	93	1.80537	-3.11135	-0.04027	H	187	2.04518	-3.03872	-0.72257
C	94	1.79228	-3.17105	-0.1514	H	188	2.04271	-3.21081	-0.54786

Table S4. Fractional atomic coordinates for the unit cell of Pt-Tpy-COF with AA stacking.

P1									
a = 29.71 Å, b = 25.02 Å, c = 3.72 Å, $\alpha = \beta$ = 90°, γ = 113.15°									
Element	Number	x	y	z	Element	Number	x	y	z
C	1	4.17694	1.1594	0.72102	C	96	4.80226	1.62413	0.89662
C	2	4.12847	1.13349	0.84242	C	97	4.77721	1.56557	0.99276
C	3	4.10085	1.07429	0.79228	C	98	4.80003	1.52637	0.95711
C	4	4.12353	1.03905	0.65716	C	99	4.84629	1.34511	0.56828
C	5	4.1729	1.06306	0.54737	C	100	4.84766	1.54494	0.81445
C	6	4.19891	1.12378	0.57256	C	101	4.84696	1.44479	0.68631
C	7	4.20286	1.2238	0.73232	C	102	4.87244	1.40904	0.60719
C	8	4.19669	1.02478	0.40386	C	103	4.92376	1.43437	0.57948
C	9	4.25396	1.25072	0.77812	C	104	4.94958	1.49292	0.66365
C	10	4.27754	1.31139	0.78375	C	105	4.92381	1.52624	0.7735
C	11	4.25016	1.34586	0.75513	C	106	4.87267	1.50425	0.7617
C	12	4.19939	1.31932	0.71747	C	107	4.6491	0.95154	0.44707
C	13	4.17612	1.25918	0.69653	C	108	4.38349	0.80659	0.08469

C	14	4.16856	0.97104	0.24137	C	109	4.39957	0.85726	-0.12685
C	15	4.19	0.93315	0.13447	C	110	4.37439	0.89391	-0.1315
C	16	4.24019	0.94814	0.18047	C	111	4.32941	0.87746	0.04092
C	17	4.26903	1.00239	0.32944	C	112	4.30922	0.82279	0.20884
C	18	4.24745	1.04011	0.4427	C	113	4.33615	0.78804	0.23446
C	19	4.27332	1.40946	0.75149	C	114	4.69516	0.97596	0.27798
C	20	4.26073	0.90486	0.09686	C	115	4.72073	1.03633	0.26541
C	21	4.04718	1.05131	0.83928	C	116	4.70045	1.07316	0.41834
C	22	4.02158	1.0844	0.70322	C	117	4.65495	1.04936	0.5848
C	23	3.97069	1.06113	0.72014	C	118	4.63057	0.98939	0.61117
N	24	3.94826	1.00855	0.86934	N	119	4.3075	0.91903	0.07456
C	25	3.96973	0.97478	1.00505	N	120	4.72597	1.13486	0.41496
C	26	4.02093	0.99557	0.99179	Pt	121	3.8761	0.97572	0.86158
C	27	3.93678	1.08624	0.57185	Pt	122	5.16992	1.62475	0.84759
C	28	3.93435	0.91804	1.14596	H	123	4.11125	1.15955	0.9694
C	29	3.95155	1.14086	0.40803	H	124	4.10202	0.99299	0.63342
C	30	3.91572	1.15816	0.26803	H	125	4.23551	1.14364	0.46358
C	31	3.86624	1.12096	0.28887	H	126	4.27569	1.22508	0.8126
C	32	3.85263	1.06728	0.46243	H	127	4.31691	1.33134	0.81585
N	33	3.88794	1.05187	0.60131	H	128	4.17779	1.34531	0.69338
N	34	3.88586	0.90891	1.11615	H	129	4.13711	1.24072	0.64666
C	35	3.84925	0.85999	1.23602	H	130	4.1298	0.95765	0.19408
C	36	3.86087	0.81595	1.38792	H	131	4.16708	0.89175	0.01786
C	37	3.91003	0.82348	1.41749	H	132	4.30786	1.01462	0.37283
C	38	3.9473	0.87493	1.29799	H	133	4.27043	1.08008	0.5745
C	39	4.6213	1.88699	0.46288	H	134	4.25173	1.43271	0.84103
C	40	4.57007	1.85958	0.39775	H	135	4.23602	0.86013	0.06323
C	41	4.54525	1.79902	0.44949	H	136	4.04095	1.1258	0.57298
C	42	4.57133	1.76631	0.57838	H	137	4.03995	0.96978	1.0948

C	43	4.62319	1.79185	0.60056	H	138	3.98977	1.16934	0.38419
C	44	4.64709	1.85212	0.54746	H	139	3.92637	1.19988	0.13598
C	45	4.54251	1.89089	0.28791	H	140	3.83897	1.13355	0.16672
C	46	4.49264	1.86443	0.23701	H	141	3.81464	1.03817	0.48654
C	47	4.46727	1.8038	0.25655	H	142	3.81165	0.85534	1.21137
C	48	4.49392	1.77098	0.37763	H	143	3.83211	0.77646	1.48188
C	49	4.4693	1.71062	0.44234	H	144	3.91931	0.78968	1.53627
C	50	4.49513	1.68169	0.61543	H	145	3.98518	0.88069	1.32468
C	51	4.54442	1.70922	0.69102	H	146	4.68648	1.87249	0.57358
C	52	4.41619	1.77518	0.17651	H	147	4.55812	1.93688	0.24447
C	53	4.39409	1.7144	0.2134	H	148	4.47531	1.89427	0.19853
C	54	4.4192	1.68164	0.3504	H	149	4.47793	1.63743	0.69957
C	55	4.65324	1.75626	0.65548	H	150	4.56099	1.68466	0.83917
C	56	4.39124	1.61771	0.40608	H	151	4.35602	1.69197	0.13998
C	57	4.63859	1.70037	0.50278	H	152	4.60704	1.68311	0.32928
C	58	4.66446	1.66561	0.5687	H	153	4.65152	1.6223	0.4551
C	59	4.70795	1.68715	0.76338	H	154	4.75762	1.76162	1.06021
C	60	4.72489	1.74419	0.8995	H	155	4.71049	1.82073	0.97226
C	61	4.69761	1.77821	0.84844	H	156	4.32857	1.62694	0.65199
C	62	4.34492	1.59712	0.57031	H	157	4.28512	1.52492	0.77825
C	63	4.31974	1.53795	0.64188	H	158	4.40118	1.4875	0.2895
C	64	4.33998	1.49764	0.54342	H	159	4.44541	1.59012	0.17075
C	65	4.38524	1.51782	0.37051	H	160	5.075	1.41076	1.01804
C	66	4.41028	1.5768	0.29892	H	161	5.14279	1.38826	1.26525
N	67	4.31588	1.43613	0.60435	H	162	5.2248	1.46706	1.35191
N	68	4.73357	1.64965	0.81251	H	163	5.2389	1.56882	1.18636
C	69	5.11066	1.44526	1.05673	H	164	5.21867	1.76146	0.78827
C	70	5.149	1.43256	1.19621	H	165	5.18715	1.83498	0.5719
C	71	5.19532	1.47696	1.24552	H	166	5.10279	1.80271	0.33788

C	72	5.2033	1.53401	1.15126	H	167	5.04936	1.69816	0.32313
N	73	5.16578	1.54515	1.01137	H	168	5.01572	1.44671	0.86832
N	74	5.15283	1.69105	0.65842	H	169	5.00446	1.602	0.42997
C	75	5.18237	1.74819	0.67605	H	170	4.78832	1.13373	0.64902
C	76	5.16456	1.78929	0.55862	H	171	4.80181	1.71101	0.95083
C	77	5.1167	1.77099	0.42808	H	172	4.78147	1.34751	0.31164
C	78	5.08657	1.71188	0.41926	H	173	4.73765	1.24209	0.28811
C	79	5.11986	1.50275	0.96354	H	174	4.86119	1.22055	0.77615
C	80	5.10539	1.67186	0.54073	H	175	4.90392	1.32521	0.82061
C	81	5.03253	1.49098	0.77207	H	176	4.9074	1.61969	0.58591
C	82	5.0831	1.52233	0.80294	H	177	4.86918	1.68771	0.67966
N	83	5.10148	1.57857	0.70806	H	178	4.74032	1.55043	1.09865
C	84	5.07634	1.60845	0.57687	H	179	4.78047	1.48194	1.04383
C	85	5.02609	1.57919	0.53113	H	180	4.80742	1.42631	0.69182
C	86	5.00351	1.52041	0.64349	H	181	4.94369	1.40859	0.49218
C	87	4.7704	1.15984	0.53236	H	182	4.94407	1.57012	0.86756
C	88	4.77884	1.66574	0.9101	H	183	4.4329	0.87039	-0.27708
C	89	4.79904	1.32038	0.41887	H	184	4.38991	0.93513	-0.27139
C	90	4.77409	1.26002	0.40246	H	185	4.27476	0.80928	0.34854
C	91	4.79615	1.22342	0.53268	H	186	4.32138	0.74919	0.39788
C	92	4.84355	1.24792	0.67388	H	187	4.71083	0.94856	0.14766
C	93	4.8682	1.308	0.69459	H	188	4.75544	1.05442	0.12647
C	94	4.8718	1.60376	0.71334	H	189	4.63932	1.07738	0.70802
C	95	4.84983	1.643	0.76271	H	190	4.59663	0.97281	0.75633

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