Supplementary Information for

Construction of porphyrin-based two-dimensional covalent organic frameworks for photocatalytic hydrogen production

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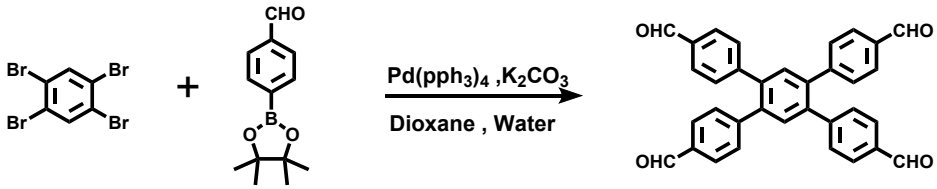
1. Materials and methods

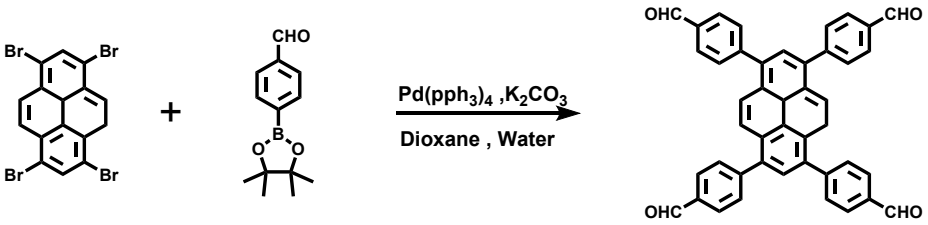
1.1 Materials

Unless otherwise indicated, all chemicals were purchased from a commercial resource without further purification. Column chromatography was carried out on silica gel (200-300 mesh). TLC analysis was performed on precoated silica gel plates (0.2 mm thick). Tetrakis-(triphenylphosphine) palladium (0), 4-formylbenzeneboronic acid, 1,2,4,5-tetrabromo-benzen, N,N'-dimethylacetamide, dioxane, and 1,2-dichlorobenzene were purchased from TCI. Other chemicals were purchased from Sinopharm Co, Shanghai, China.

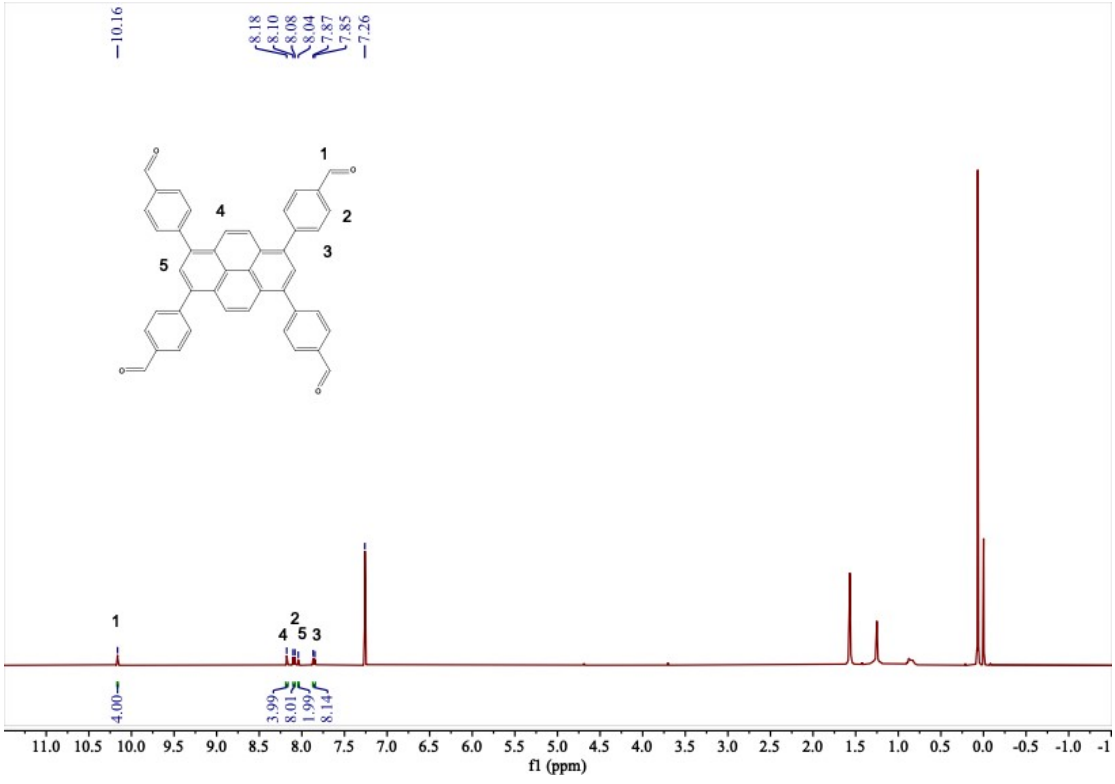
1.2 Synthesis

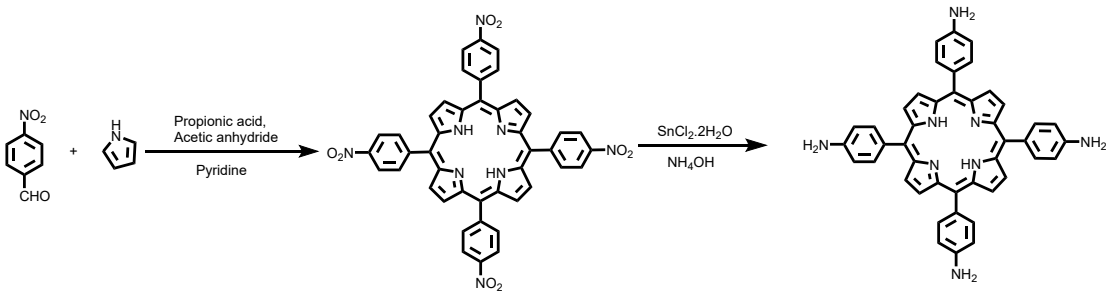


Synthesis of 1,2,4,5-tetrakis-(4-formylphenyl)benzene (TPB). TPB was synthesized according to a modified procedure reported in the literature.[S1] Typically, a mixture of 1,2,4,5-tetrabromo-benzen (0.79 g, 2 mmol), 4-formylphenylboronic acid (1.50 g, 10 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol%), and potassium carbonate (2.1 g, 15 mmol) in dry dioxane (30 mL) was stirred under argon for three days at 90 ℃. After completing the reaction, the mixture underwent 3 extractions with ethyl acetate and water, followed by washing with saturated salt water to eliminate the excess water. Next, the solution was dried by anhydrous magnesium sulphate overnight, and the solvent was then removed by vacuum filtration. The crude product, a grey solid, was subsequently concentrated using the rotary evaporation. The product was purified via column chromatography (petroleum ether/ethyl acetate = 5:1), producing a white solid of 0.853 g (in 86.3% yield).

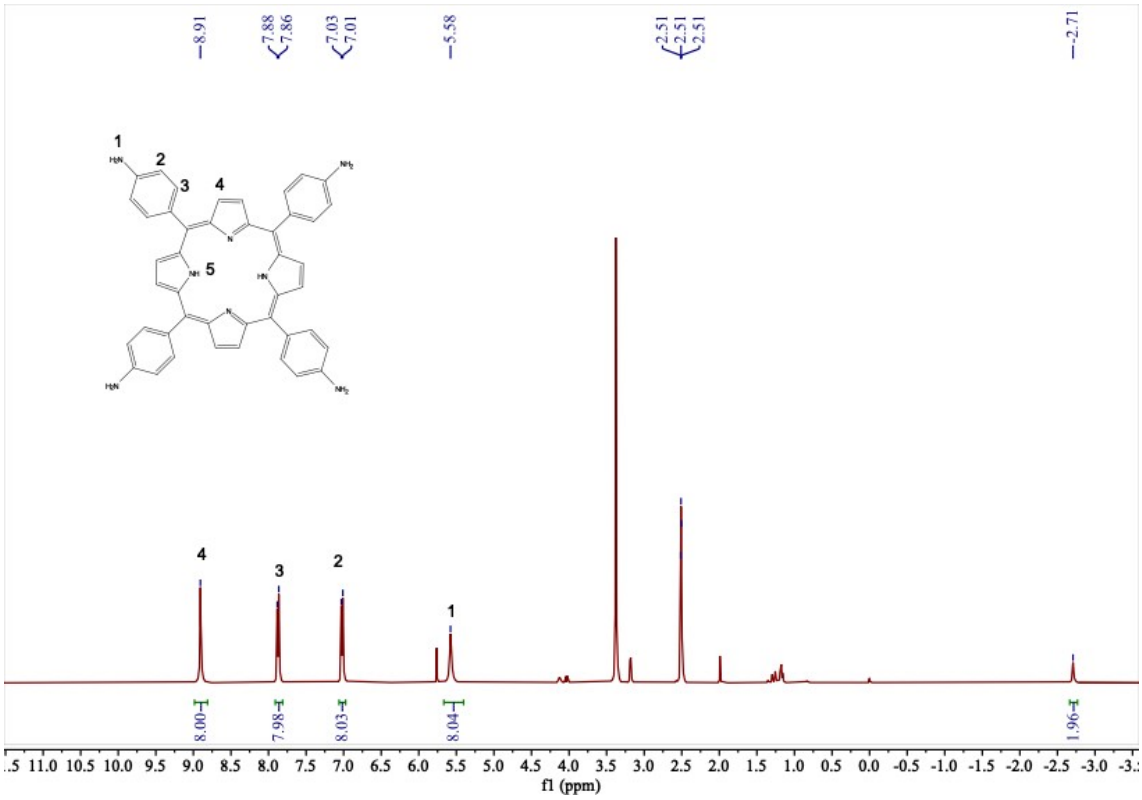


Synthesis of 1,3,6,8-tetrakis(p-formylphenyl)pyrene (TFPPy). TFPPy was synthesized according to a modified procedure reported in the literature.[2] A mixture of 1,3,6,8-tetrabromopyrene (1.00 g, 1.93 mmol), 4-formylphenylboronic acid (1.74 g, 11.6 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol, 5.2 mol%), and potassium carbonate (2.1 g, 15 mmol) in dry dioxane (30 mL) was stirred under argon for three days at 85 °C. Subsequently, the yellow suspension was poured into a solution of ice-cold concentrated hydrochloric acid. The yellow solid was filtered and washed thrice with 20 mL of 2 M HCl. After that, the solid was washed with 10 mL of acetone three times and extracted with $CHCl_3$ in 5 lots of 100 mL each. The solution was evaporated under reduced pressure, and the resulting solid residue was recrystallized from hot $CHCl_3$ to yield bright yellow TFPPy powder (0.85 g, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$, d): 10.17 (s, 4H, Ar H), 8.18 (s, 4H, Ar H), 8.09 (d, J = 6 Hz, 8H, Ar H), 8.05 (s, 2H, Ar H), 7.86 (d, J = 6 Hz, 8H, Ar H).





Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP). TAPP was synthesized in accordance with published literature.[S3] In the typical procedure, 4-nitrobenzaldehyde (22.0 g, 0.145 mol) and acetic anhydride (24.0 mL, 0.254 mol) were dissolved in propionic acid (600 mL) and subjected to reflux. Pyrrole (10.0 mL, 0.144 mol) was then slowly added to the solution. After refluxing for 30 min, the resulting mixture was cooled, yielding a precipitate that was collected by filtration, washed with H_2O and methanol, then dried under vacuum. The powder obtained was dissolved in pyridine (160 mL) and refluxed for an hour. After cooling down to room temperature, the precipitate was collected via filtration and washed with acetone, generating 5,10,15,20-tetrakis(4-nitrophenyl)-21H,23H-porphine crystals (14% in yield). The intermediate product (4.13 g, 5.19×10^{-3} mol) was dissolved in hot HCl (500 mL) at 70 ℃, to which $SnCl_2 \cdot 2H_2O$ (18.0 g, 7.97×10^{-2} mol) was added. The resulting mixture was stirred at 70 ℃ for 30 min and then cooled to 0 ℃. After neutralization with aqueous NH_3, the resulting grey crystalline product was filtered and dissolved in acetone. The solvent was removed by Rotary evaporation and the product was vacuum-dried to yield a purple powder in 92% yield. ^{1}H NMR (400 MHz, DMSO) δ 8.91 (s, 8H), 7.87 (d, J = 8.4 Hz, 8H), 7.02 (d, J = 8.4 Hz, 8H), 5.58 (s, 8H), 2.71 (s, 2H).



1.3 Methods

Power X-ray diffraction (PXRD) patterns were recorded on a SmartLab X-ray diffractometer. The sample is dried under vacuum and then mounted on a glass flat sample plate. Patterns were collected in the range of $2° < 2\theta < 30°$ with a step size of 0.02° and exposure time of 10° min^{-1}. Fourier transform infrared (FT-IR) spectra were recorded in a Jasco FT/IR-4000 accessory with a spectral range of 4000-400 cm^{-1}, and signals are given in wavenumbers (cm^{-1}). Thermogravimetric analyses (TGA) were run on a Thermbalance TGA Q600 thermal gravimetric analyser with samples under N_2 atmosphere. The samples were heated at 10 °C min^{-1} within a temperature range of 25-700 °C. N_2 adsorption and desorption isotherms (BET) were done at 77 K using Quantachrome Autosorb-iQ. Before the test, the sample was vacuum dried overnight at 120 °C. The pore volume of COFs was calculated from the sorption curve using the nonlocal density functional theory (NLDFT) model. Scanning Electron Microscopy (SEM) images were performed on a thermoscientific Hitachi Regulus8100. The sample was dispersed in ethanol, and dropped on a piece of clean conductive tape, coated with gold. Ultraviolet visible infrared spectrophotometer (UV-vis) spectra were recorded in

a Jasco V-770 accessory with a spectral range of 200-700 nm, and signals are given in wavenumbers (nm). ^{1}H NMR and ^{13}C NMR were tested with a 400M NMR spectrometer (Bruker AVANCE NEO 400MHz NMR spectrometer). Steady-state photoluminescence (PL) decay spectra measurements Time-resolved fluorescence decay spectra were measured at room temperature using Jasco FP-8600 spectrometer. The data was fit with the exponential reconvolution function and the non-linear least square method. COFs (20 mg) were used to fill the sample cell (the same volume). A 450 W ozone free xenon arc lamp is used as an excitation light source in the steady-state PL emission test.

Structural modellings of TPB-TAPP-COF and TFPPY-TAPP-COF were performed using the Accelrys Materials Studio software package. The space groups were obtained from the Reticular Chemistry Structure Resource. The theoretical models were then optimized by the Forcite module. Pawley refinements of the PXRD patterns were done in the Reflex module. The integrated intensities were extracted using Pseudo-Voigt profile. The unit cell parameters a, b, c, FWHM parameters U, V, W, profile parameters NA, NB, and zero point were refined.

The photocurrent measurements were conducted with an electrochemical workstation (IVIUM) and the working electrodes irradiated from the front side. The visible light was generated by a 300W xenon lamp (PerfectLight, PLS-SXE300E) with a 420 nm cut-off filter, and was chopped manually. The three-electrode cell was applied with 0.2 M Na_2SO_4 aqueous solution as the electrolyte, where Pt foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. The COFs were deposited on ITO as the working electrodes. Electrochemical impedance spectroscopy. The electrochemical impedance spectroscopy (EIS) was tested by an electrochemical workstation (IVIUM). A 300 W xenon lamp (PerfectLight, PLS-SXE300E) with a 420 nm cut-off filter as the visible light source. The EIS was measured over a range from 0.01 to 100 kHz with an amplitude of 0.01 V under the open-circle potential and visible-light irradiation.

The photocatalytic hydrogen generation experiments of the photocatalysts were performed on a set of photocatalytic equipment (Labsolar-6A). First of all, the as-

synthesized COFs (5 mg) were ultrasonically dispersed in 0.1 M ascorbic acid to form a well-dispersed polymer suspension. 125 μl (5 wt.% H_2PtCl_6) was then added to the reaction system. After the photocatalytic system was degassed to remove the dissolved air, the suspension was irradiated with a 300 W Xe lamp under vacuum with stirring. Circulating cooling water was used to keep the photocatalytic reaction temperature at 5 ℃. A 420 nm cut-off filter was used to filter off ultraviolet light to obtain the simulated visible light irradiation ($\lambda > 420$ nm). The produced hydrogen was measured online by using a gas chromatograph (GC-2014). Hydrogen was detected with a thermal conductivity detector (TCD) referencing standard gas with a known concentration of hydrogen. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. The hydrogen evolution rates were determined from a linear regression fit.

General procedure for recycling the COF samples. The COF sample used for catalysis was collected by filtration, washed several times with water, then dried under vacuum at 120 °C overnight and reused for the next cycle.

Table S1. Fractional atomic coordinates for unit cell of TPB-TAPP-COF calculated

using the density functional tight-binding method after performing the Pawley refinement.

Slipped TPB-TAPP-COF AA structure	Space group: Triclinic P-1 a = 5.0597 Å, b = 19.6579 Å, c = 22.1670 Å α = 95.7157°, β = 87.3825°, γ = 82.0961°		
C	1.26654	0.56744	0.40424
C	1.04852	0.55604	0.36487
C	0.99032	0.494	0.37175
C	1.16943	0.46486	0.41561
N	1.32998	0.51114	0.43433
C	1.38906	0.62841	0.40915
C	1.18493	0.39631	0.43122
C	1.3074	0.37286	0.48346
C	1.32668	0.30578	0.4995
C	1.46301	0.30356	0.55137
C	1.53378	0.36853	0.56499
N	1.42905	0.41111	0.52467
C	1.70349	0.3851	0.61168
C	1.82169	0.44649	0.61779
C	2.02877	0.45903	0.65981
C	2.09022	0.52069	0.65245
C	1.92323	0.54842	0.60575
N	1.76773	0.5015	0.58567
C	1.91399	0.61634	0.58869
C	1.79822	0.63917	0.53549
C	1.79459	0.70495	0.51715
C	1.65688	0.70725	0.46545
C	1.56755	0.64397	0.45447
N	1.66441	0.60199	0.49604
C	2.0194	0.66688	0.6323
C	1.78267	0.33323	0.65496
C	1.07281	0.34644	0.38807
C	1.30843	0.68027	0.36563
C	1.92256	0.67528	0.69338
C	2.03162	0.71847	0.73574
C	2.23412	0.7557	0.71797
C	2.32713	0.74896	0.65655
C	2.22125	0.70446	0.61446
C	1.94227	0.27053	0.63488
C	2.05034	0.22691	0.67657
C	2.00787	0.24636	0.73883
C	1.83879	0.30747	0.75923

C	1.72381	0.35008	0.71752
C	1.14946	0.34098	0.32584
C	1.02979	0.29884	0.28451
C	0.83866	0.25919	0.3044
C	0.7683	0.26263	0.36698
C	0.88289	0.30647	0.40794
C	1.17809	0.74654	0.38613
C	1.06801	0.79079	0.34508
C	1.06586	0.76756	0.28364
C	1.20681	0.70253	0.26243
C	1.33493	0.66047	0.3029
N	2.34795	0.79612	0.7644
N	2.1446	0.20445	0.78045
N	0.72358	0.22076	0.26185
N	0.91775	0.80746	0.24713
C	2.51373	0.84021	0.75724
C	2.26846	0.2298	0.82526
C	0.80676	0.78333	0.1965
C	0.66041	0.82846	0.1612
C	2.62256	0.87429	0.81067
C	2.41261	0.18431	0.8658
C	2.55693	0.85785	0.86952
C	2.66092	0.89032	0.91965
C	2.82733	0.94086	0.91221
C	2.90074	0.95573	0.85345
C	2.79823	0.92281	0.80301
C	2.34487	0.11862	0.87304
C	2.47831	0.07694	0.91305
C	2.69958	0.09716	0.94246
C	2.76298	0.16389	0.93552
C	2.61882	0.20717	0.89837
C	0.70533	0.89715	0.16046
C	0.56179	0.94093	0.1235
C	0.34644	0.92015	0.09159
C	0.30517	0.85034	0.09289
C	0.46492	0.80495	0.12547
C	0.55096	0.17487	0.27078
C	0.4347	0.14356	0.22154
C	0.47123	0.16381	0.16273
C	0.35805	0.1314	0.11394
C	0.21563	0.07584	0.12206
C	0.16918	0.05752	0.18118
C	0.27656	0.09131	0.23046

C	1.86433	1.05014	0.98052
C	1.97188	1.07922	1.0323
C	2.1278	1.03945	1.07094
C	2.18026	0.96595	1.05761
C	2.07115	0.93758	1.00517
C	1.91997	0.97776	0.96662
H	0.94264	0.59172	0.33695
H	0.83227	0.471	0.35008
H	1.2596	0.26155	0.47575
H	1.51194	0.25787	0.57461
H	1.4308	0.46379	0.52659
H	2.12439	0.4244	0.69005
H	2.24235	0.5444	0.67583
H	1.87489	0.74827	0.53899
H	1.62144	0.75195	0.44039
H	1.6445	0.55055	0.49691
H	1.76518	0.64727	0.70844
H	1.95858	0.72283	0.78284
H	2.4859	0.77589	0.64088
H	2.29566	0.69928	0.56777
H	1.98872	0.25616	0.58697
H	2.17852	0.1796	0.66037
H	1.80008	0.32269	0.80727
H	1.6005	0.39808	0.73398
H	1.29873	0.37051	0.30913
H	1.08769	0.29678	0.23661
H	0.62014	0.23379	0.38477
H	0.82465	0.3093	0.45549
H	1.15225	0.76322	0.43413
H	0.96275	0.84095	0.3621
H	1.21976	0.68427	0.21476
H	1.43905	0.6102	0.2858
H	2.57689	0.85208	0.71253
H	2.28188	0.28457	0.83088
H	0.79844	0.72851	0.18808
H	2.42465	0.82005	0.87698
H	2.60791	0.87696	0.96457
H	3.03495	0.99309	0.84675
H	2.85538	0.9354	0.75804
H	2.18231	0.1006	0.84923
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H	0.14156	0.83036	0.07102
H	0.4246	0.75218	0.12536
H	0.50532	0.16058	0.31572
H	0.58808	0.20459	0.15404
H	0.39459	0.14735	0.06906
H	0.052	0.01678	0.18913
H	0.2402	0.07555	0.27541
H	1.9222	1.13411	1.04496
H	2.11833	0.88317	0.99055

Table S2. Fractional atomic coordinates for unit cell of TFPPY-TAPP-COF

calculated using the density functional tight-binding method after performing the Pawley refinement.

Slipped TFPPY-TAPP-COF AA structure	Space group: Triclinic P-1 a = 27.6452 Å, b = 23.4692 Å, c = 8.3549 Å α = 89.9052°, β = 90.1894°, γ = 90.1560°		
C	0.60711	0.29575	0.50137
H	0.57672	0.28267	0.57445
C	0.64834	0.26149	0.49699
H	0.64893	0.2225	0.56637
C	0.18274	0.88165	0.21367
H	0.18285	0.92502	0.25769
C	0.22483	0.84952	0.22866
H	0.25569	0.87021	0.28206
C	0.39249	0.35579	0.2274
H	0.39666	0.39279	0.1512
C	0.35231	0.32012	0.20529
H	0.32577	0.33098	0.11496
C	0.88008	0.80329	0.11024
H	0.90574	0.78808	0.02212
C	0.84195	0.76784	0.15712
H	0.83848	0.72603	0.10343
N	0.76643	0.2495	0.29939
C	0.60007	0.52955	0.46733
H	0.63312	0.55083	0.5023
C	0.55844	0.56023	0.42421
C	0.55928	0.6201	0.40694
C	0.6047	0.34594	0.41022
C	0.68811	0.2769	0.40218
C	0.72983	0.23793	0.39163
H	0.72789	0.19842	0.45748
C	0.03656	0.82542	0.20996
H	0.05931	0.79228	0.25923
C	0.05129	0.87922	0.13654
C	0.09905	0.8976	0.1081
C	0.10816	0.95358	0.05436
C	0.15263	0.97198	-0.02449
H	0.18133	0.9454	-0.06943
C	0.14148	0.85936	0.13813
C	0.22629	0.79265	0.17478
C	0.42235	0.70747	0.43354
H	0.44909	0.71939	0.52209
C	0.38315	0.74355	0.40896

H	0.3806	0.78223	0.47929
C	0.85099	0.12376	0.29071
H	0.85378	0.08187	0.34407
C	0.81284	0.15898	0.33693
H	0.78786	0.1426	0.42491
C	0.64454	0.6387	0.31491
H	0.64309	0.60115	0.23966
C	0.68636	0.67209	0.31428
H	0.71663	0.65894	0.24076
C	0.14274	0.19753	0.08543
H	0.11169	0.21634	0.02709
C	0.18479	0.23037	0.10325
H	0.18508	0.27396	0.06074
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C	0.4703	0.4394	0.38402
C	0.47131	0.37911	0.36943
C	0.4274	0.65692	0.34497
C	0.34757	0.73007	0.29583
C	0.3067	0.76983	0.27608
H	0.30861	0.80918	0.34257
C	0.98881	0.17521	0.20909
H	0.96665	0.20938	0.25523
C	0.97278	0.12118	0.13948
C	0.92433	0.10274	0.12468
C	0.91191	0.04661	0.07729
C	0.86322	0.02814	0.03144
H	0.83231	0.05484	0.00511
C	0.88459	0.14176	0.17496
C	0.80741	0.21338	0.26796
C	0.60711	0.70425	0.50137
H	0.57672	0.71733	0.57445
C	0.64834	0.73851	0.49699
H	0.64893	0.7775	0.56637
C	0.18274	0.11835	0.21367
H	0.18285	0.07498	0.25769
C	0.22483	0.15048	0.22866
H	0.25569	0.12979	0.28206
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C	0.72983	0.76207	0.39163
H	0.72789	0.80158	0.45748
C	0.03656	0.17458	0.20996
H	0.05931	0.20772	0.25923
C	0.05129	0.12078	0.13654
C	0.09905	0.1024	0.1081
C	0.10816	0.04642	0.05436
C	0.15263	0.02802	-0.02449
H	0.18133	0.0546	-0.06943
C	0.14148	0.14064	0.13813
C	0.22629	0.20735	0.17478
C	0.42235	0.29253	0.43354
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H	0.39208	0.55086	0.39161
C	0.4703	0.5606	0.38402
C	0.47131	0.62089	0.36943

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C	0.97278	0.87882	0.13948
C	0.92433	0.89726	0.12468
C	0.91191	0.95339	0.07729
C	0.86322	0.97186	0.03144
H	0.83231	0.94516	0.00511
C	0.88459	0.85824	0.17496
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N	0.94004	0	0.09819
C	0.51596	0.64907	0.37825
C	0.51435	0.53027	0.40321
H	0.51715	0.3052	0.36077
C	0.51596	0.35093	0.37825
C	0.51435	0.46973	0.40321
H	0.51715	0.6948	0.36077
N	0.0117	0.90957	0.09483
N	0.0117	0.09043	0.09483
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H	0.97396	0	0.15083
C	0.68927	0.29253	0.93354
H	0.66254	0.28061	1.02209
C	0.72848	0.25645	0.90896
H	0.73103	0.21777	0.97929
C	0.26063	0.87624	0.79071
H	0.25785	0.91813	0.84407
C	0.29879	0.84102	0.83693
H	0.32377	0.8574	0.92491
C	0.46709	0.3613	0.81491
H	0.46854	0.39885	0.73966
C	0.42527	0.32791	0.81428
H	0.395	0.34106	0.74076
C	0.96889	0.80247	0.58543
H	0.99994	0.78366	0.52709
C	0.92684	0.76963	0.60325
H	0.92655	0.72604	0.56074
N	0.84312	0.24299	0.69241
C	0.68489	0.52969	0.88723

H	0.71955	0.55086	0.89161
C	0.64132	0.5606	0.88402
C	0.64032	0.62089	0.86943
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C	0.76406	0.26993	0.79583
C	0.80493	0.23017	0.77608
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C	0.12282	0.82479	0.70909
H	0.14497	0.79062	0.75523
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C	0.1873	0.89726	0.62468
C	0.19972	0.95339	0.57729
C	0.24841	0.97186	0.53144
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C	0.30422	0.78662	0.76796
C	0.50452	0.70425	1.00138
H	0.53491	0.71733	1.07445
C	0.46329	0.73851	0.99699
H	0.4627	0.7775	1.06637
C	0.92889	0.11835	0.71367
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C	0.8868	0.15048	0.72866
H	0.85594	0.12979	0.78206
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C	0.26968	0.23216	0.65712
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H	1.05232	0.20772	0.75923

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C	1.01258	0.1024	0.6081
C	1.00347	0.04642	0.55436
C	0.959	0.02802	0.47551
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C	0.68928	0.70747	0.93354
H	0.66254	0.71939	1.02209
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H	0.73103	0.78223	0.97929
C	0.26064	0.12376	0.79071
H	0.25785	0.08187	0.84407
C	0.29879	0.15898	0.83693
H	0.32377	0.1426	0.92491
C	0.46709	0.6387	0.81492
H	0.46854	0.60115	0.73966
C	0.42527	0.67209	0.81428
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C	0.96889	0.19753	0.58543
H	0.99994	0.21634	0.52709
C	0.92684	0.23037	0.60325
H	0.92655	0.27396	0.56074
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C	0.76406	0.73007	0.79583
C	0.80493	0.76983	0.77608
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C	0.12282	0.17521	0.70909
H	0.14497	0.20938	0.75523
C	0.13885	0.12118	0.63948
C	0.1873	0.10274	0.62468
C	0.19972	0.04661	0.57729
C	0.24841	0.02814	0.53144
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C	0.30422	0.21338	0.76796
C	0.50451	0.29575	1.00137
H	0.53491	0.28267	1.07445

C	0.46329	0.26149	0.99699
H	0.4627	0.2225	1.06637
C	0.92889	0.88165	0.71367
H	0.92878	0.92502	0.75769
C	0.8868	0.84952	0.72866
H	0.85594	0.87021	0.78206
C	0.71913	0.35579	0.72741
H	0.71497	0.39279	0.6512
C	0.75932	0.32012	0.70529
H	0.78586	0.33098	0.61496
C	0.23155	0.80329	0.61024
H	0.20589	0.78808	0.52212
C	0.26968	0.76784	0.65712
H	0.27315	0.72603	0.60343
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H	0.47851	0.55083	1.0023
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C	0.55235	0.6201	0.90694
C	0.50693	0.34595	0.91022
C	0.42352	0.2769	0.90218
C	0.3818	0.23793	0.89163
H	0.38374	0.19842	0.95748
C	1.07507	0.82542	0.70996
H	1.05232	0.79228	0.75923
C	1.06034	0.87922	0.63654
C	1.01258	0.8976	0.6081
C	1.00347	0.95358	0.55436
C	0.959	0.97198	0.47551
H	0.9303	0.9454	0.43057
C	0.97015	0.85936	0.63813
C	0.88534	0.79265	0.67478
N	0.17159	0	0.59819
N	1.02925	0	0.59811
C	0.59566	0.64907	0.87826
C	0.59729	0.53027	0.9032
H	0.59448	0.3052	0.86077
C	0.59567	0.35093	0.87825
C	0.59727	0.46973	0.90321
H	0.59448	0.6948	0.86077
N	0.09993	0.90957	0.59483
N	0.09993	0.09043	0.59483
H	0.13767	0	0.65083

H	1.05783	0	0.67946

Table S3. Comparison between representative photocatalysts from literature and TFPPY-TAPP-COF reported in this work.

photocatalyst	cocatalyst	Mass fraction of cocatalyst	sacrificial agent	Hydrogen production efficiency	Wavelength and quantum yield and	Ref.
2Br-COF	H_2PtCl_6	3wt %	L-ascorbic acid	13610 μmol $g^{-1}h^{-1}$	6.6 % 400 nm	S4
ZCS-COF-20	H_2PtCl_6	3 wt%	L-ascorbic acid	11300 μmol $g^{-1}h^{-1}$	5.3 % 500 nm	S5
CN-COF	H_2PtCl_6	n.a.	TEOA	10 100 μmol h^{-1} g^{-1}	20.7% 425 nm	S6
TFPPY-TAPP-COF	H_2PtCl_6	5 wt%	L-ascorbic acid	8700 μmol h^{-1} g^{-1}	0.12% 420 nm	This work
Th-TZ-COF	H_2PtCl_6	8 wt%	L-ascorbic acid	5220 μmol h^{-1} g^{-1}	1.38% 450 nm	S7
DABT-Py-COF	H_2PtCl_6	3 wt%	L-ascorbic acid	5458 μmol $h^{-1}g^{-1}$	n.a.	S8
A CdS-COF	H_2PtCl_6	0.5 wt%	lactic acid	3700 μmol g^{-1} h^{-1}	4.2% 420 nm	S9
$En_{TAPT\text{-}TDOEB}$	H_2PtCl_6	3 wt%	L-ascorbic acid	2396.7 μmol $h^{-1}g^{-1}$	n.a.	S10
sp^2c-COF	H_2PtCl_6	3wt %	triethanolamine	1360 μmol $h^{-1}g^{-1}$	0.48% 495 nm	S11
TpDTz COF	$Ni(OAc)_2$	6 wt%	TEOA	941 μmol h^{-1} g^{-1}	0.2% 400 nm	S12
$Qu_{TAPT\text{-}TFB}$	H_2PtCl_6	3 wt%	L-ascorbic acid	787.6 μmol $h^{-1}g^{-1}$	n.a.	S13
N_2-COF	H_2PtCl_6	8 wt%	TEOA	780 μmol g^{-1} h^{-1}	0.16% 400 nm	S14
TP-BDDA COF	H_2PtCl_6	n.a.	TEOA	324 μmol g^{-1} h^{-1}	1.8% 520 nm	S15
PTP-COF	H_2PtCl_6	8 wt%	TEOA	83 μmol g^{-1} h^{-1}	n.a.	S16

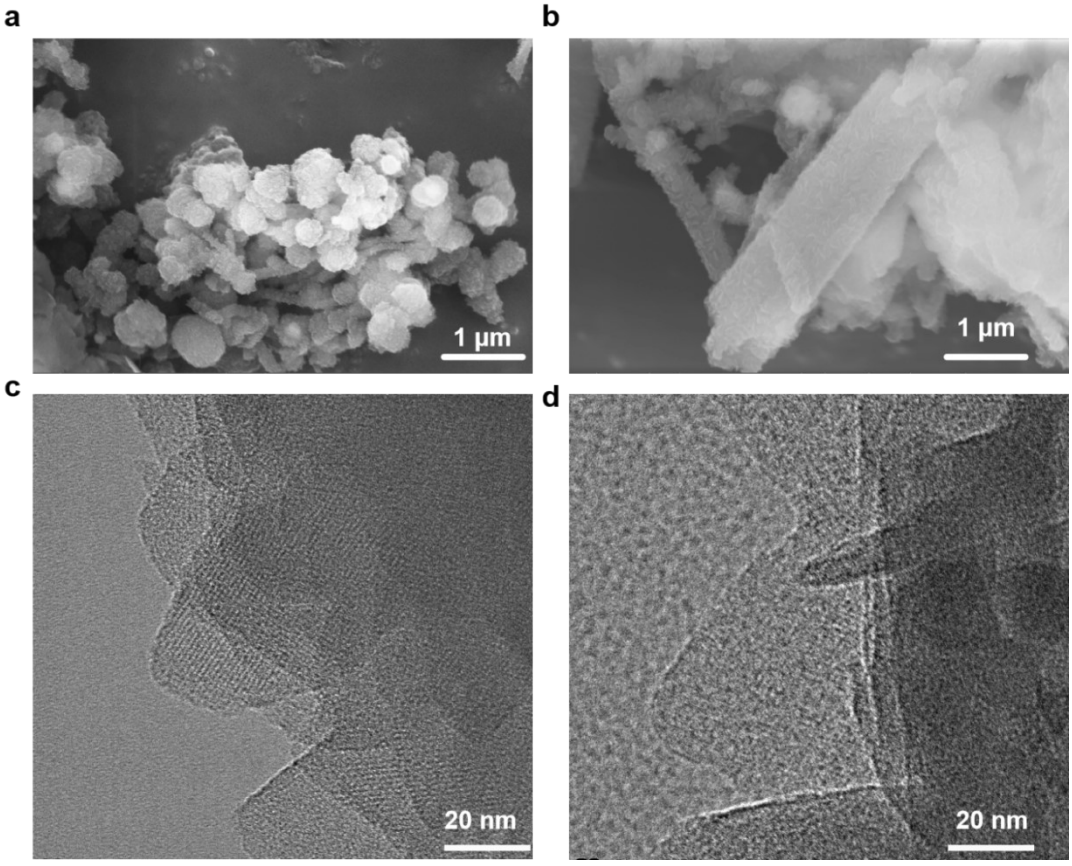

Fig S1. SEM and TEM images of TPB-TAPP-COF (a, c) and TFPPY-TAPP-COF (b, d).

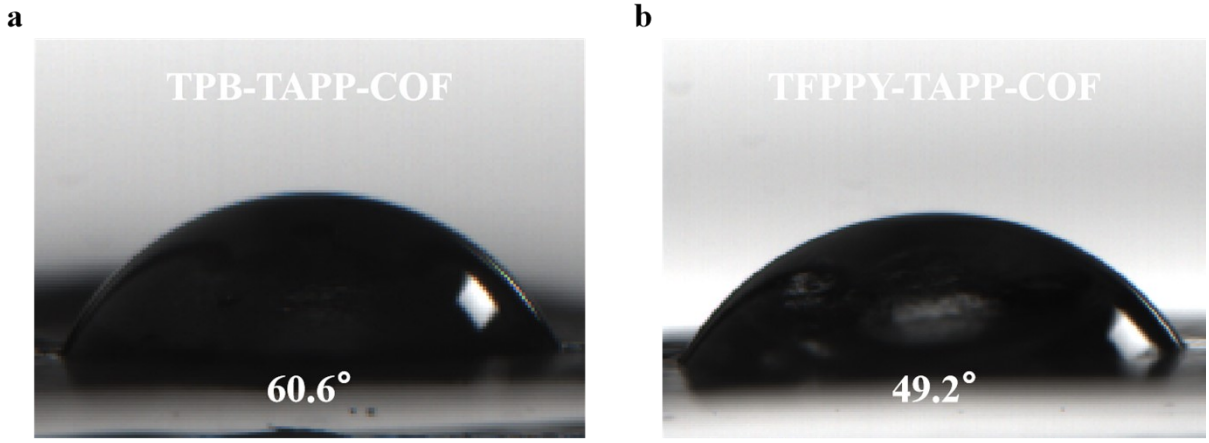

Fig S2. Contact angles of TPB-TAPP-COF (a) and TFPPY-TAPP-COF (b).

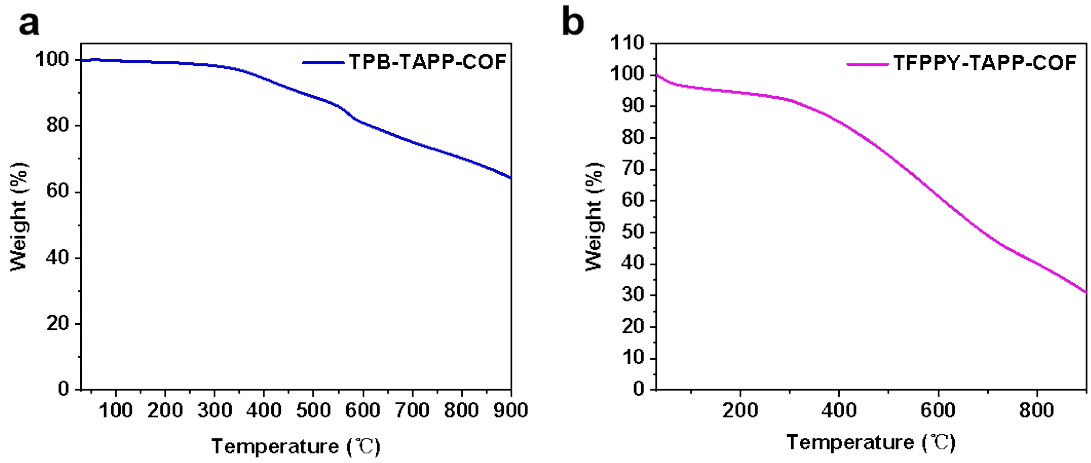

Fig S3. Thermogravimetric Analysis (TGA) curves of TPB-TAPP-COF (a) and TFPPY-TAPP-COF (b).

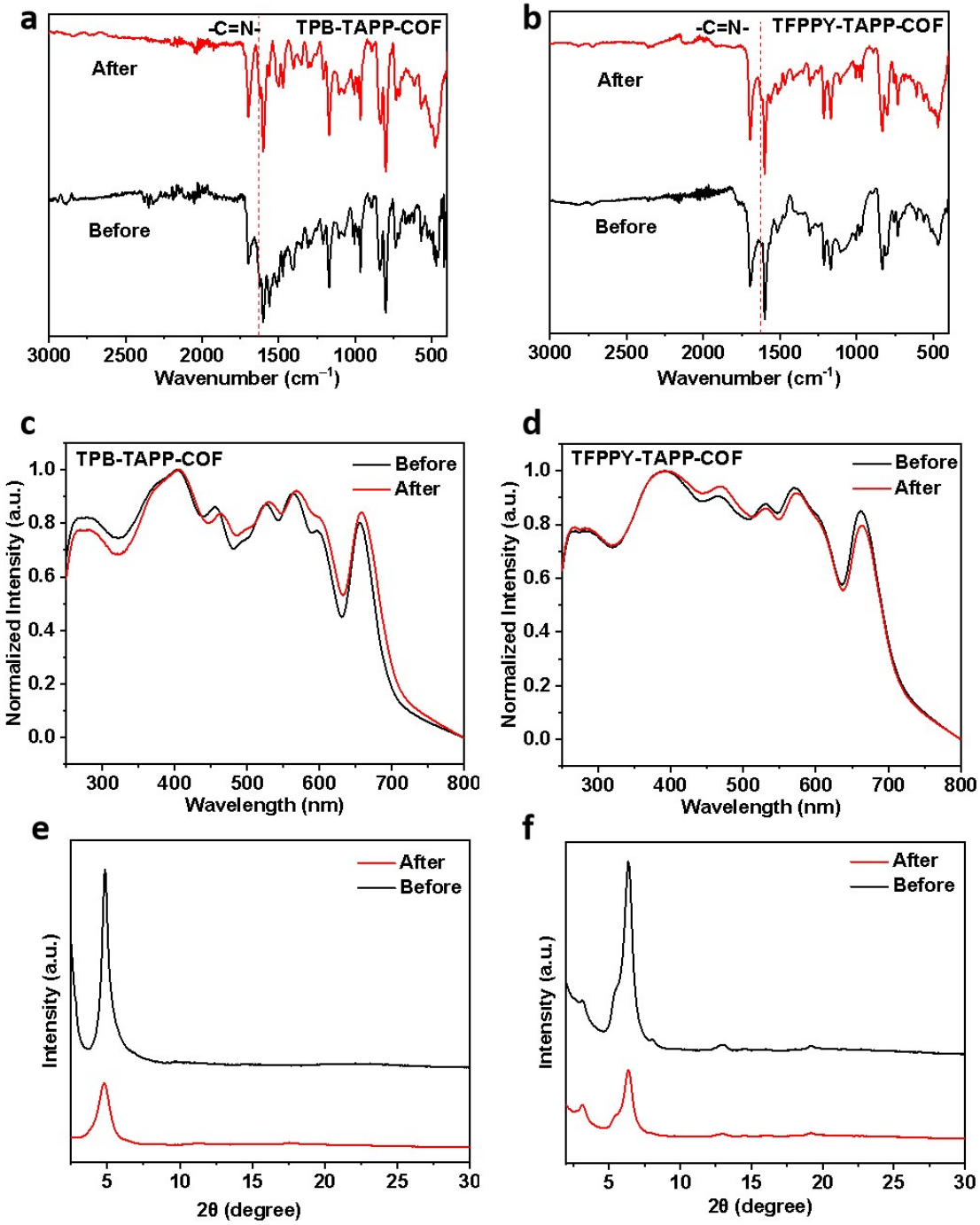

Fig S4. FT-IR (a, b), UV-vis (c, d) spectra and PXRD patterns (e, f) of TPB-TAPP-COF and TFPPY-TAPP-COF before and after photocatalysis.

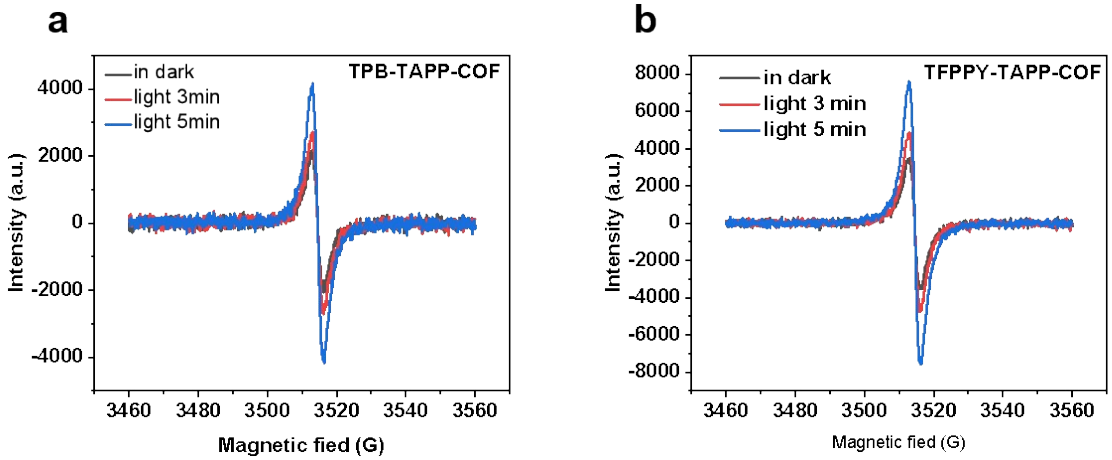

Fig S5. EPR maps of TPB-TAPP-COF and TFPPY-TAPP-COF under different lighting times.

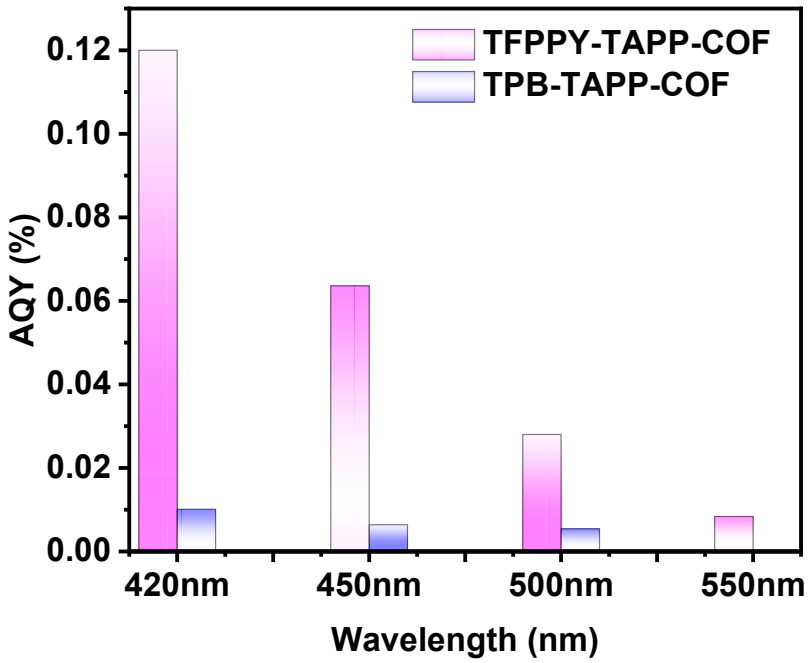

Fig S6. The quantum efficiency of TPB-TAPP-COF and TFPPY-TAPP-COF, tested with different filters.

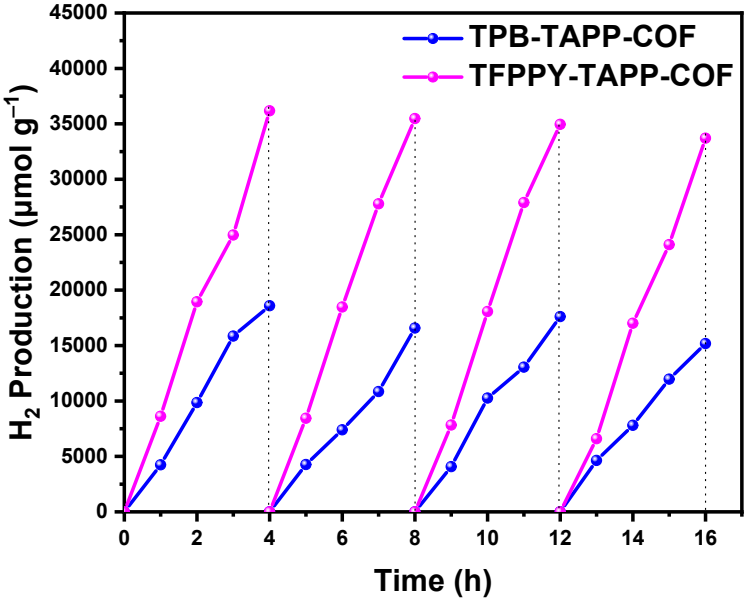

Figure S7. Recyclability of TPB-TAPP-COF and TFPPY-TAPP-COF.

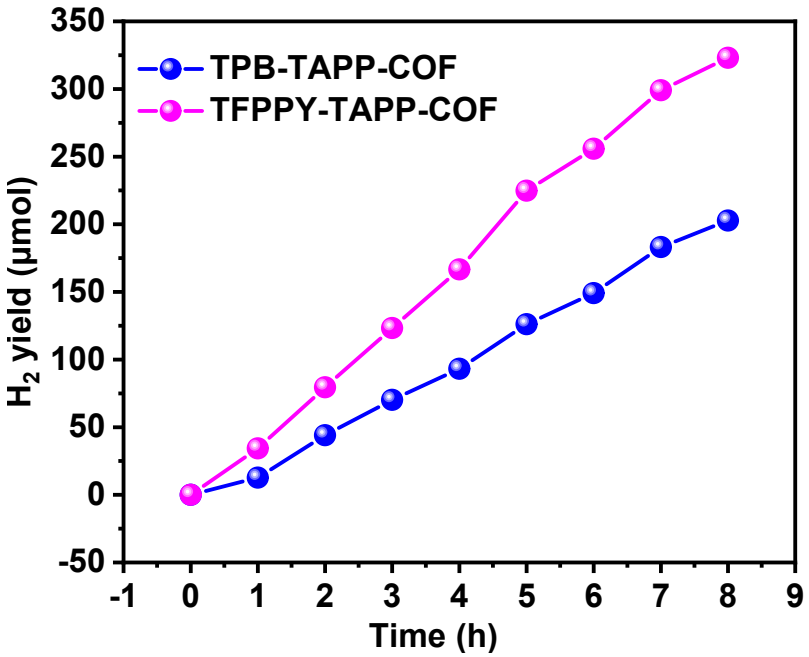

Figure S8. The time-resolved HER profile of TPB-TAPP-COF and TFPPY-TAPP-COF.

Quantum Efficiency (AQY):

An optical power/energy meter (Newport, Model: 842-PE) was used for determination of the number of incident photons ($N_{photons}$). The value of $N_{photons}$ was calculated using the following equation:

$$N_{photon} = \frac{P\lambda t}{hc}$$

$$N_{photon} = \frac{800\,J\,s^{-1}m^{-2} \times 39.69 \times 10^{-4}\,m^2 \times 420 \times 10^{-9}\,m \times 3600\,s}{6.626 \times 10^{-34}\,J\,s \times 3 \times 10^{8}\,m\,s^{-1}} \quad (1)$$

$$= 2.4 \times 10^{22}$$

here, power of the light (P) = 80 mW cm^{-2} = 800 Wm^{-2} = 800 J $s^{-1}m^{-2}$ area of lamp (a) = 39.69 cm^2 = 39.69 × 10^{-4} m^2, λ is the wavelength of the light = 420 nm = 420 × 10^{-9} m, t is the duration of irradiation 1 h = 3600 s, h is the Planck's constant (6.626 x 10^{-34} J s) and c is the velocity of light (3 × 10^8 m s^{-1}).

Number of incident photon ($N_{photons}$) is unitless.

The light intensity was absorbed by the photocatalysts is 800 Wm^{-2} which is required to calculated AQY.

$$AQY = \frac{2 \times numbers\ of\ evolved\ H_2\ molecule}{numbers\ of\ incident\ photons\ (N_{photon})} \times 100$$

$$(AQY)TFPPY - TAPP - COF = \frac{2 \times 24.4 \times 10^{-6} \times 6.023 \times 10^{23}}{2.4 \times 10^{22}} \times 100$$

$$(AQY)TFPPY - TAPP - COF = 0.12\ \%$$

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