Supplementary Information

Isomeric Cyano-vinylene-linked Covalent Organic Frameworks and their Impact on Photocatalytic Hydrogen Evolution

Amit Nagar,[a] Akhtar Alam,[b] Pradip Pachfule,[b] and C. M. Nagaraja*[a]

[a] Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India, Tel: 91-1881-232357. Email: cmnraja@iitrpr.ac.in

[b] Department of Chemical and Biological Sciences, S. N. Bose National Centre for Basic Sciences, JD Block, Salt Lake - Sector-III, Kolkata - 700 106, India

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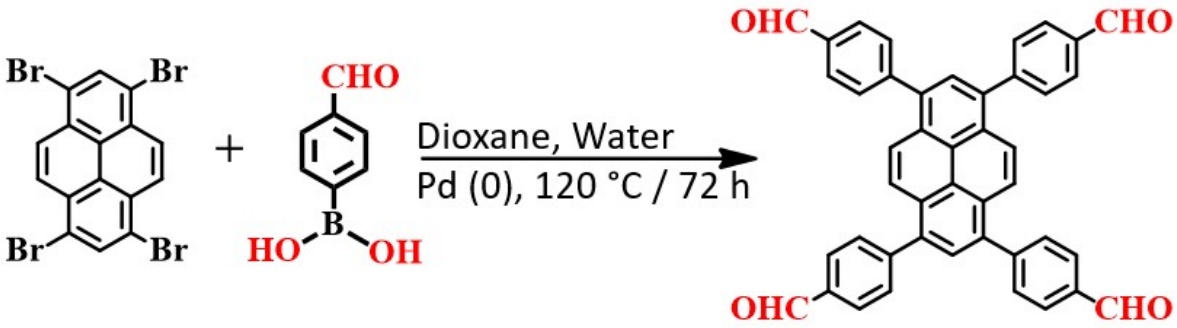
Experimental section

Material

All reagents and solvents were obtained from commercial suppliers and used as received: dichloromethane (DCM), tetrahydrofuran (THF), ethanol, methanol (MeOH), dioxane, n-butyl alcohol (*n*-BuOH) and o-dichlorobenzene (*o*-DCB) were obtained from Spectrochem Pvt. Ltd. 1,3,6,8-tetrabromopyrene, 4-formylphenylboronic acid, potassium carbonate, 4-(cyanomethyl)phenylboronic acid, were obtained from Acros Organics. H_2PtCl_6, $Pd(PPh_3)_4$ were obtained from ChemScene India Pvt. Ltd.

Synthesis of 1,3,6,8-tetrakis(4-formylphenyl) pyrene.



1,3,6,8-tetrabromopyrene (1.04 g, 2.0 mmol), 4-formylphenylboronic acid (1.26 g, 8.4 mmol), palladium tetrakis(triphenylphosphine) (0.231 g, 0.20 mmol), and potassium carbonate (1.525g, 11.0 mmol) in dioxane/water (60 mL/15 mL) were stirred under reflux in nitrogen for three days. After cooling to room temperature, the resulting product was filtrated, and washed with water and methanol three times. Yield: 68 %. ^{1}H NMR (400 MHz, $CDCl_3$): 10.16 (s, 4 H, CHO), 8.18 (s, 4 H), 8.09 (d, *J* = 7.9 Hz, 8 H), 8.04 (s, 2 H), 7.86 (d, *J* = 7.9 Hz, 8 10H).

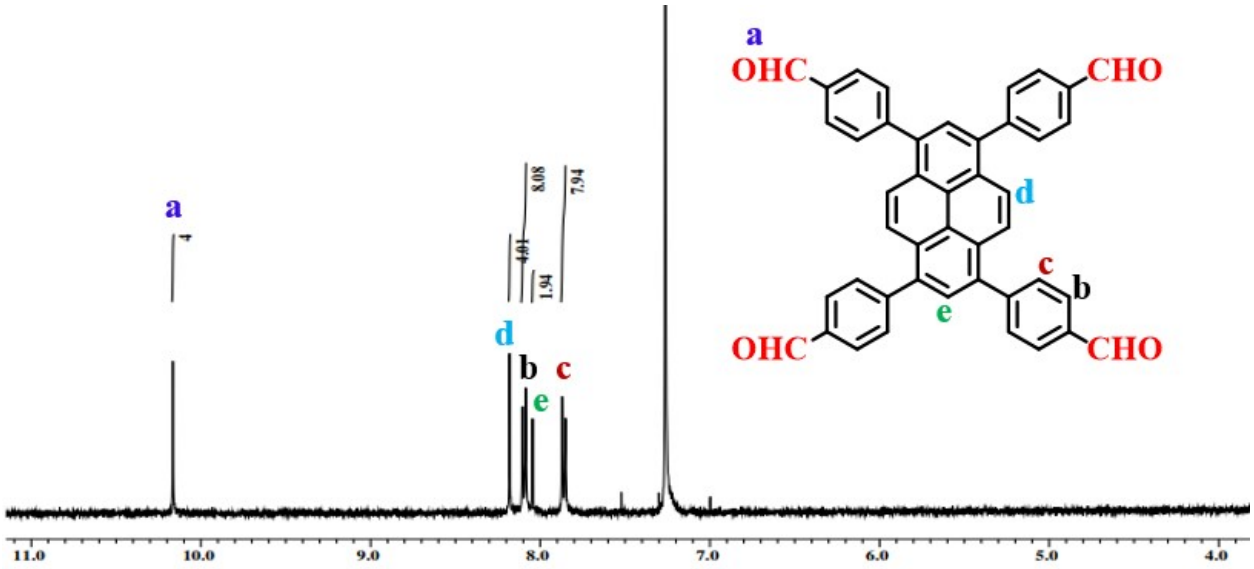
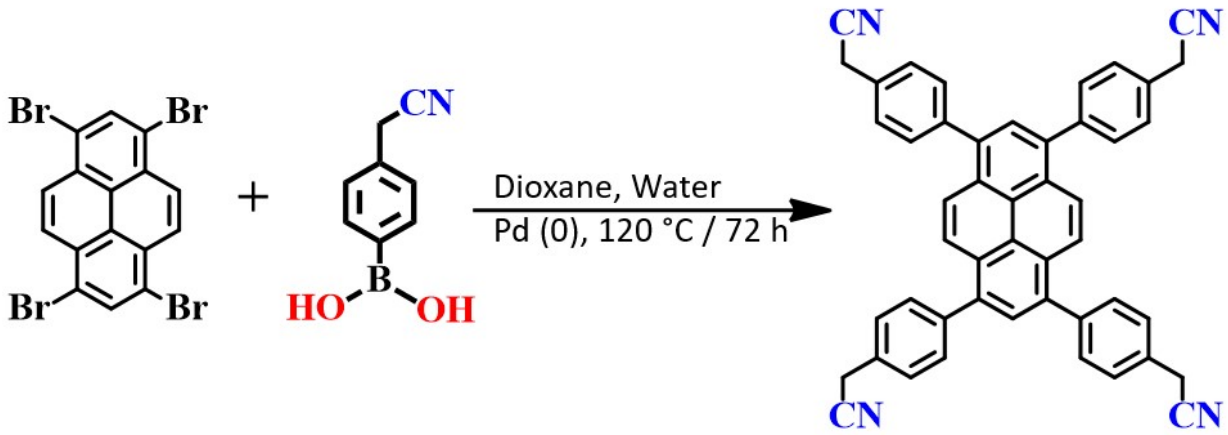


Figure S1. *^{1}H NMR ($CDCl_3$, 400 MHz) spectra of 1,3,6,8-tetrakis(4-formylphenyl) pyrene (PyCHO) linker.*

Synthesis of 1,3,6,8-tetrakis[4-(cyanomethyl)phenyl]pyrene (PyCN).



1,3,6,8-tetrabromopyrene (1.04 g, 2.0 mmol), 4-(cyanomethyl)phenylboronic acid (1.35 g, 8.4 mmol), palladium tetrakis(triphenylphosphine) (0.231 g, 0.20 mmol), potassium carbonate (1.52 g, 11 mmol) in dioxane/water (60 mL/15 mL) were stirred under reflux in nitrogen for three days. After cooling to room temperature, the resulting product was filtrated, and washed with water and methanol three times. Yield: 50 %. ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (s, 4 H), 7.96 (s, 2 H), 7.69 (d, *J* = 8.1 Hz, 8 H), 7.53 (d, *J* = 8.2 Hz, 8 H),3.90 (s, 8 H).

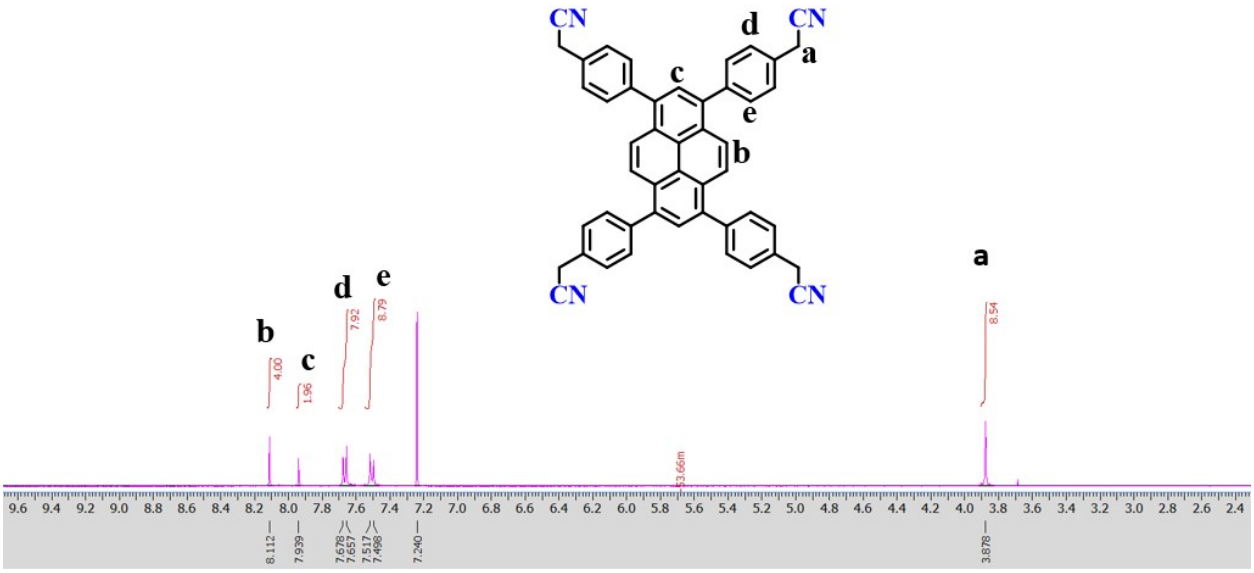


Figure S2. *^{1}H NMR ($CDCl_3$, 400 MHz) spectra of 1,3,6,8-tetrakis[4-(cyanomethyl)phenyl]pyrene (PyCN) linker.*

Experimental section

Synthesis of Py-PaCN COF: To synthesize Py-PaCN COF, we followed previously reported methods. [S1] A mixture of Py-CHO (30.0 mg, 0.048 mmol) and 1,4-phenylenediacetonitrile (PaCN) (22.6 mg, 0.096 mmol) was prepared in 1,4- dioxane (2.0 mL) along with KOH catalyst (0.2 mL, 4 M) in a Pyrex tube. The tube was then sonicated for 30 min to achieve a homogeneous dispersion. The dispersion was subsequently flash-frozen in a liquid-nitrogen bath and subjected to four freeze−pump−thaw cycles to remove trapped gases. The tube was sealed under vacuum and heated at 85 °C for 72 h to promote the polymerization reaction. After completion of the reaction, the resulting precipitate was collected by filtration. It was then washed four times with dry THF and subjected to Soxhlet extraction with THF for 24 h to remove any impurities. The purified solid was finally dried under vacuum at 80 °C for 12 h to obtain the pure Py-PaCN COF material.

Synthesis of PyCN-Pa COF: We synthesized PyCN-Pa COF following the same procedure used for the synthesis of Py-PaCN COF. A mixture of PyCN (32.0 mg, 0.048 mmol) and 1, 4-p-phenyldiformaldehyde (Pa) (11.9 mg, 0.096 mmol) was prepared in 1,4-dioxane (2.0 mL) along with a KOH catalyst (0.2 mL, 4 M) in a Pyrex tube. The tube was then sonicated for 30 min to achieve a homogeneous dispersion. The dispersion was subsequently flash-frozen in a liquid-nitrogen bath and subjected to three freeze−pump−thaw cycles to remove trapped gases. The tube was sealed under vacuum and heated at 85 °C for 72 h to promote the polymerization reaction. After completion of the reaction, the resulting precipitate was collected by filtration. It was then washed four times with dry THF and subjected to Soxhlet extraction with THF for 24 h to remove any impurities. The purified solid was finally dried under vacuum at 80 °C for 12 h to obtain pure PyCN-Pa COF material.

Physical measurements

Powder X-ray diffraction measurements were conducted in the range of 2-50° on PAN analytical's X'PERT PRO X-Ray diffractometer with a scan rate of 2°/min using Cu-Kα radiation (λ = 1.54184 Å, 40 kV, 20 mA) for confirming phase purity of as-synthesized samples. Thermogravimetric analyses of the as-synthesized samples were carried out using a Metler Toledo thermogravimetric analyzer under an air atmosphere with a flow rate of 30 mL/ min from 40-800 °C (heating rate of 5 °C/min). Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Bruker Tensor-F27 instrument in ATR mode. SEM images and EDAX patterns were recorded on the FEI Nova SEM-450 instrument. UV-Vis (Diffuse Reflectance) spectra were recorded on the Shimadzu spectrophotometer using $BaSO_4$ as a reference. The ^{1}H NMR spectra of organic linkers synthesized were recorded in $CDCl_3$ on a JEOL JNM-ECS-400 spectrometer operating at a frequency of 400 MHz using $CDCl_3$ solvent. ^{13}C CP-MAS (Cross Polarization Magic Angle Spinning) solid-state NMR (600MHz) spectra were recorded on Bruker Advance 400 (DRX400) instrument. The evolved H_2 was quantified using gas chromatography (PerkinElmer, Clarus 580) equipped with 5 Å molecular sieves and N_2 as a carrier gas. The apparent quantum yield (AQY) for hydrogen evolution was measured under the illumination of white LED lights. The AQY values were calculated using the following equation:

AQY (%) = 2 × Number of evolved H_2 molecules/ Number of incident photons × 100 %

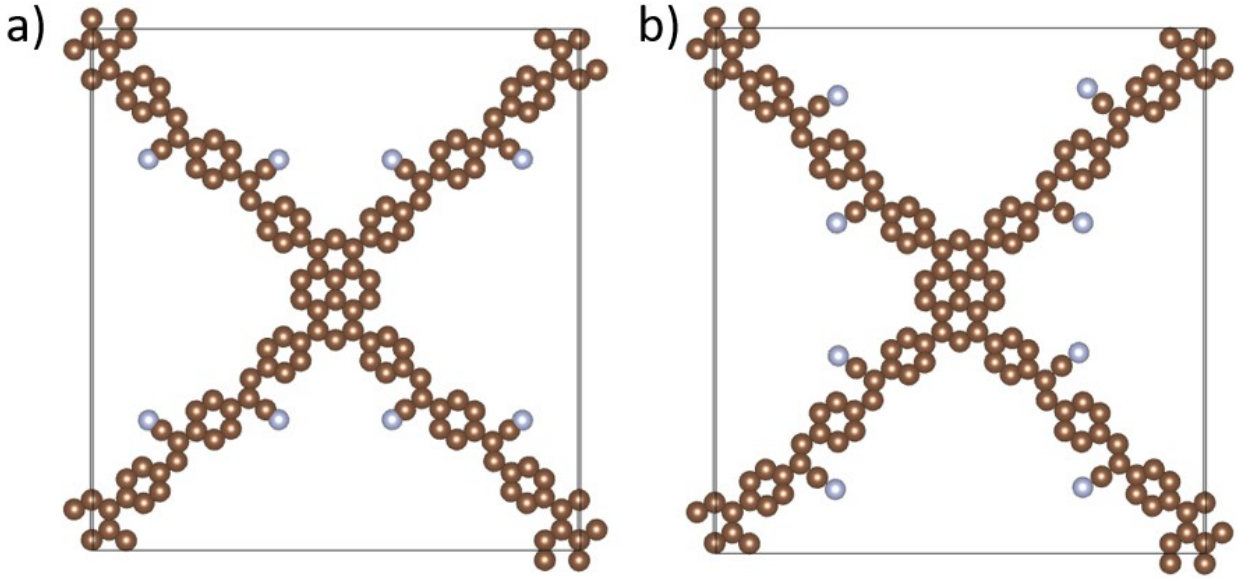


Figure S3. *A unit cell of (a) Py-PaCN COF, and (b) PyCN-Pa COF.*

Table S1: Fractional atomic coordinates for the unit cell of Py-PaCN COF.

Space group: P1	
a = 34.90 Å	α = 90 °
b = 35.18 Å	β = 90 °
c = 4.07 Å	γ = 90 °

C1	0.035028	0.918681	0.446583
C2	0.034791	0.959131	0.425035
C3	0.067395	0.980487	0.315433
C4	0.929999	0.895326	0.575151
C5	0.930672	0.858865	0.719352
C6	0.899182	0.834851	0.717577
C7	0.864633	0.846243	0.571241
C8	0.863711	0.88305	0.432427
C9	0.89542	0.90682	0.432642
C10	0.169957	0.823463	0.455625
C11	0.785657	0.767844	0.568391
C12	0.751942	0.789029	0.524453
C13	0.71757	0.771276	0.453924
C14	0.677897	0.713081	0.365888
C15	0.649465	0.262636	0.212545
C16	0.534918	0.418723	0.447762
C17	0.534712	0.459153	0.426012
C18	0.56733	0.480459	0.315995
C19	0.429836	0.395359	0.575808
C20	0.430434	0.358814	0.718625
C21	0.398886	0.334861	0.716898
C22	0.364316	0.346409	0.571887
C23	0.363501	0.383249	0.43354
C24	0.395259	0.406961	0.433827
C25	0.669372	0.32299	0.457259
C26	0.284729	0.268519	0.572333
C27	0.251062	0.289752	0.527818
C28	0.216639	0.272022	0.457925

C29	0.17703	0.213699	0.368672
C30	0.150674	0.763155	0.20647
C31	0.96512	0.91868	0.552077
C32	0.965316	0.959114	0.573796
C33	0.932689	0.980404	0.683904
C34	0.070188	0.895335	0.423956
C35	0.069591	0.858779	0.281056
C36	0.10114	0.834833	0.283025
C37	0.135699	0.8464	0.428246
C38	0.136511	0.883254	0.566616
C39	0.104753	0.906956	0.566151
C40	0.830562	0.82309	0.542724
C41	0.215278	0.768515	0.427492
C42	0.248943	0.789753	0.472052
C43	0.283375	0.772036	0.54168
C44	0.322989	0.713723	0.630668
C45	0.349349	0.263177	0.793206
C46	0.465003	0.418703	0.553235
C47	0.465235	0.459149	0.574919
C48	0.432631	0.480486	0.684773
C49	0.570044	0.395359	0.424798
C50	0.569323	0.358873	0.280796
C51	0.600783	0.334829	0.282619
C52	0.635347	0.346208	0.428779
C53	0.636332	0.383046	0.567332
C54	0.604652	0.406858	0.566992
C55	0.33005	0.323476	0.544661
C56	0.714195	0.267685	0.431954
C57	0.747926	0.288885	0.475095
C58	0.782324	0.271182	0.545546
C59	0.822015	0.213015	0.634539
C60	0.850374	0.762762	0.787754
C61	0.964977	0.081042	0.552172
C62	0.965243	0.0406	0.573854
C63	0.932656	0.019259	0.683829
C64	0.070025	0.104467	0.424614
C65	0.069324	0.140925	0.280273
C66	0.100754	0.165007	0.282231
C67	0.135303	0.153678	0.428871
C68	0.136283	0.116863	0.567572
C69	0.104623	0.09302	0.567189
C70	0.830048	0.176313	0.543773
C71	0.214186	0.232147	0.433411

C72	0.247872	0.21093	0.477812
C73	0.28226	0.228651	0.548442
C74	0.322012	0.286798	0.636175
C75	0.350561	0.737268	0.785712
C76	0.465053	0.581071	0.553067
C77	0.465263	0.540641	0.574761
C78	0.432641	0.51934	0.684526
C79	0.570137	0.604439	0.425449
C80	0.569505	0.640978	0.282438
C81	0.601032	0.664958	0.284043
C82	0.635629	0.653464	0.429049
C83	0.636475	0.616624	0.56737
C84	0.604748	0.592871	0.567182
C85	0.330667	0.67688	0.541838
C86	0.715149	0.731408	0.429707
C87	0.748839	0.71021	0.473897
C88	0.783244	0.727969	0.543836
C89	0.82283	0.786294	0.632484
C90	0.849407	0.23663	0.79107
C91	0.034911	0.081075	0.44731
C92	0.034737	0.04064	0.425568
C93	0.067375	0.019343	0.315905
C94	0.929804	0.104378	0.574828
C95	0.930447	0.140923	0.718025
C96	0.898927	0.164921	0.716429
C97	0.86433	0.153411	0.571358
C98	0.863473	0.116564	0.432923
C99	0.895195	0.092804	0.433029
C100	0.169324	0.176883	0.45797
C101	0.784756	0.231326	0.570601
C102	0.75106	0.210111	0.526979
C103	0.71663	0.227826	0.457044
C104	0.677038	0.286165	0.367691
C105	0.650484	0.736667	0.209503
C106	0.534983	0.581082	0.44801
C107	0.534739	0.54064	0.426185
C108	0.56734	0.519315	0.316093
C109	0.429924	0.604438	0.575775
C110	0.430652	0.640936	0.719571
C111	0.399227	0.665017	0.717283
C112	0.364663	0.653651	0.571032
C113	0.363654	0.616788	0.432928
C114	0.395311	0.592946	0.433547

C115	0.669901	0.676373	0.45659
C116	0.285836	0.732162	0.565968
C117	0.25215	0.710944	0.521429
C118	0.217758	0.728645	0.450983
C119	0.177995	0.786785	0.363918
C120	0.149503	0.237201	0.212929
C121	0.499977	0.479487	0.500519
C122	0.499967	0.400001	0.500616
C123	0.000043	0.979461	0.499422
C124	0.000071	0.899965	0.499239
C125	0.499999	0.520312	0.500572
C126	0.500018	0.599781	0.500662
C127	0.000005	0.020293	0.499546
C128	-6.7E-05	0.099758	0.499688
N1	0.628255	0.242341	0.079202
N2	0.129668	0.742839	0.071081
N3	0.370371	0.242866	0.928277
N4	0.871549	0.742476	0.921387
N5	0.371795	0.757537	0.919083
N6	0.870502	0.256894	0.926004
N7	0.629387	0.756931	0.074775
N8	0.128343	0.257414	0.078359
H1	0.092624	0.965313	0.223828
H2	0.956519	0.849242	0.840119
H3	0.901494	0.807007	0.831495
H4	0.837641	0.892482	0.313082
H5	0.893951	0.934189	0.308641
H6	0.193072	0.837913	0.582846
H7	0.752244	0.819854	0.552713
H8	0.691777	0.788361	0.425224
H9	0.592533	0.465243	0.224368
H10	0.456284	0.349073	0.838622
H11	0.401167	0.306969	0.830029
H12	0.337429	0.392792	0.314845
H13	0.393825	0.434367	0.310453
H14	0.69262	0.337305	0.58384
H15	0.251411	0.320587	0.555482
H16	0.190868	0.289145	0.429172
H17	0.907498	0.965174	0.775535
H18	0.043747	0.849015	0.161027
H19	0.098861	0.806923	0.169939
H20	0.162572	0.892808	0.685451
H21	0.106177	0.934379	0.689503

H22	0.807336	0.837419	0.416092
H23	0.248588	0.820588	0.444611
H24	0.309146	0.789165	0.570476
H25	0.407413	0.465307	0.776475
H26	0.543465	0.34925	0.160165
H27	0.598428	0.306963	0.168948
H28	0.662425	0.392475	0.686427
H29	0.606165	0.434265	0.690545
H30	0.306929	0.337929	0.417712
H31	0.74764	0.319696	0.445984
H32	0.808118	0.288292	0.573609
H33	0.907433	0.034439	0.775482
H34	0.043469	0.150489	0.159278
H35	0.098397	0.192842	0.168182
H36	0.162361	0.107463	0.686956
H37	0.106139	0.065647	0.691058
H38	0.806929	0.161782	0.417193
H39	0.247553	0.180101	0.449622
H40	0.308031	0.21153	0.577209
H41	0.407429	0.534543	0.776064
H42	0.54365	0.650689	0.162304
H43	0.598726	0.692838	0.170715
H44	0.662551	0.607097	0.686093
H45	0.606226	0.565466	0.690619
H46	0.307429	0.662524	0.415517
H47	0.748519	0.679375	0.446241
H48	0.809023	0.710859	0.572467
H49	0.092594	0.034556	0.224659
H50	0.956312	0.150639	0.838072
H51	0.901239	0.192799	0.829937
H52	0.837381	0.107027	0.314321
H53	0.893708	0.065383	0.309651
H54	0.192539	0.162552	0.584678
H55	0.751398	0.179279	0.554897
H56	0.690859	0.210689	0.428664
H57	0.59255	0.534514	0.224497
H58	0.456513	0.650537	0.840267
H59	0.401594	0.692895	0.830765
H60	0.337567	0.607362	0.313695
H61	0.393788	0.565535	0.310082
H62	0.693025	0.66189	0.583311
H63	0.252468	0.680117	0.549432
H64	0.191995	0.711515	0.422089

H65	0.499984	0.369022	0.500706
H66	0.000068	0.868986	0.499155
H67	0.500009	0.630761	0.500604
H68	-7.3E-05	0.13074	0.499653

Table S2. Fractional atomic coordinates for the unit cell of dual-pore PyCN-Pa COF with AA stacking.

Space group: P1	
a = 32.13 Å	α = 90 °
b = 38.13 Å	β = 90 °
c = 4.06 Å	γ = 90 °

C1	0.038207	0.925346	0.461938
C2	0.037831	0.962623	0.436883
C3	0.073366	0.982335	0.335465
C4	0.923539	0.903908	0.54458
C5	0.922702	0.870097	0.685508
C6	0.887589	0.848959	0.669508
C7	0.85108	0.860471	0.510763
C8	0.85148	0.894451	0.375838
C9	0.88679	0.915392	0.390407
C10	0.187363	0.839437	0.51519
C11	0.780173	0.777295	0.525893
C12	0.737661	0.78465	0.467295
C13	0.708949	0.757669	0.449528
C14	0.687335	0.696274	0.469662
C15	0.538116	0.425268	0.460541
C16	0.537766	0.462548	0.435086
C17	0.573254	0.48223	0.332177
C18	0.423399	0.404061	0.543642
C19	0.422406	0.370256	0.684392
C20	0.387113	0.349323	0.669348
C21	0.350633	0.36107	0.511924
C22	0.351195	0.395055	0.377201
C23	0.386701	0.415759	0.39014
C24	0.687074	0.339129	0.517795
C25	0.280002	0.277778	0.516708
C26	0.237394	0.285238	0.464025
C27	0.208614	0.258325	0.445843
C28	0.186936	0.196944	0.46191
C29	0.962013	0.925168	0.539659
C30	0.962159	0.962475	0.564216
C31	0.926538	0.982109	0.665481

C32	0.076855	0.904337	0.455828
C33	0.077953	0.870633	0.312843
C34	0.113306	0.849768	0.326617
C35	0.149748	0.861494	0.484779
C36	0.149124	0.895428	0.621002
C37	0.113541	0.916061	0.609402
C38	0.813599	0.838285	0.478821
C39	0.220283	0.7781	0.479459
C40	0.262913	0.785391	0.533024
C41	0.291529	0.758358	0.552347
C42	0.312826	0.696869	0.537836
C43	0.461947	0.425195	0.538836
C44	0.462147	0.462483	0.564069
C45	0.42659	0.482118	0.666777
C46	0.576725	0.404203	0.454931
C47	0.577762	0.370408	0.313568
C48	0.61306	0.349484	0.328683
C49	0.64952	0.361237	0.486449
C50	0.648972	0.395249	0.620916
C51	0.613445	0.415943	0.607984
C52	0.313011	0.339031	0.481325
C53	0.719999	0.277834	0.481313
C54	0.762641	0.285187	0.533505
C55	0.79131	0.258191	0.551646
C56	0.812699	0.196733	0.53618
C57	0.961603	0.074957	0.537518
C58	0.961954	0.037666	0.563093
C59	0.926442	0.017949	0.66493
C60	0.076358	0.096277	0.456091
C61	0.077403	0.130068	0.314844
C62	0.11261	0.151105	0.331487
C63	0.149013	0.139493	0.491043
C64	0.148425	0.105515	0.62583
C65	0.113009	0.0847	0.611122
C66	0.812818	0.161317	0.476764
C67	0.219977	0.222627	0.481744
C68	0.262585	0.215149	0.534237
C69	0.291391	0.24207	0.551732
C70	0.312965	0.303528	0.5363
C71	0.46168	0.574944	0.539042
C72	0.462007	0.537653	0.564252
C73	0.42652	0.517954	0.666971
C74	0.576482	0.596041	0.456544

C75	0.577674	0.629911	0.317272
C76	0.613034	0.65075	0.334367
C77	0.649406	0.638848	0.492606
C78	0.648656	0.604793	0.625665
C79	0.613084	0.58418	0.610397
C80	0.312951	0.661439	0.479
C81	0.7203	0.722019	0.490519
C82	0.762805	0.714682	0.549729
C83	0.791502	0.741663	0.56807
C84	0.813165	0.803022	0.545494
C85	0.037816	0.075089	0.460316
C86	0.037641	0.037784	0.436232
C87	0.073288	0.018167	0.335379
C88	0.923025	0.096083	0.54207
C89	0.922042	0.129918	0.682644
C90	0.886802	0.150908	0.666986
C91	0.850354	0.139217	0.508514
C92	0.850892	0.105216	0.374004
C93	0.886328	0.084421	0.388364
C94	0.186559	0.161587	0.523898
C95	0.779781	0.222511	0.516753
C96	0.737134	0.215146	0.464956
C97	0.708461	0.242154	0.446859
C98	0.687106	0.303649	0.461294
C99	0.537867	0.574978	0.460176
C100	0.537623	0.537694	0.434786
C101	0.573175	0.518062	0.332015
C102	0.423109	0.596095	0.544269
C103	0.422182	0.629945	0.684586
C104	0.38697	0.65098	0.668742
C105	0.35048	0.639311	0.510851
C106	0.350941	0.605271	0.377058
C107	0.386348	0.584449	0.391258
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C109	0.279955	0.722692	0.517245
C110	0.237332	0.715385	0.463596
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C114	0.500062	0.40792	0.499919
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N5	0.252622	0.87296	0.722518
N6	0.747827	0.128168	0.259202
N7	0.74913	0.871001	0.246793
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H1	0.101004	0.968412	0.251743
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H3	0.888442	0.823499	0.791143
H4	0.823875	0.904282	0.250346
H5	0.886283	0.940872	0.2697
H6	0.727	0.811524	0.437344
H7	0.676315	0.764061	0.404096
H8	0.657263	0.707586	0.402756
H9	0.600838	0.468296	0.24747
H10	0.449535	0.360622	0.817583
H11	0.387738	0.323874	0.791328
H12	0.323591	0.405034	0.252653
H13	0.386371	0.441244	0.269474
H14	0.226729	0.31216	0.438086
H15	0.175924	0.26482	0.404272
H16	0.156964	0.208215	0.391686
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H18	0.050841	0.861025	0.179226
H19	0.112752	0.824387	0.203153
H20	0.176721	0.905394	0.745854
H21	0.113816	0.941486	0.731411
H22	0.273725	0.81228	0.558594
H23	0.324243	0.764716	0.594366
H24	0.34293	0.708072	0.605455

H25	0.399054	0.468116	0.751352
H26	0.550652	0.360764	0.180202
H27	0.612464	0.324034	0.206538
H28	0.676586	0.405252	0.745251
H29	0.613771	0.441443	0.728607
H30	0.773428	0.312085	0.558786
H31	0.824045	0.26458	0.592451
H32	0.842813	0.207935	0.603487
H33	0.898793	0.031878	0.748441
H34	0.050355	0.13966	0.180418
H35	0.111939	0.176549	0.209468
H36	0.175957	0.095602	0.751781
H37	0.113379	0.059229	0.732004
H38	0.273254	0.188222	0.559523
H39	0.324101	0.235579	0.592361
H40	0.343178	0.29224	0.599628
H41	0.398946	0.531893	0.751815
H42	0.550646	0.639704	0.183801
H43	0.612532	0.676269	0.213666
H44	0.676161	0.594684	0.750628
H45	0.61328	0.558634	0.729838
H46	0.773449	0.687814	0.580767
H47	0.824113	0.735283	0.614617
H48	0.843038	0.791865	0.619737
H49	0.100865	0.032171	0.251732
H50	0.949145	0.139548	0.816207
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H55	0.675722	0.235767	0.40631
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H58	0.449322	0.639576	0.817677
H59	0.387706	0.67647	0.790091
H60	0.323311	0.595317	0.252621
H61	0.385892	0.558909	0.271392
H62	0.226516	0.688502	0.438086
H63	0.175999	0.736078	0.402443
H64	0.157229	0.792714	0.394191
H65	0.500113	0.379315	0.500094
H66	0.000283	0.879352	0.500783
H67	0.499734	0.62087	0.499376

H68	-0.000438	0.120926	0.497444
H66	0.000283	0.879352	0.500783
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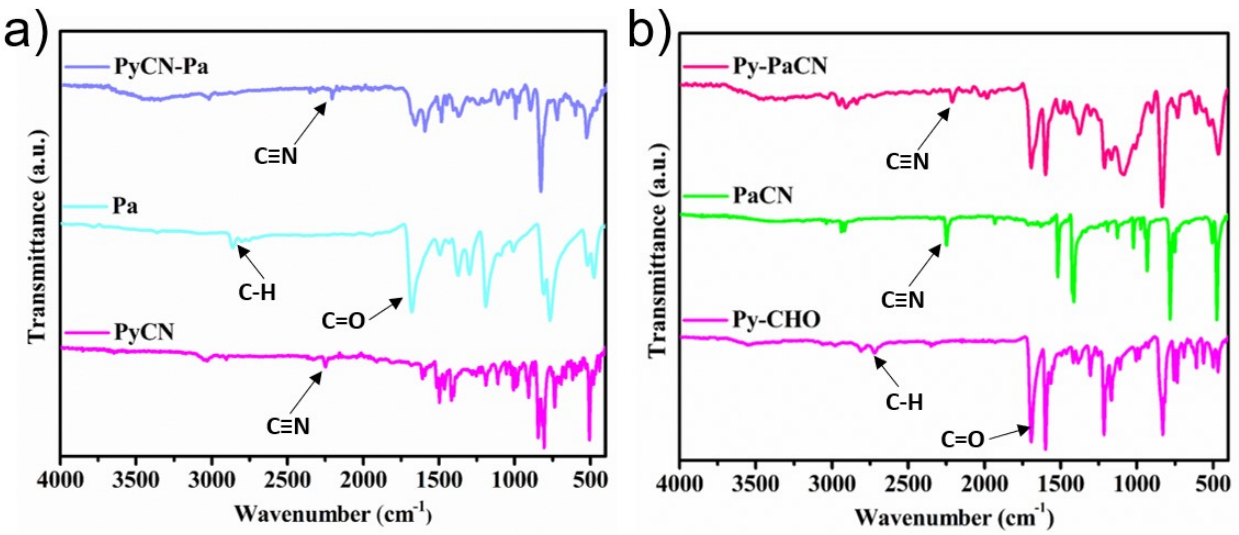

Figure S4. *FT-IR spectra of (a) Py-PaCN and (b) PyCN-Pa COFs.*

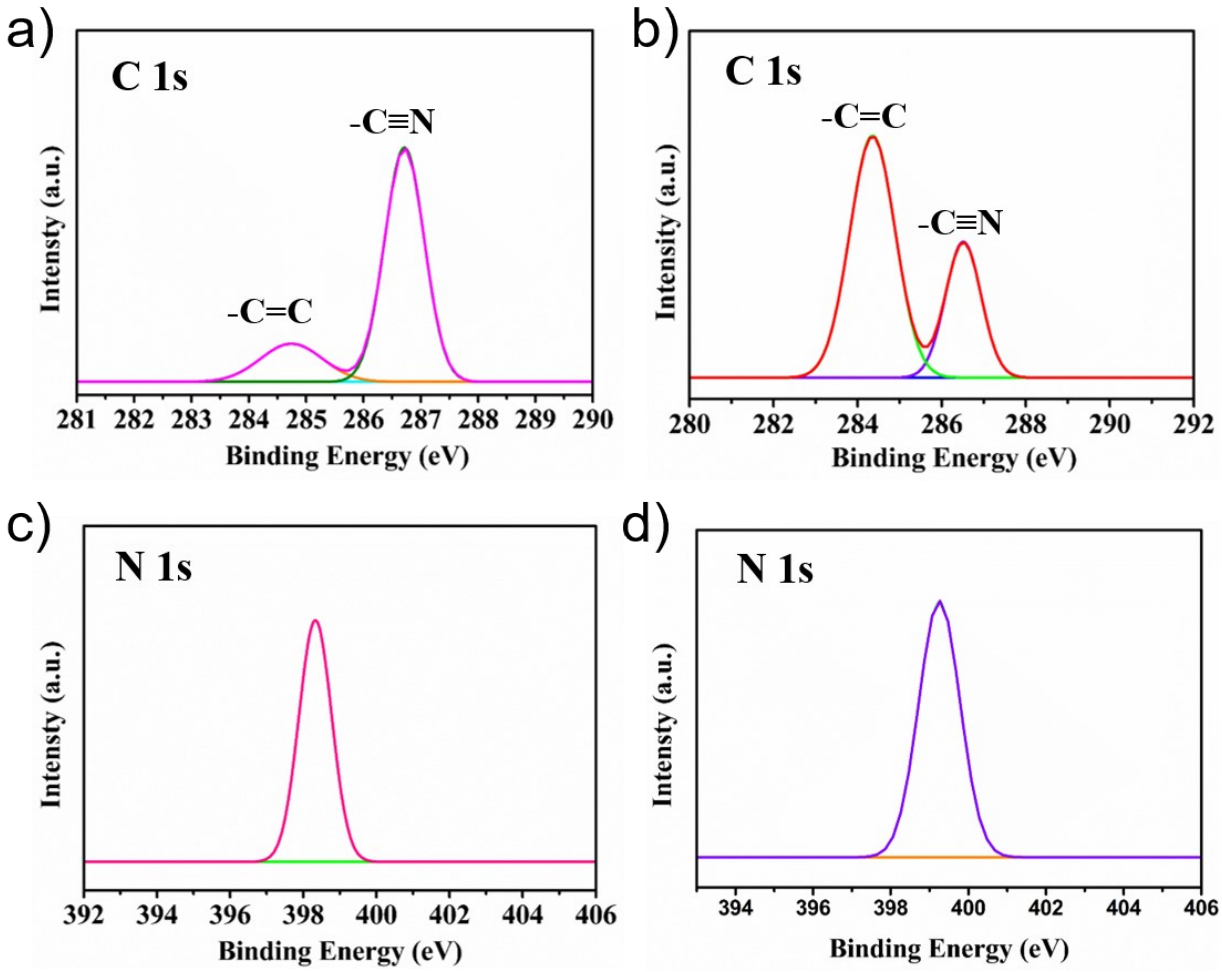

Figure S5. *XPS spectra of Py-PaCN COF (a) C 1s, and (c) N 1s. XPS spectra of PyCN-Pa COF (b) C 1s, and (d) N 1s.*

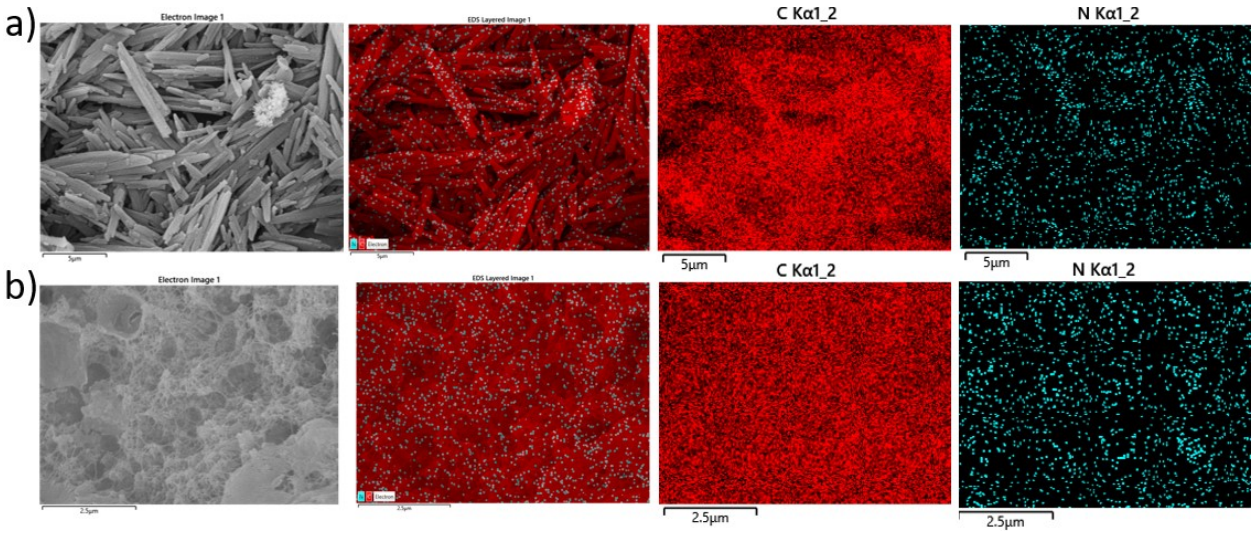

***Figure S6**. FE-SEM Elemental mapping (a) Py-PaCN COF, and (b) PyCN-Pa COF.*

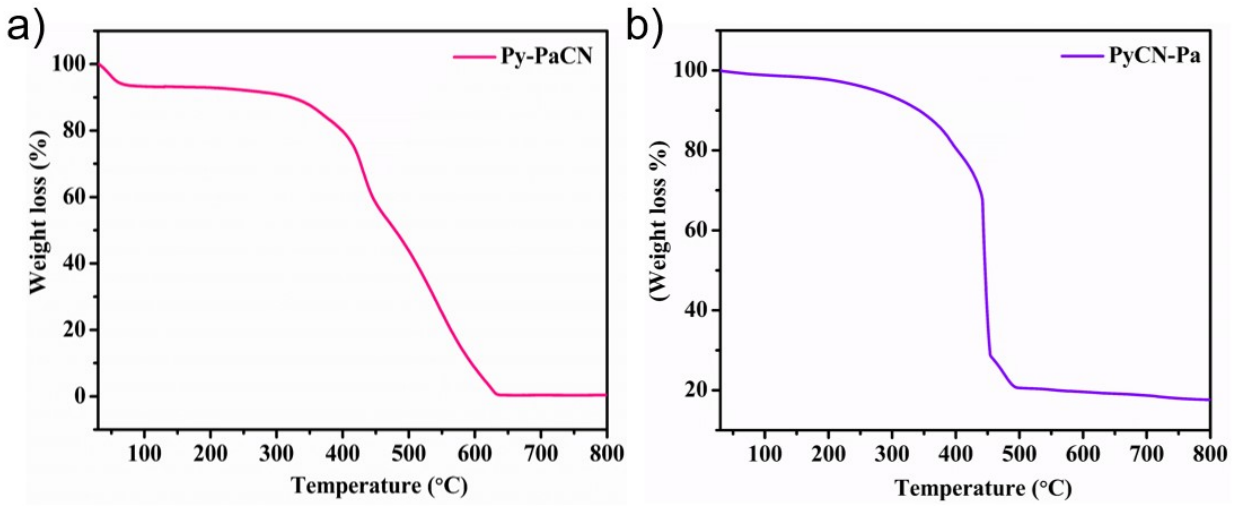

Figure S7. *TGA data of (a) Py-PaCN COF and (b) PyCN-Pa COF.*

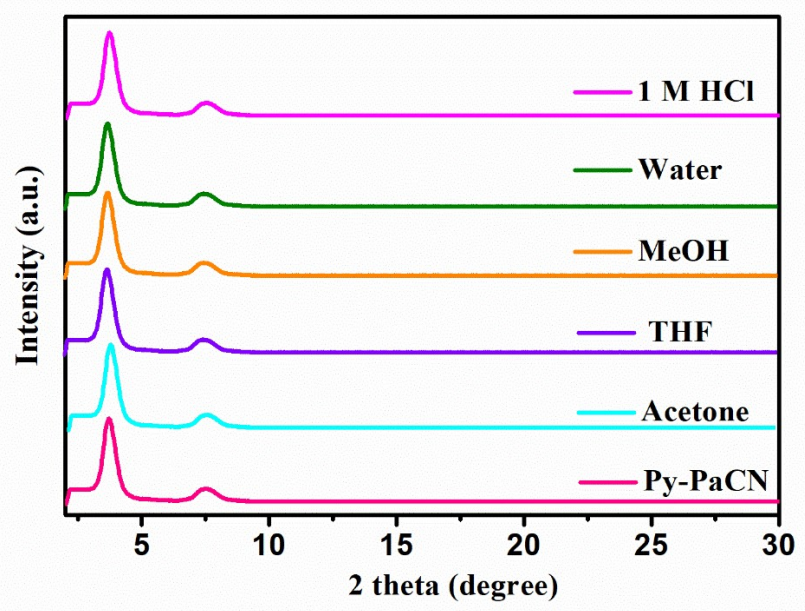

Figure S8. *XRD patterns of Py-PaCN COF after soaking in different solvents for 24 hours.*

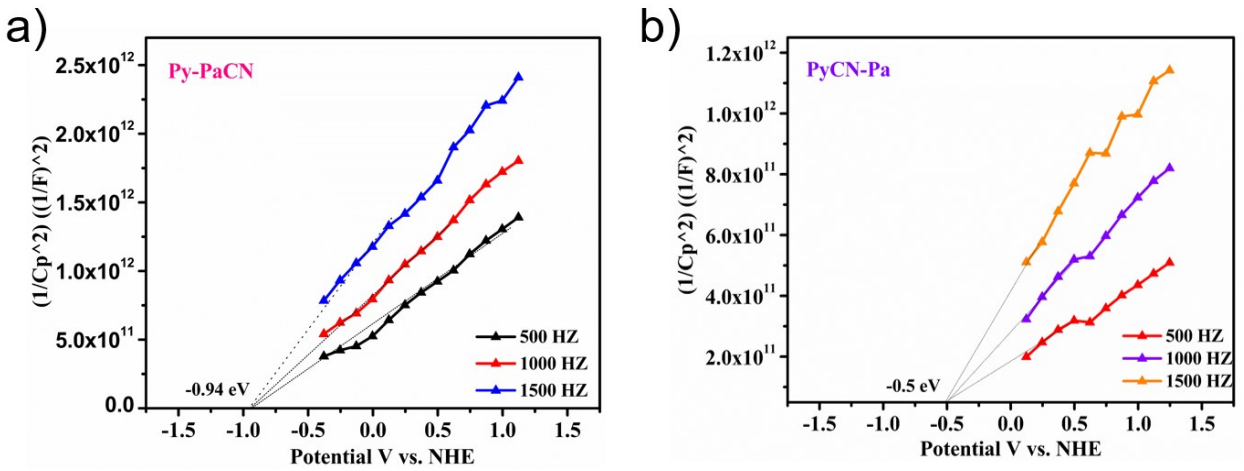

Figure S9. *Mott-Schottky plots of (a) Py-PaCN and (b) PyCN-Pa COFs.*

Photocatalytic hydrogen production: A mixture of 6 mg of COF powder, 30 mL aqueous solution, and 0.1 M aqueous ascorbic acid solution was prepared. The mixture was sonicated for 30 minutes to create a well-dispersed suspension. A 3 wt.% aqueous solution of hexachloroplatinic acid (H_2PtCl_6), acting as a co-catalyst, was added to the suspension. This mixture was transferred to a Pyrex glass reactor vessel connected to a closed gas system. To remove any residual air, the reaction mixture was purged with Ar gas before being irradiated with 3 x 30 W LED light source. The photocatalytic hydrogen generation was carried out over 5 hours, with H_2 generation measured hourly using gas chromatography (PerkinElmer, Clarus 580) with a thermal conductivity detector (TCD), and helium as the carrier gas. The concentration of hydrogen was calibrated against a known standard, and dissolved hydrogen in the reaction mixture was not estimated, with any pressure changes due to H_2 generation being ignored in the calculations. The photocatalytic cycling test followed the same procedure, with each cycle lasting 5 hours.

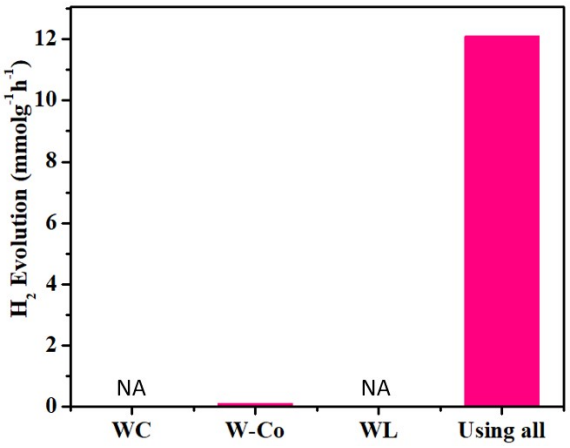

Figure S10. *Optimized conditions for photocatalytic hydrogen production without catalyst (WC), without co-catalyst (W-Co), without light (WL), and by using of all.*

Table S3. *The photocatalytic performance comparison with other representative COF-based photocatalysts.*

Catalyst	**Co-catalyst**	**SED**	**Solvent**	**Illumination**	**Activity, mmol g $^{-1}$ h $^{-1}$**	**AQY%**	**Ref.**
TP-BDDA COF	Pt	TEOA	Water	> 395 nm	0.324	1.8	S2
sp^2 c-COFERDN	Pt	TEOA	Water	λ ≥ 420 nm	2.12	0.48	S3
Py-ClTP-BT-COF	Pt	Ascorbic acid	Water	> 420 nm	8.875	8.45	S4
FS-COF	Pt	Ascorbic acid	Water	> 420 nm	10.20	3.2	S5
NKCOF-108	Pt	Ascorbic acid	Water	> 420 nm	11.60	6.8	S6
PyTz-COF	Pt	Ascorbic acid	Water	AM 1.5G	2.07	-	S7
COF-alkene	Pt	TEOA	Water	> 400 nm	2.33	6.7	S8
TZ-COF-4	Pt	Ascorbic acid	Water	> 400 nm	4.296	1.3	S9
TFPT-COF	Pt	TEOA	Water	> 420 nm	1.97	-	S10
BTTh-TZ-COF	Pt	AA	Xe lamp	> 420 nm	5.22	1.38	S11
RuCOF-ETTA	Pt	AA	Xe lamp	> 420 nm	6.42	6.95	S12
COF-OH-3	Pt	AA	Xe lamp	> 420 nm	9.89	0.15	S13
Py-PaCN-COF	Pt	Ascorbic acid	Water	> 420 nm	12.1	7.15	This work
PyCN-Pa COF	Pt	Ascorbic acid	Water	> 420 nm	4.3	2.54	This work

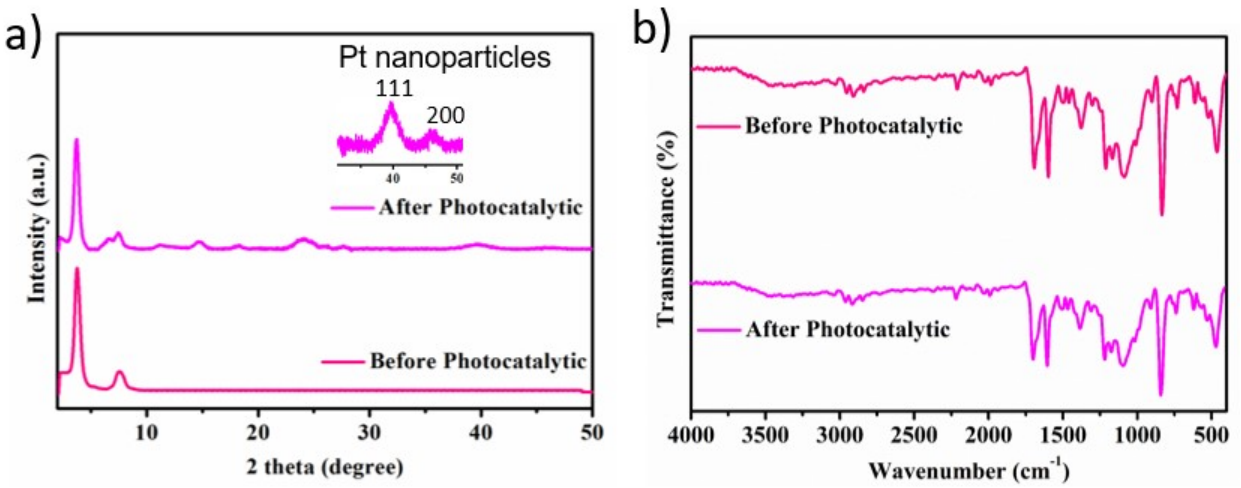

Figure S11. *(a) PXRD, and (b) FT-IR spectra of Py-PaCN COF after photocatalytic hydrogen evolution experiment.*

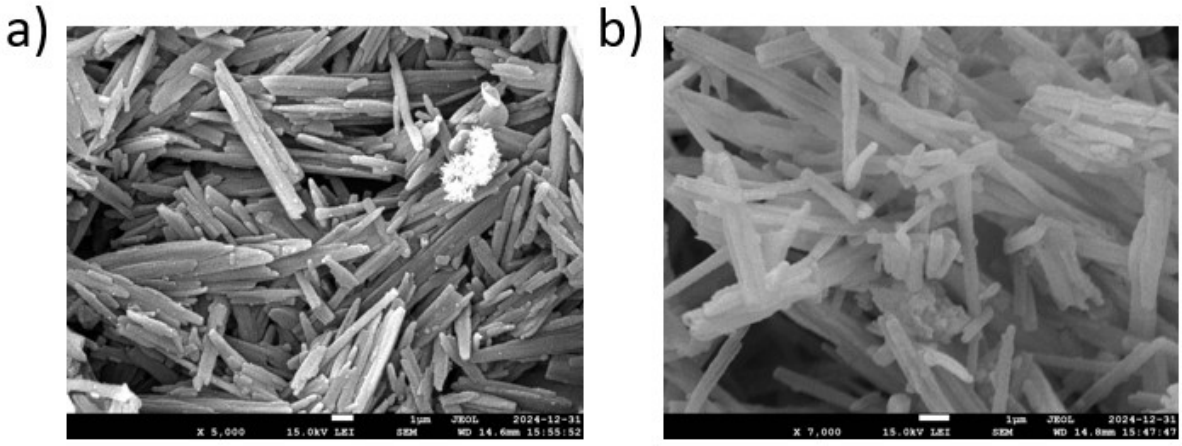

Figure S12. *FE-SEM images of Py-PaCN COF (a) as-synthesized, and (b) recycled COF after hydrogen evolution activity.*

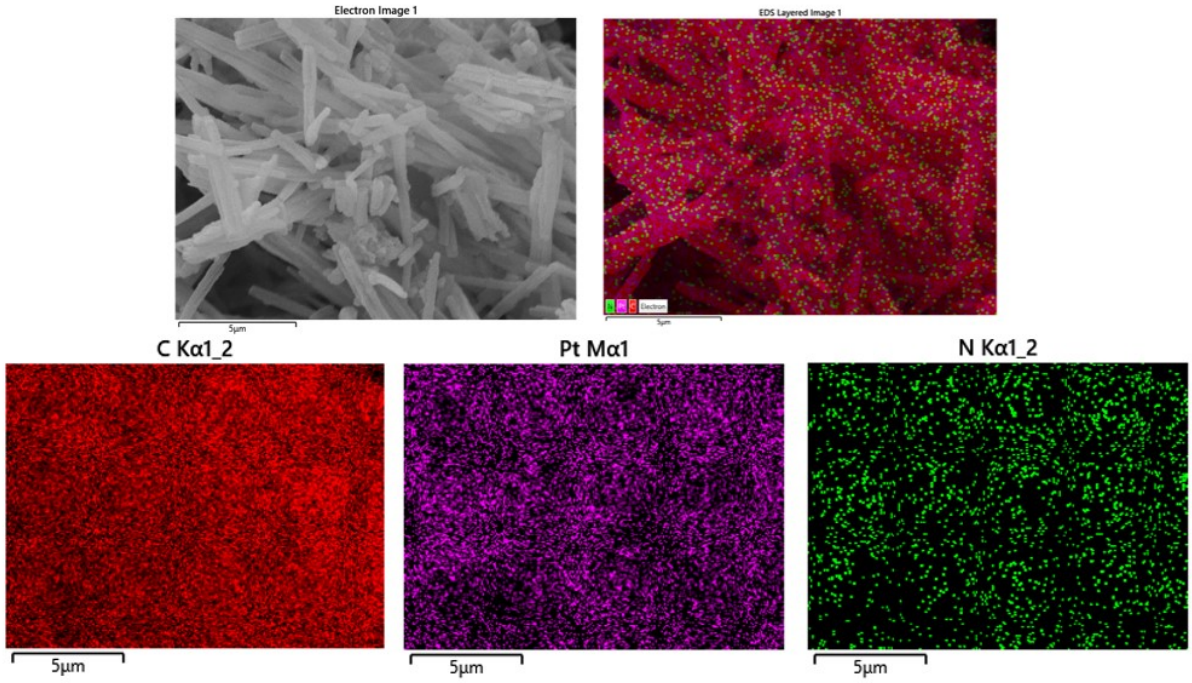

Figure S13. *Elemental mapping of Py-PaCN COF after photocatalytic reaction.*

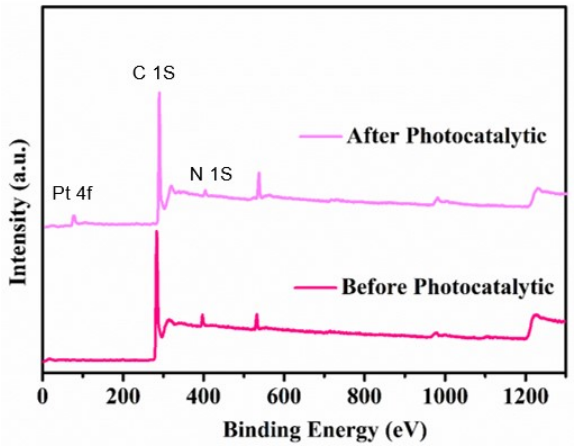

Figure S14. *XPS survey spectra of Py-PaCN COF before and after photocatalysis.*

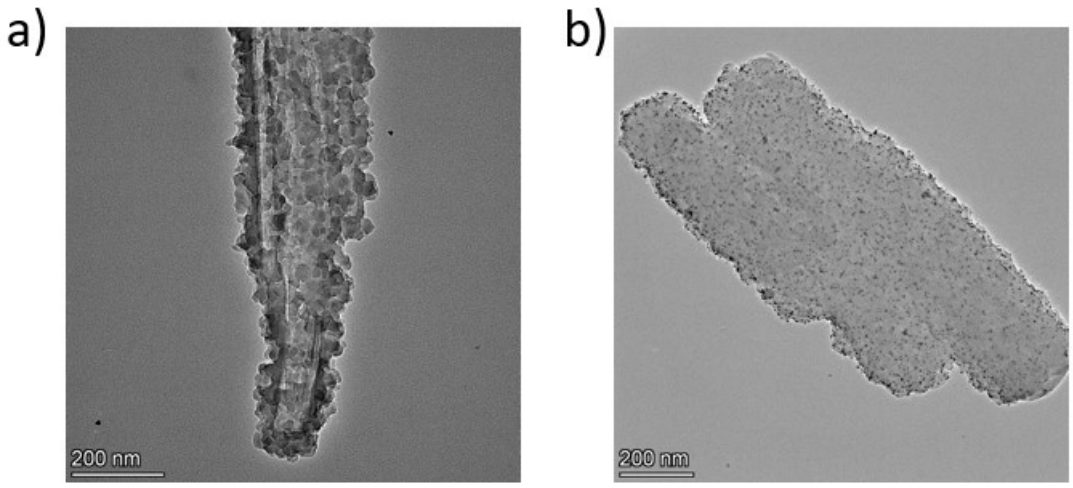

Figure S15. *HR-TEM images of Py-PaCN COF (a) as-synthesized, and (b) recycled COF after hydrogen evolution activity.*

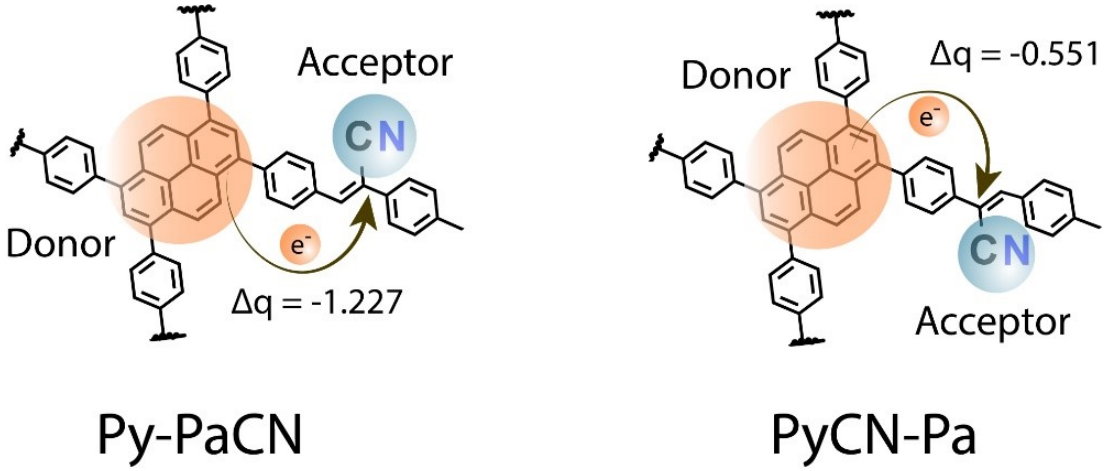

Figure S16: *Change in the partial charge distribution (Δq) at the donor (pyrene) and acceptor (cyano) sites of the COF isomers as determined by Natural Population Analysis (NPA).*

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