Supplementary Information (SI) for Sustainable Energy & Fuels.

Supplementary Information

Benzothiadiazole-based Donor-Acceptor Covalent Organic Framework for Photocatalytic Hydrogen Generation

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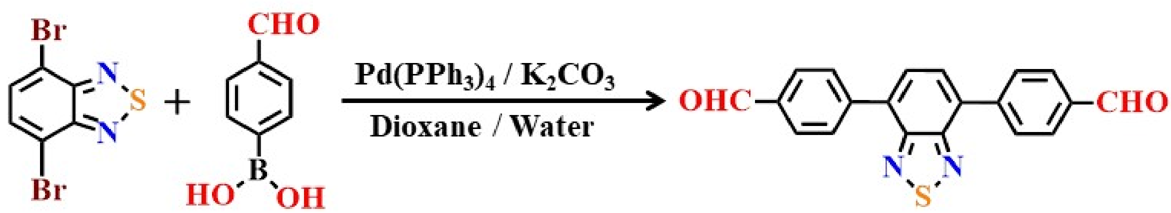
Experimental section

Materials

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 SD Fine Chemicals. 4,7-dibromo-2,1,3-benzothiadiazole and 1,4-Dibromobenzene were obtained from Acros Organics. H_2PtCl_6, $Pd(PPh_3)_4$ were obtained from ChemScene India Pvt. Ltd.

Synthesis of 4,4'-(Benzothiadiazole-4,7-diyl) dibenzaldehyde (BT)



It was synthesized according to a literature method with some modifications.[41] To a K_2CO_3/H_2O solution (0.64 g/3 mL) in a 50 mL two-necked flask was added distilled dioxane (15 mL), 4,7-dibromo-2,1,3-benzothiadiazole (250 mg, 0.85 mmol), 4-formylphenylboronic acid (383 mg, 2.55 mmol), and $Pd(PPh_3)_4$ (60 mg, 0.052 mmol), which was degassed three times. After reflux in N_2 over 72 h, the mixture was poured into water and extracted with chloroform three times and the organic solvents in the obtained solution were removed. ^1H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 2 H, CHO), 8.18 (d, 4 H, J = 8.0 Hz, Ph-H), 8.08 (d, 4 H, J = 8.0 Hz, Ph-H), 7.92 (s, 2H, Ph-H) ppm.

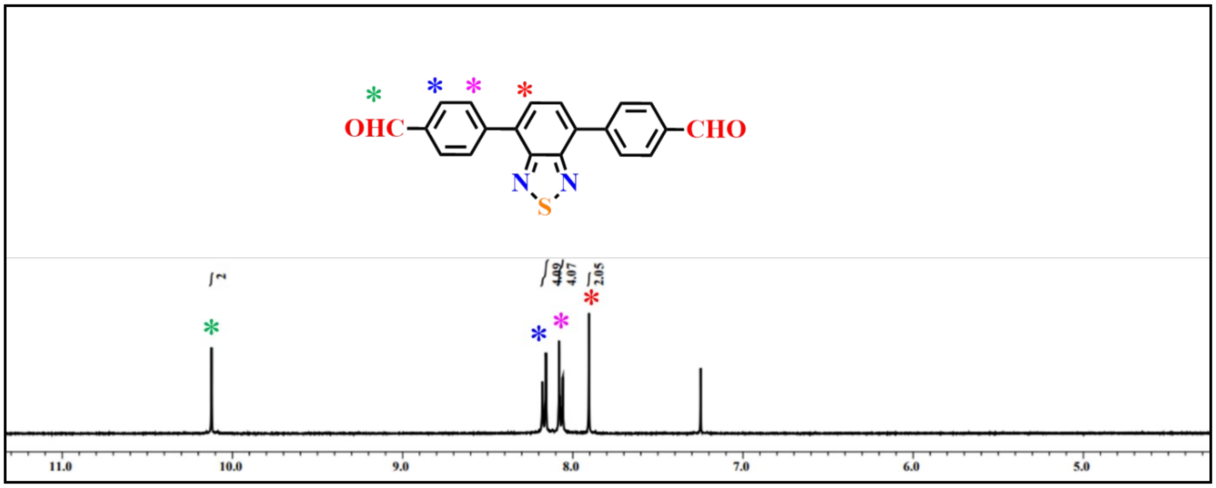


Figure S1. *[1]H NMR ($CDCl_3$, 400 MHz) spectra of 4,4'-(Benzothiadiazole-4,7-diyl) dibenzaldehyde (BT) linker.*

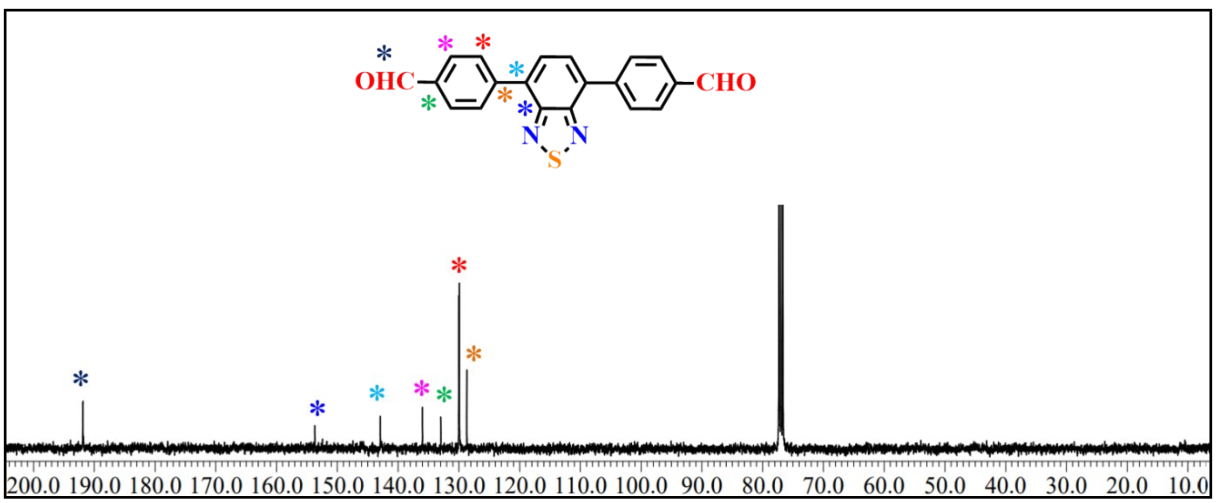
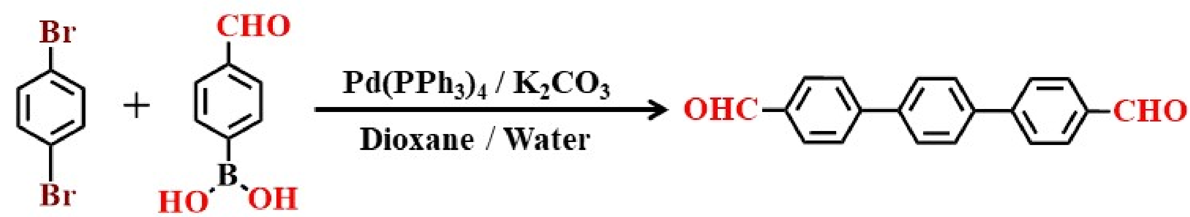


Figure S2. *[13]C NMR ($CDCl_3$, 100 MHz) spectra of 4,4'-(Benzothiadiazole-4,7-diyl) dibenzaldehyde (BT) linker.*

Synthesis of 4,4''-p-Terphenyldicarboxaldehyde (TP)



1,4-Dibromobenzene (0.30 g, 1.27 mmol), tetrakis(triphenylphosphine) palladium (0.20 g, 0.17 mmol), potassium carbonate (0.35 g, 2.54 mmol), were added to 1,4-dioxane containing 4-formylphenylboronic acid (0.40 g, 2.67 mmol), and the mixture was stirred at 100 °C under nitrogen for 3 days. After the solvents were evaporated under vacuum, the residue solid was purified using dichloromethane/hexane (4/1, v/v) as fluent phase, and finally dried in the vacuum oven to give TPDA (0.30 g, 1.05 mmol, 82.4%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 10.07 (s, 2H, CHO), 7.97-7.99 (d, 4H, Ar-H), 7.80-7.82 (d, 4H, Ar-H), 7.76 (s, 4H, Ar-H).

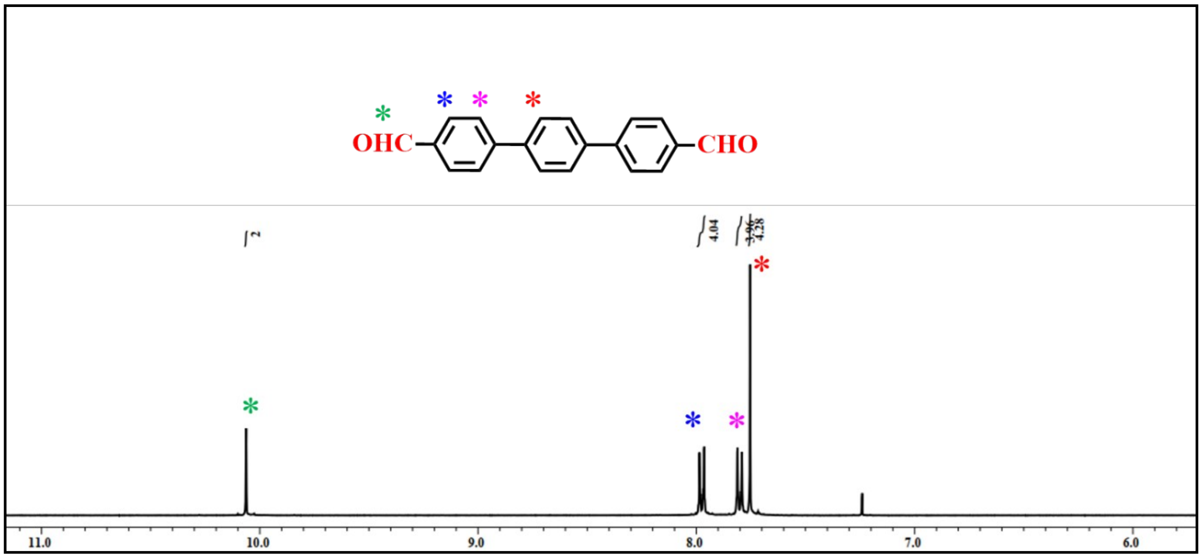


Figure S3. *^{1}H NMR ($CDCl_3$, 400 MHz) spectra of 4,4''-p-Terphenyldicarboxaldehyde (TP) linker.*

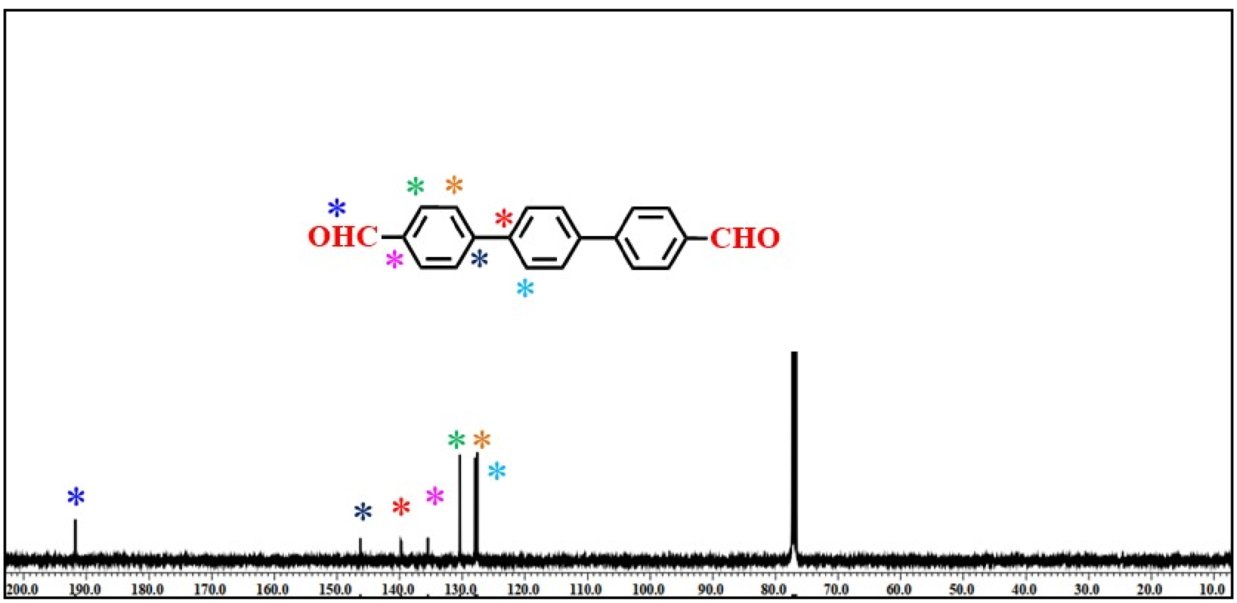


Figure S4. *^{13}C NMR ($CDCl_3$, 400MHz) spectra of 4,4''-p-Terphenyldicarboxaldehyde (TP) linker.*

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 products of catalytic reactions were identified and the catalytic conversions were determined by ^1H NMR spectra 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 (400 MHz) 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 determined following equation:

$$AQY (\%) = 2 \times \text{Number of evolved } H_2 \text{ molecules} / \text{Number of incident photons} \times 100 \%$$

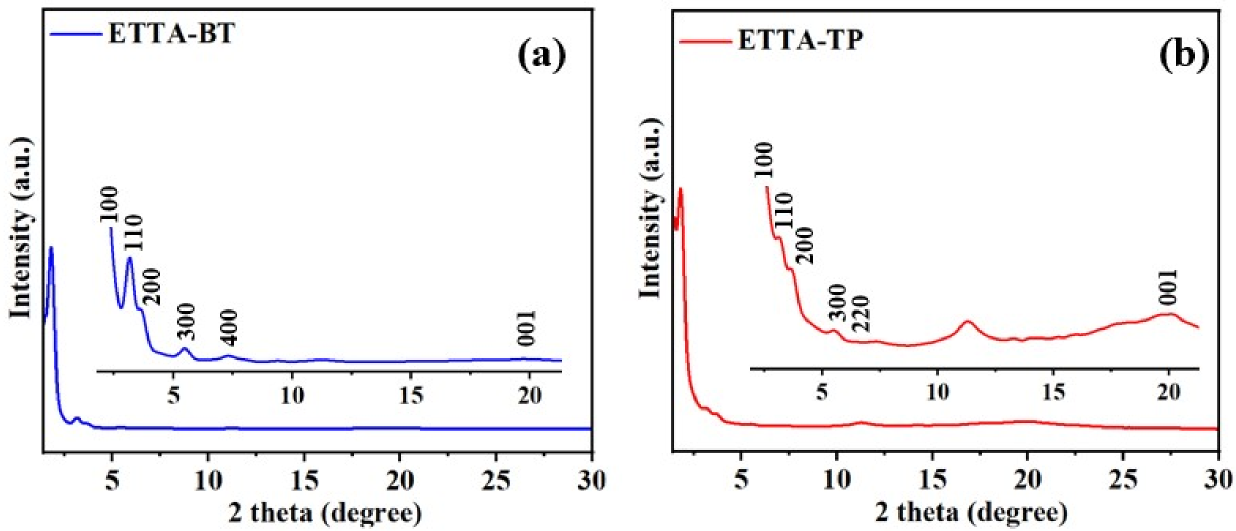


Figure S5. *PXRD patterns of (a) ETTA-BT COF, and (b) ETTA-TP COF.*

Table S1: Fractional atomic coordinates for the unit cell of ETTA-BT COF (adopted from the previous literature.

Space group: P1							
a = 55.7 Å				α = 90°			
b = 56.0 Å				β = 90°			
c = 5.9 Å				γ = 120°			
C	0.49482	0.0051	0.4668	C	0.59176	0.0853	0.3829
C	0.51956	0.0045	0.4495	C	0.57299	0.0734	0.2044
C	0.47381	0.9774	0.9897	C	0.54991	0.0471	0.2295
C	0.46539	0.9803	0.4805	C	0.62464	0.1313	0.5059
C	0.49983	0.9854	0.9328	C	0.65129	0.1571	0.4792
C	0.5235	0.9792	0.4533	C	0.67187	0.1585	0.3337
C	0.442	0.9831	0.4321	C	0.69802	0.1822	0.3265
C	0.4154	0.96	0.4136	C	0.70375	0.205	0.4614
C	0.41123	0.9336	0.4462	C	0.68296	0.2042	0.6006
C	0.43339	0.9307	0.5213	C	0.65697	0.1802	0.6113
C	0.45971	0.9536	0.54	C	0.73192	0.2291	0.4677
C	0.50758	0.9549	0.3242	C	0.73767	0.255	0.3885
C	0.5118	0.9326	0.3341	C	0.7539	0.2265	0.5573
C	0.5315	0.9328	0.4773	C	0.76376	0.2774	0.3987
C	0.54826	0.9565	0.6042	C	0.7807	0.2495	0.569
C	0.54464	0.9795	0.589	C	0.786	0.2755	0.4904
C	0.38079	0.8862	0.3414	C	0.81431	0.2997	0.5013
C	0.35302	0.8616	0.321	C	0.83693	0.2973	0.4267
C	0.54437	0.9009	0.6506	C	0.86368	0.32	0.434
C	0.54182	0.8734	0.642	C	0.86836	0.3454	0.5178
C	0.32885	0.8628	0.362	C	0.84583	0.3478	0.5958
C	0.30291	0.8387	0.357	C	0.81897	0.325	0.5873

C	0.3008	0.8131	0.312	C	0.89666	0.3693	0.5132
C	0.32495	0.8121	0.2659	N	0.38429	0.9099	0.4081
C	0.35079	0.8361	0.2688	N	0.53317	0.908	0.4912
C	0.27369	0.7874	0.3265	N	0.24937	0.8029	0.0757
C	0.27074	0.7651	0.4594	N	0.20488	0.7616	0.116
C	0.25005	0.7844	0.2157	N	0.1062	0.6197	0.3866
C	0.24478	0.7411	0.4824	N	0.10977	0.4954	0.5862
C	0.22137	0.7389	0.3733	N	0.29618	0.5254	0.8095
C	0.19387	0.7143	0.4029	N	0.2571	0.532	0.874
C	0.22487	0.761	0.2383	N	0.3922	0.4949	0.3699
C	0.17227	0.7168	0.4991	N	0.56947	0.7581	0.6498
C	0.14591	0.6937	0.5214	N	0.57759	0.8046	0.6531
C	0.14069	0.6677	0.4454	N	0.51586	0.6186	0.5186
C	0.16244	0.6653	0.3495	N	0.61769	0.5148	0.6387
C	0.18892	0.6884	0.3302	N	0.71606	0.4877	0.2155
C	0.11267	0.6436	0.4723	N	0.75515	0.4813	0.1549
C	0.08007	0.5948	0.4162	N	0.90002	0.5118	0.4968
C	0.06282	0.5909	0.6029	N	0.4959	0.3921	0.4844
C	0.03832	0.5659	0.6339	N	0.44923	0.2521	0.5487
C	0.0306	0.5441	0.4798	N	0.44542	0.2073	0.5701
C	0.04787	0.5479	0.2941	N	0.50151	0.1111	0.5169
C	0.07247	0.573	0.2633	N	0.61596	0.1119	0.3536
C	0.00514	0.5171	0.5168	N	0.90268	0.3924	0.6107
C	0.00606	0.4934	0.537	N	0.76543	0.3001	0.3073
C	0.03282	0.4937	0.5537	N	0.71931	0.2606	0.2907
C	0.03923	0.4781	0.404	S	0.21719	0.7914	0.9697
C	0.06462	0.479	0.4186	S	0.28836	0.5433	0.998
C	0.0842	0.4956	0.5796	S	0.59778	0.79	0.6589
C	0.07792	0.511	0.7318	S	0.72433	0.4704	0.025
C	0.05237	0.51	0.7187	S	0.4235	0.2197	0.6064

C	0.13335	0.515	0.6613	S	0.73434	0.294	0.2085
C	0.15797	0.5117	0.6488	H	0.46113	0.9569	0.0609
C	0.155	0.4856	0.6106	H	0.46533	0.9908	0.9671
C	0.17822	0.4826	0.5871	H	0.50781	0.9714	0.94
C	0.20499	0.5056	0.6007	H	0.51307	0.0053	0.8651
C	0.20799	0.5317	0.6436	H	0.44396	0.003	0.4015
C	0.18465	0.5347	0.6677	H	0.39815	0.9627	0.3667
C	0.22947	0.5023	0.5615	H	0.4307	0.9107	0.5643
C	0.08007	0.5948	0.4162	N	0.90002	0.5118	0.4968
C	0.06282	0.5909	0.6029	N	0.4959	0.3921	0.4844
C	0.03832	0.5659	0.6339	N	0.44923	0.2521	0.5487
C	0.0306	0.5441	0.4798	N	0.44542	0.2073	0.5701
C	0.04787	0.5479	0.2941	N	0.50151	0.1111	0.5169
C	0.07247	0.573	0.2633	N	0.61596	0.1119	0.3536
C	0.00514	0.5171	0.5168	N	0.90268	0.3924	0.6107
C	0.00606	0.4934	0.537	N	0.76543	0.3001	0.3073
C	0.03282	0.4937	0.5537	N	0.71931	0.2606	0.2907
C	0.03923	0.4781	0.404	S	0.21719	0.7914	0.9697
C	0.06462	0.479	0.4186	S	0.28836	0.5433	0.998
C	0.0842	0.4956	0.5796	S	0.59778	0.79	0.6589
C	0.07792	0.511	0.7318	S	0.72433	0.4704	0.025
C	0.05237	0.51	0.7187	S	0.4235	0.2197	0.6064
C	0.13335	0.515	0.6613	S	0.73434	0.294	0.2085
C	0.15797	0.5117	0.6488	H	0.46113	0.9569	0.0609
C	0.155	0.4856	0.6106	H	0.46533	0.9908	0.9671
C	0.17822	0.4826	0.5871	H	0.50781	0.9714	0.94
C	0.20499	0.5056	0.6007	H	0.51307	0.0053	0.8651
C	0.20799	0.5317	0.6436	H	0.44396	0.003	0.4015
C	0.18465	0.5347	0.6677	H	0.39815	0.9627	0.3667
C	0.22947	0.5023	0.5615	H	0.4307	0.9107	0.5643

C	0.25344	0.5155	0.6963	H	0.47557	0.9499	0.6025
C	0.22907	0.4849	0.3858	H	0.48935	0.9503	0.2312
C	0.25169	0.4808	0.3511	H	0.4982	0.9144	0.2377
C	0.27557	0.5118	0.6603	H	0.564	0.9574	0.7155
C	0.27531	0.4943	0.4891	H	0.55786	0.9967	0.6936
C	0.29865	0.4893	0.4586	H	0.39854	0.8839	0.3024
C	0.29503	0.4631	0.4999	H	0.5538	0.914	0.7968
C	0.31756	0.4587	0.487	H	0.33021	0.8823	0.4017
C	0.34392	0.4805	0.4297	H	0.28452	0.8399	0.3952
C	0.34727	0.5065	0.3796	H	0.32382	0.7926	0.2292
C	0.32479	0.511	0.3959	H	0.3692	0.8348	0.235
C	0.36785	0.4761	0.4384	H	0.28839	0.7666	0.5494
C	0.41681	0.4932	0.3968	H	0.24286	0.7244	0.5888
C	0.4208	0.4807	0.5885	H	0.17599	0.7368	0.557
C	0.44544	0.4803	0.6166	H	0.12953	0.6961	0.5967
C	0.46646	0.4924	0.4535	H	0.15888	0.6455	0.29
C	0.46251	0.505	0.2627	H	0.20547	0.6863	0.2548
C	0.43798	0.5057	0.2362	H	0.09748	0.6464	0.5642
C	0.49304	0.4929	0.4861	H	0.06865	0.6067	0.7303
C	0.51736	0.517	0.4992	H	0.02614	0.5632	0.7837
C	0.49264	0.4663	0.4812	H	0.04241	0.5311	0.1772
C	0.51775	0.5436	0.507	H	0.08583	0.5754	0.1216
C	0.54382	0.5174	0.5366	H	0.0252	0.4657	0.2718
C	0.54736	0.5051	0.7311	H	0.06943	0.4672	0.3012
C	0.57169	0.5042	0.7633	H	0.09242	0.5234	0.8622
C	0.59318	0.5164	0.6054	H	0.04791	0.522	0.8359
C	0.5897	0.5288	0.4103	H	0.13556	0.5343	0.7198
C	0.56515	0.5292	0.3759	H	0.13459	0.4675	0.5973
C	0.52723	0.5618	0.3222	H	0.17521	0.4622	0.5576
C	0.52624	0.5862	0.3292	H	0.22841	0.5498	0.6525

C	0.51554	0.5928	0.5189	H	0.18737	0.555	0.6951
C	0.50593	0.5744	0.7038	H	0.21137	0.4747	0.2739
C	0.50697	0.55	0.6969	H	0.25093	0.4674	0.2154
C	0.48372	0.4486	0.6693	H	0.27493	0.4462	0.549
C	0.48501	0.4244	0.6659	H	0.31452	0.4385	0.5261
C	0.49537	0.4175	0.4766	H	0.36743	0.5235	0.3343
C	0.50451	0.4353	0.2884	H	0.32766	0.5312	0.3619
C	0.50316	0.4595	0.2917	H	0.36486	0.4569	0.5082
C	0.52585	0.8546	0.4716	H	0.40522	0.472	0.7199
C	0.52173	0.8279	0.4707	H	0.44831	0.4713	0.769
C	0.53379	0.8196	0.6385	H	0.47876	0.5146	0.1376
C	0.55036	0.8385	0.8061	H	0.43531	0.5159	0.0906
C	0.55421	0.8653	0.8085	H	0.53092	0.4959	0.8548
C	0.52873	0.7911	0.6388	H	0.57402	0.4941	0.9117
C	0.50151	0.7684	0.6296	H	0.6057	0.5374	0.282
C	0.55063	0.7856	0.6454	H	0.56262	0.538	0.2213
C	0.49678	0.7413	0.6294	H	0.53475	0.5568	0.1705
C	0.54605	0.7592	0.6419	H	0.53362	0.6001	0.186
C	0.51919	0.7363	0.634	H	0.49801	0.5788	0.855
C	0.51435	0.7079	0.6339	H	0.49924	0.5359	0.8385
C	0.49644	0.6887	0.7935	H	0.47657	0.4539	0.8214
C	0.49257	0.662	0.7994	H	0.47812	0.4109	0.812
C	0.50637	0.6541	0.6443	H	0.51269	0.4309	0.1388
C	0.5239	0.6732	0.4816	H	0.51063	0.4733	0.1483
C	0.5279	0.6999	0.4768	H	0.51605	0.8605	0.3416
C	0.50286	0.6262	0.6585	H	0.50912	0.8138	0.3388
C	0.6423	0.5342	0.5821	H	0.55991	0.8325	0.9366
C	0.66629	0.53	0.5961	H	0.56658	0.8795	0.9412
C	0.66269	0.5035	0.6232	H	0.48398	0.7718	0.625
C	0.68542	0.4994	0.6106	H	0.4757	0.7241	0.6231

C	0.71205	0.5219	0.5748	H	0.48599	0.6946	0.9169
C	0.71584	0.5485	0.5578	H	0.47907	0.6477	0.9269
C	0.69306	0.5525	0.5662	H	0.53478	0.6675	0.3604
C	0.73572	0.5174	0.545	H	0.54169	0.7145	0.3517
C	0.75872	0.5301	0.6898	H	0.48937	0.6123	0.7879
C	0.73615	0.5007	0.3701	H	0.64545	0.5538	0.5186
C	0.7812	0.5257	0.6606	H	0.64218	0.4859	0.6466
C	0.75832	0.4969	0.337	H	0.68234	0.4788	0.6257
C	0.78169	0.5092	0.4808	H	0.73632	0.566	0.5301
C	0.80636	0.5056	0.4471	H	0.69627	0.5732	0.5453
C	0.80391	0.4811	0.3573	H	0.75893	0.5429	0.8287
C	0.82729	0.4782	0.3298	H	0.79797	0.535	0.7819
C	0.85344	0.4993	0.3986	H	0.78392	0.4639	0.3123
C	0.85598	0.5236	0.4881	H	0.82486	0.4592	0.2598
C	0.83289	0.5269	0.5093	H	0.87601	0.5403	0.5408
C	0.87793	0.4958	0.3809	H	0.83598	0.5463	0.5739
C	0.92567	0.5117	0.4985	H	0.8768	0.4791	0.2796
C	0.93459	0.5021	0.3151	H	0.9218	0.4935	0.1666
C	0.96076	0.5044	0.3201	H	0.96746	0.497	0.1789
C	0.97816	0.5162	0.5082	H	0.98134	0.5331	0.8445
C	0.96892	0.5251	0.693	H	0.9362	0.5305	0.8281
C	0.94302	0.5232	0.686	H	0.96995	0.476	0.8878
C	0.98007	0.4665	0.5599	H	0.9253	0.4321	0.919
C	0.96349	0.4609	0.7539	H	0.93837	0.409	0.2549
C	0.93814	0.4363	0.7701	H	0.98166	0.4525	0.222
C	0.9292	0.417	0.5944	H	0.51493	0.3937	0.1775
C	0.94548	0.4229	0.3979	H	0.48235	0.3467	0.6867
C	0.97049	0.4477	0.3802	H	0.47936	0.3018	0.7371
C	0.5056	0.3824	0.3315	H	0.52151	0.3125	0.0998
C	0.50389	0.3555	0.3654	H	0.52474	0.3575	0.0508

C	0.49112	0.3395	0.5586	H	0.54136	0.2913	0.3671
C	0.48934	0.3138	0.5869	H	0.53728	0.2455	0.3869
C	0.50034	0.3039	0.4226	H	0.45637	0.1795	0.2333
C	0.51319	0.32	0.23	H	0.45291	0.1341	0.2057
C	0.51491	0.3456	0.2014	H	0.5212	0.1607	0.6707
C	0.49829	0.2766	0.4494	H	0.52471	0.2063	0.6984
C	0.47322	0.2529	0.5062	H	0.46892	0.1021	0.2994
C	0.52153	0.2735	0.4096	H	0.48615	0.0766	0.1503
C	0.47101	0.2275	0.5169	H	0.48354	0.032	0.134
C	0.51929	0.2474	0.4229	H	0.51424	0.0436	0.8196
C	0.49371	0.2239	0.4737	H	0.51746	0.0881	0.8305
C	0.49084	0.1962	0.4674	H	0.5597	0.0347	0.7741
C	0.47051	0.1755	0.3304	H	0.60135	0.0798	0.7261
C	0.46862	0.1498	0.3139	H	0.57572	0.0848	0.0497
C	0.48701	0.1443	0.4341	H	0.53407	0.0389	0.1026
C	0.50706	0.1648	0.5746	H	0.61238	0.1285	0.6566
C	0.50906	0.1907	0.5901	H	0.66791	0.1408	0.2316
C	0.48503	0.1172	0.4079	H	0.71393	0.1827	0.2178
C	0.50082	0.0852	0.4971	H	0.68719	0.2218	0.7053
C	0.49179	0.0693	0.2985	H	0.64132	0.1796	0.7238
C	0.49025	0.0437	0.2891	H	0.75018	0.2068	0.6204
C	0.49693	0.033	0.4789	H	0.79722	0.2471	0.6419
C	0.50732	0.0498	0.6731	H	0.83383	0.278	0.3586
C	0.50951	0.0757	0.6798	H	0.88077	0.3178	0.3725
C	0.54569	0.0318	0.4277	H	0.84903	0.3673	0.6599
C	0.56385	0.0446	0.6107	H	0.80177	0.3272	0.648
C	0.58701	0.0708	0.5866	H	0.91248	0.3671	0.425

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

Space group: P1	
a = 55.3 Å	α = 90°
b = 55.3 Å	β = 90°
c = 4.5 Å	γ = 120°

C	1.50698	0.47975	0.55579	C	1.35527	0.85325	0.31858
C	1.53072	0.50462	0.63838	N	1.63729	0.09397	0.54366
C	1.53143	0.53156	0.73716	N	1.91934	0.37937	0.22017
C	1.55939	0.50778	0.6105	C	1.91746	0.3552	0.25039
C	1.50794	0.45373	0.46235	C	1.89037	0.33016	0.22324
C	1.47793	0.4761	0.5265	C	1.64237	0.11841	0.45561
C	1.55671	0.55742	0.73353	C	1.67089	0.14126	0.43549
C	1.55766	0.58216	0.80718	C	1.69423	0.13982	0.53655
C	1.53357	0.58269	0.89093	C	1.72092	0.16197	0.50779
C	1.50874	0.55695	0.91562	C	1.7263	0.18743	0.37086
C	1.5079	0.53215	0.84604	C	1.70248	0.18888	0.27593
C	1.56977	0.49672	0.8226	C	1.67595	0.16656	0.30717
C	1.59603	0.49977	0.79239	C	1.86662	0.33016	0.11038
C	1.61425	0.51632	0.56665	C	1.84105	0.30617	0.09715
C	1.60478	0.5296	0.37056	C	1.8372	0.28019	0.20404
C	1.57772	0.52484	0.38693	C	1.8616	0.28016	0.30479
C	1.47352	0.49674	0.39939	C	1.88705	0.30434	0.31475
C	1.44695	0.49283	0.36446	C	1.16841	0.66121	0.6964
C	1.42324	0.46787	0.45109	C	1.1922	0.68552	0.6235
C	1.42751	0.44683	0.57145	C	1.1965	0.71201	0.7149
C	1.45412	0.4507	0.60613	C	1.17565	0.71156	0.90466
C	1.52236	0.44318	0.62294	C	1.15197	0.68694	0.97824

C	1.52206	0.41903	0.53924	C	1.33692	0.85591	0.51512
C	1.50606	0.40292	0.29808	C	1.30919	0.83588	0.53491
C	1.48984	0.41222	0.14992	C	1.29774	0.81094	0.36375
C	1.49116	0.43718	0.22587	C	1.31613	0.80932	0.15352
N	1.53482	0.60829	0.94285	C	1.34383	0.82945	0.13665
N	1.64072	0.51882	0.54809	C	1.2204	0.73766	0.60972
N	1.50517	0.37786	0.21782	C	1.27035	0.78711	0.42688
N	1.39669	0.46507	0.41461	C	1.75437	0.21028	0.32321
C	1.66118	0.53378	0.36926	C	1.80971	0.25594	0.23304
C	1.37353	0.44733	0.543	C	1.77742	0.21307	0.49284
C	1.6853	0.53002	0.37086	C	1.80385	0.23482	0.44934
C	1.34871	0.44945	0.49487	C	1.78673	0.25288	0.06036
C	1.68751	0.51085	0.55891	C	1.76031	0.23114	0.10372
C	1.71032	0.50724	0.55234	C	1.23759	0.73732	0.37628
C	1.73287	0.52264	0.35253	C	1.26136	0.76077	0.29025
C	1.73074	0.54242	0.16742	C	1.25232	0.78781	0.64892
C	1.70775	0.54575	0.1774	C	1.22857	0.76424	0.73714
C	1.34738	0.46809	0.29097	H	1.57687	0.55967	0.67043
C	1.32369	0.47001	0.25774	H	1.57768	0.60181	0.78986
C	1.29944	0.45366	0.43312	H	1.48943	0.55622	0.98894
C	1.3006	0.43407	0.63034	H	1.48782	0.51306	0.87841
C	1.32442	0.43233	0.65935	H	1.55747	0.48563	1.01928
C	1.75625	0.51792	0.33404	H	1.60285	0.48956	0.95494
C	1.27603	0.45849	0.43308	H	1.6184	0.54327	0.19314
C	1.27916	0.48473	0.34566	H	1.57104	0.53516	0.22426
C	1.25808	0.49056	0.38024	H	1.4913	0.51688	0.33524
C	1.23176	0.47062	0.50315	H	1.44458	0.50981	0.26864
C	1.2283	0.44405	0.58043	H	1.40965	0.42672	0.63908
C	1.24937	0.43821	0.54485	H	1.45588	0.43316	0.69508

C	1.20966	0.47698	0.54792	H	1.5329	0.45204	0.83209
C	1.75393	0.4922	0.42794	H	1.534	0.41225	0.67699
C	1.77609	0.48784	0.41484	H	1.47622	0.39987	-0.0346
C	1.8027	0.50883	0.30859	H	1.47834	0.4436	0.09971
C	1.80487	0.53434	0.20858	H	1.66082	0.54843	0.20619
C	1.7827	0.53872	0.22185	H	1.37186	0.43129	0.70001
C	1.82664	0.50497	0.31662	H	1.67084	0.4982	0.71831
C	1.51612	0.61359	0.83876	H	1.71089	0.49217	0.70742
C	1.52067	0.64172	0.85472	H	1.74712	0.55458	0.0035
C	1.52373	0.37155	0.30458	H	1.70707	0.56088	0.02413
C	1.51781	0.34296	0.29073	H	1.36553	0.48171	0.15209
C	1.54283	0.6637	1.01167	H	1.32408	0.48512	0.09618
C	1.54665	0.69024	1.01289	H	1.28298	0.42129	0.77912
C	1.52814	0.69657	0.85386	H	1.32429	0.41751	0.82327
C	1.5053	0.67395	0.70173	H	1.29936	0.50135	0.2617
C	1.50205	0.64769	0.7027	H	1.26199	0.51143	0.31769
C	1.49709	0.32214	0.10991	H	1.20828	0.42768	0.67071
C	1.49215	0.29519	0.11187	H	1.24559	0.4175	0.61264
C	1.50735	0.28697	0.30249	H	1.73392	0.47524	0.51186
C	1.5287	0.3084	0.4793	H	1.77315	0.46766	0.49131
C	1.53365	0.3353	0.47089	H	1.82497	0.55138	0.12804
C	1.53293	0.72441	0.82745	H	1.78571	0.55901	0.14888
C	1.50054	0.2582	0.32999	H	1.49755	0.59811	0.71593
C	1.47371	0.23559	0.25041	H	1.54307	0.38631	0.42102
C	1.46682	0.20847	0.29538	H	1.55776	0.65998	1.13671
C	1.48616	0.20146	0.42212	H	1.56435	0.7069	1.13564
C	1.51309	0.22408	0.49831	H	1.49097	0.67795	0.56897
C	1.51999	0.25114	0.45233	H	1.48461	0.63131	0.57452
C	1.56032	0.74773	0.77685	H	1.4845	0.32722	-0.0394

C	1.56412	0.77341	0.70606	H	1.47587	0.27986	-0.036
C	1.54103	0.77825	0.69215	H	1.54074	0.30348	0.63811
C	1.51382	0.75516	0.75287	H	1.54994	0.35069	0.61868
C	1.50997	0.72943	0.81817	H	1.45775	0.23978	0.15843
C	1.47966	0.17288	0.45744	H	1.44581	0.19182	0.23219
C	1.54469	0.80515	0.62294	H	1.52912	0.21993	0.58936
C	1.20784	0.49769	0.37651	H	1.5411	0.26763	0.51429
C	1.18561	0.5021	0.40576	H	1.57835	0.74442	0.77765
C	1.16377	0.48679	0.60777	H	1.58532	0.7908	0.66294
C	1.16587	0.46694	0.78505	H	1.49559	0.75811	0.74157
C	1.1879	0.46217	0.75845	H	1.48869	0.71197	0.85599
C	1.5646	0.82335	0.40898	H	1.22361	0.50955	0.20571
C	1.5672	0.84883	0.34353	H	1.185	0.51777	0.26017
C	1.55073	0.85827	0.48506	H	1.14965	0.45458	0.94991
C	1.53115	0.84041	0.69688	H	1.1884	0.44646	0.904
C	1.528	0.81483	0.76432	H	1.57747	0.81653	0.28866
C	1.45995	0.15106	0.27074	H	1.58249	0.86181	0.17335
C	1.45774	0.12517	0.26909	H	1.5178	0.84665	0.81661
C	1.47433	0.11885	0.45434	H	1.51275	0.80188	0.93513
C	1.49266	0.1398	0.6515	H	1.44789	0.15535	0.1061
C	1.49501	0.16572	0.65758	H	1.44315	0.10957	0.11003
C	1.82826	0.4861	0.52063	H	1.50568	0.13586	0.80672
C	1.85183	0.48386	0.54154	H	1.50995	0.18133	0.81408
C	1.87537	0.49981	0.3623	H	1.81102	0.47392	0.67591
C	1.8738	0.51812	0.15595	H	1.85202	0.46943	0.7086
C	1.85042	0.5207	0.1323	H	1.89149	0.53093	0.00791
C	1.14049	0.49189	0.62022	H	1.85034	0.53521	-0.0343
C	1.55395	0.88531	0.41397	H	1.14	0.50591	0.44931
C	1.47214	0.09169	0.43349	H	1.56927	0.8981	0.24287

C	1.89975	0.49683	0.40112	H	1.45644	0.07654	0.27914
N	1.12011	0.47805	0.80474	H	1.89933	0.4836	0.58648
N	1.48969	0.08713	0.57914	H	1.10078	0.50809	1.09641
N	1.53875	0.89314	0.55776	H	1.05703	0.50721	0.98896
C	1.53757	0.91784	0.54505	H	1.03936	0.44563	0.29952
C	1.09479	0.47754	0.7581	H	1.08106	0.44586	0.41514
C	1.49318	0.0637	0.56119	H	1.57188	0.94064	0.23385
N	1.92136	0.51066	0.23216	H	1.56797	0.98246	0.22872
C	1.94617	0.51092	0.30123	H	1.49878	0.94372	0.84615
C	1.08711	0.49436	0.91941	H	1.50292	0.90193	0.85638
C	1.06257	0.49428	0.85482	H	1.46033	0.04028	0.2352
C	1.04498	0.47851	0.62027	H	1.46749	0.00078	0.21638
C	1.05174	0.46002	0.47615	H	1.5347	0.04054	0.85454
C	1.07606	0.45979	0.5425	H	1.52728	0.0804	0.87995
C	1.55565	0.94107	0.37108	H	1.94185	0.48119	-0.0385
C	1.55335	0.96489	0.36764	H	1.98525	0.48208	0.09122
C	1.53274	0.96642	0.53666	H	1.9988	0.54112	0.79697
C	1.51516	0.94344	0.71408	H	1.95788	0.54156	0.65298
C	1.51737	0.91965	0.71681	H	1.57887	0.00349	0.82157
C	1.47686	0.04079	0.37515	H	1.6237	0.04633	0.82735
C	1.48111	0.01821	0.36231	H	1.59059	0.08512	0.24229
C	1.50188	0.01739	0.53472	H	1.546	0.04331	0.24735
C	1.51818	0.04024	0.71986	H	1.96541	0.45835	0.76802
C	1.51402	0.06289	0.73192	H	1.92405	0.41597	0.63293
C	1.95459	0.49439	0.14637	H	1.96977	0.40054	-0.0487
C	1.97881	0.4944	0.22396	H	2.01089	0.44443	0.06105
C	1.995	0.50945	0.46947	H	1.07371	0.53036	0.32089
C	1.98745	0.52747	0.611	H	1.11377	0.57491	0.42317
C	1.96358	0.52799	0.52914	H	1.06833	0.58964	1.11537

C	1.02005	0.50664	0.56234	H	1.02856	0.54409	1.03212
C	1.04624	0.53373	0.64838	H	1.45645	0.98154	0.80808
C	1.53031	0.9925	0.53165	H	1.41049	0.94072	0.78452
C	1.47665	0.9647	0.52397	H	1.44226	0.89964	0.21581
C	1.50476	-0.0084	0.52913	H	1.48833	0.94003	0.24385
C	1.55821	0.01954	0.53388	H	1.10565	0.6361	1.07443
C	2.01961	0.48132	0.53813	H	1.39707	0.87045	0.1259
C	1.99315	0.45459	0.4463	H	1.93519	0.35266	0.3188
C	1.58091	0.02134	0.69434	H	1.626	0.12281	0.38153
C	1.60657	0.04572	0.69704	H	1.69146	0.12064	0.64123
C	1.61099	0.06949	0.53879	H	1.73828	0.15929	0.58523
C	1.58839	0.06746	0.37499	H	1.70497	0.20798	0.17217
C	1.56276	0.04319	0.37338	H	1.65848	0.16883	0.22446
C	1.96754	0.44613	0.59037	H	1.86801	0.34966	0.03225
C	1.94349	0.42185	0.5115	H	1.82308	0.30777	0.01861
C	1.94377	0.4044	0.28771	H	1.86017	0.26078	0.3874
C	1.96895	0.4132	0.13524	H	1.90495	0.30317	0.404
C	1.99279	0.43808	0.20613	H	1.16627	0.6417	0.60768
C	1.07147	0.54279	0.49508	H	1.20744	0.68371	0.48278
C	1.09476	0.56833	0.55566	H	1.17762	0.73114	0.98807
C	1.09414	0.5863	0.77078	H	1.13638	0.688	1.12102
C	1.06957	0.57665	0.93783	H	1.34459	0.87414	0.66277
C	1.04644	0.55069	0.88307	H	1.29673	0.839	0.70466
C	1.45402	0.9637	0.67796	H	1.30913	0.79119	0.00642
C	1.42766	0.94046	0.66395	H	1.35702	0.82648	-0.0254
C	1.42245	0.91707	0.49485	H	1.77403	0.19805	0.67073
C	1.44514	0.91762	0.34758	H	1.82055	0.23657	0.59633
C	1.47156	0.94092	0.36146	H	1.79009	0.26818	-0.1142
N	1.11785	0.61272	0.80467	H	1.74357	0.22969	-0.0405

N	1.39508	0.89455	0.47924	H	1.23229	0.71788	0.25843
C	1.12165	0.63514	0.93766	H	1.27372	0.75825	0.11455
C	1.14723	0.66097	0.87209	H	1.25776	0.8073	0.76655
C	1.38474	0.87359	0.2979	H	1.21646	0.76611	0.9206

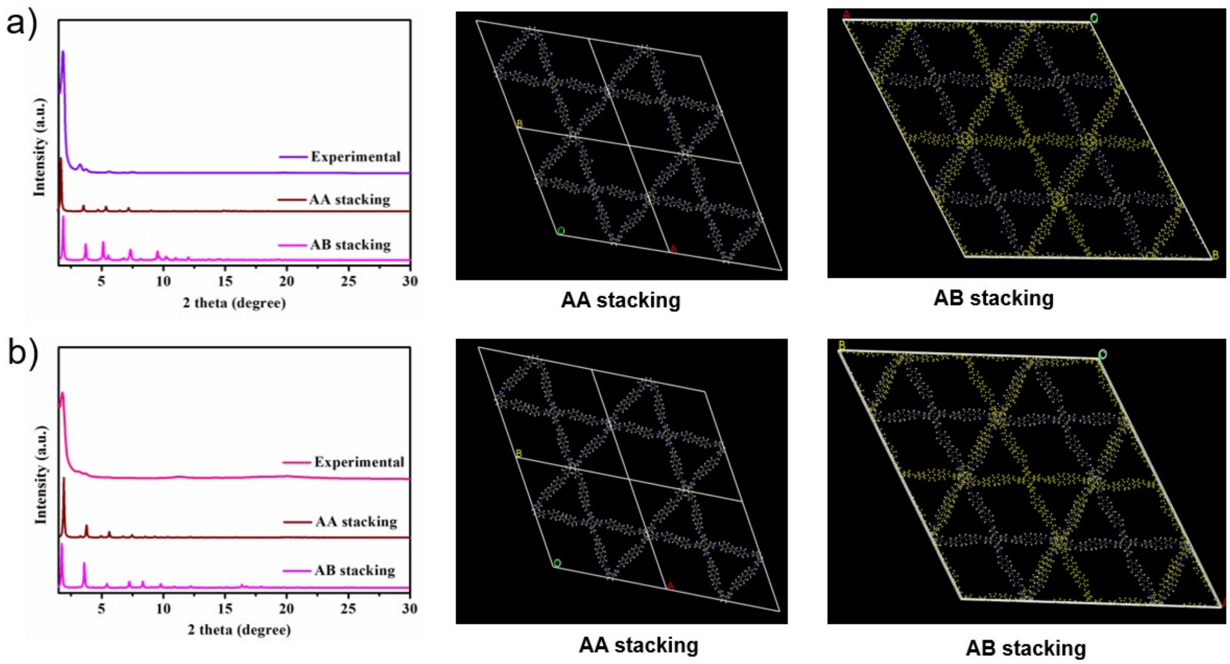


Figure S6. *Experimental and simulated powder XRD patterns of (a) ETTA-BT COF and (b) ETTA-TP COF shown in AA and AB stacking modes.*

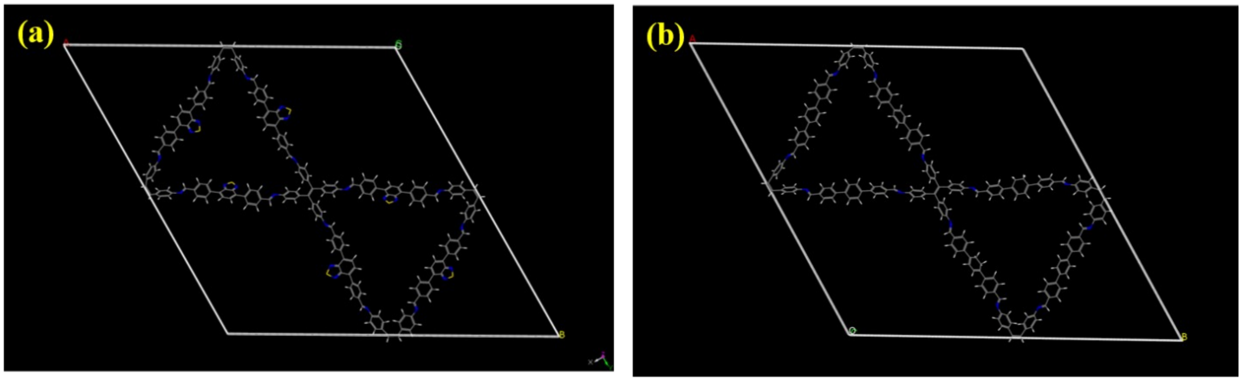


Figure S7. *A unit cell of (a) ETTA-BT COF, and (b) ETTA-TP COF (grey, carbon; yellow, sulphur; blue, nitrogen).*

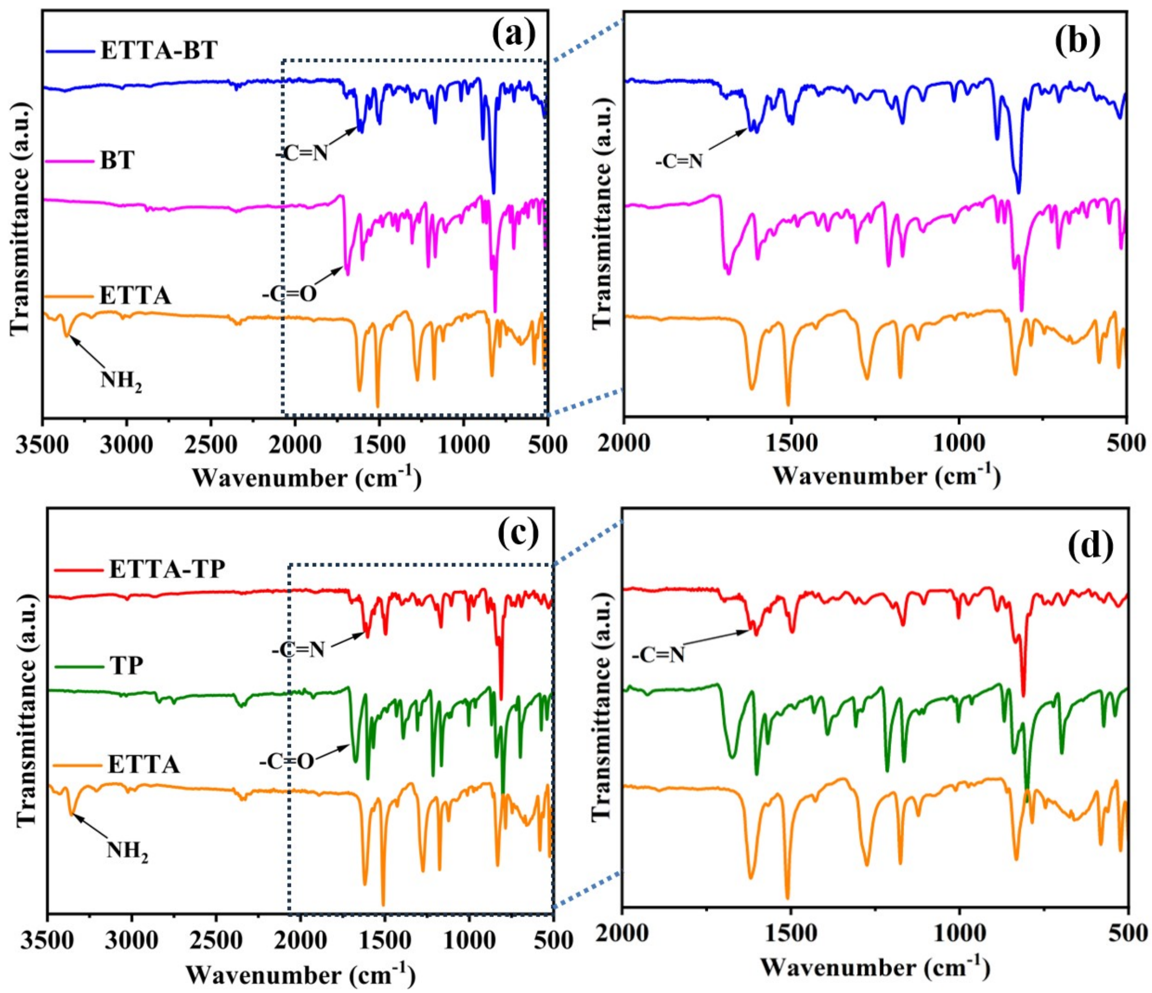


Figure S8. *FT-IR plots of (a and b) ETTA-BT COF and (c and d) ETTA-TP COF.*

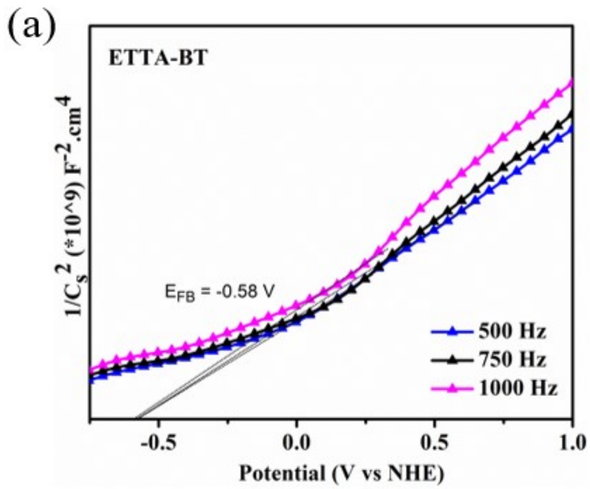


Figure S9. *Mott–Schottky plots for (a) ETTA-BT, and (b) ETTA-TP COFs.*

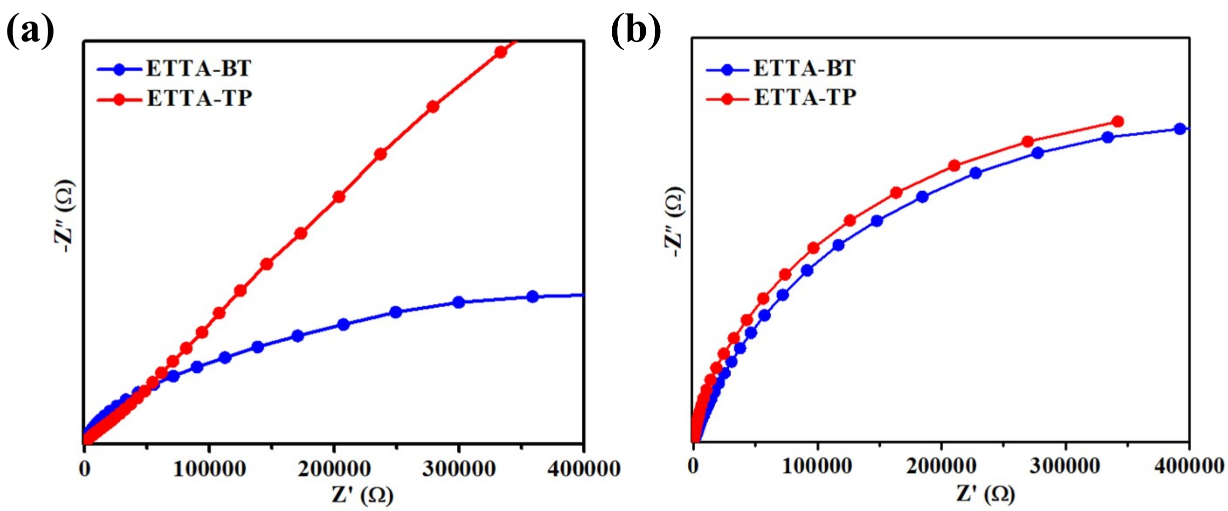


Figure S10. *Electrochemical impedance spectra (EIS) for ETTA-BT and ETTA-TP COFs in the presence of (a) light and (b) dark.*

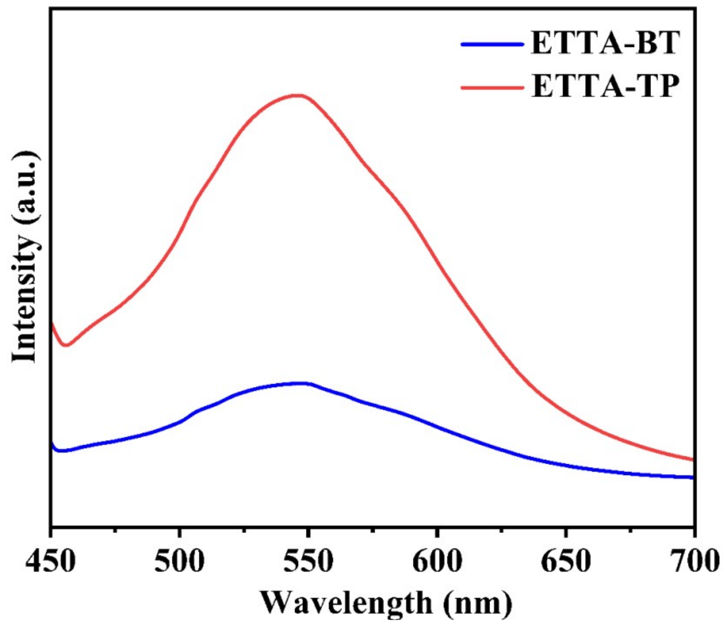


Figure S11. *Steady-state photoluminescence (PL) spectra of the COFs at excitation (λ_{ex} = 400 nm).*

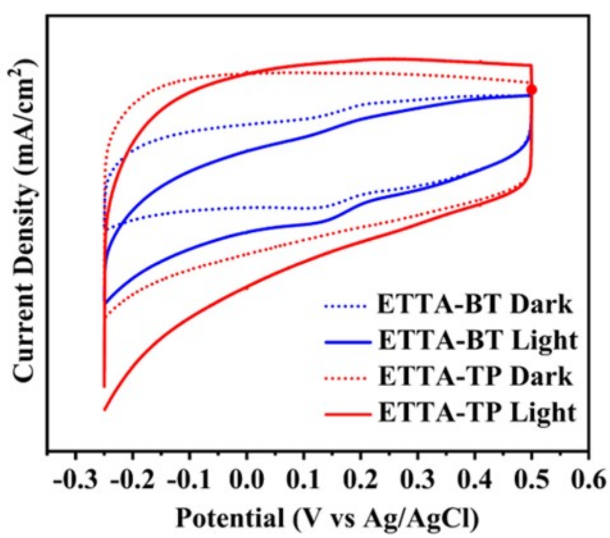


Figure S12. *Cyclic voltammetry (CV) plot of COFs in dark and light conditions.*

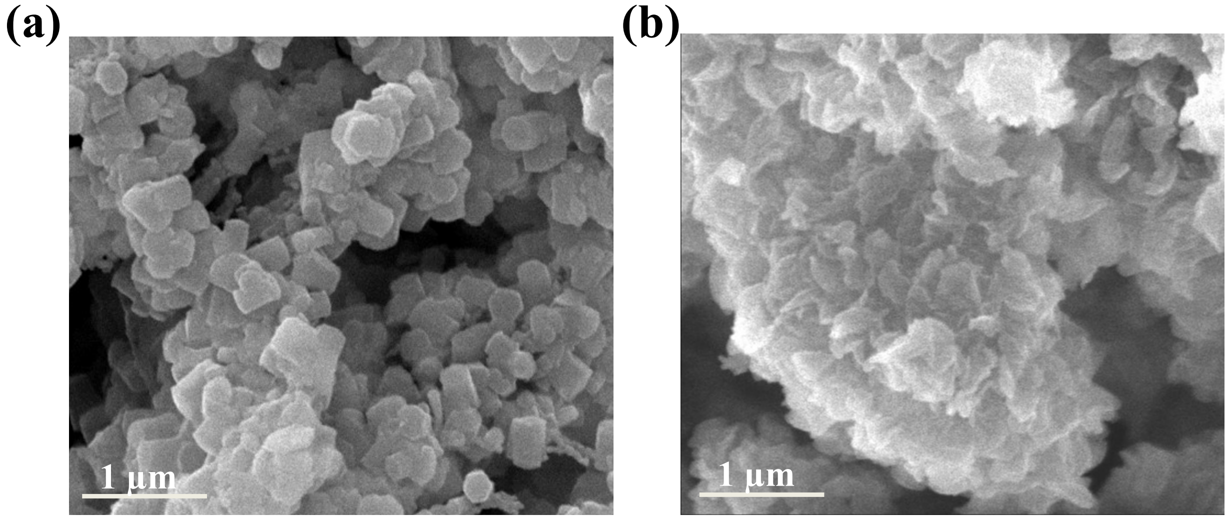


Figure S13. *FE-SEM images (a) ETTA-BT COF, and (b) ETTA-TP COF.*

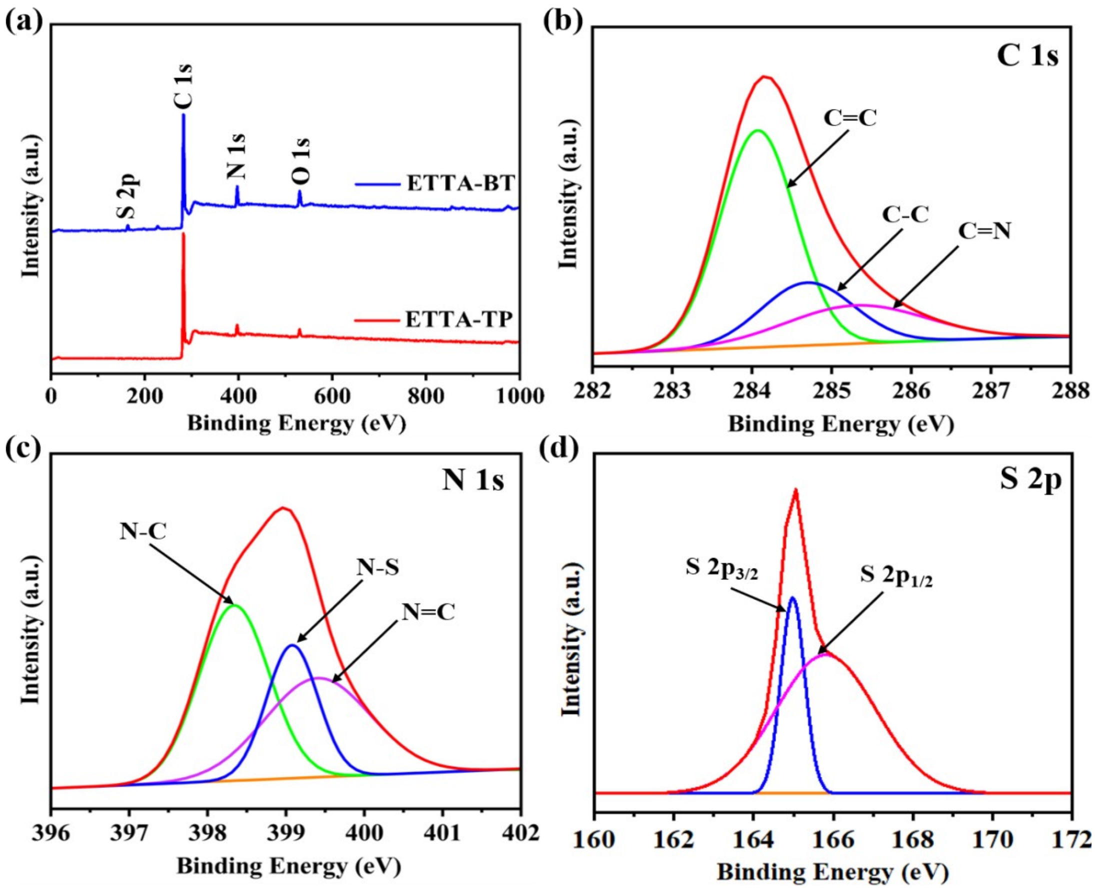


Figure S14. *(a) XPS survey scan for ETTA-BT and ETTA-TP COFs. The presence of (b) C 1S, (c) N 1S, and (d) S 2p in the ETTA-BT COF.*

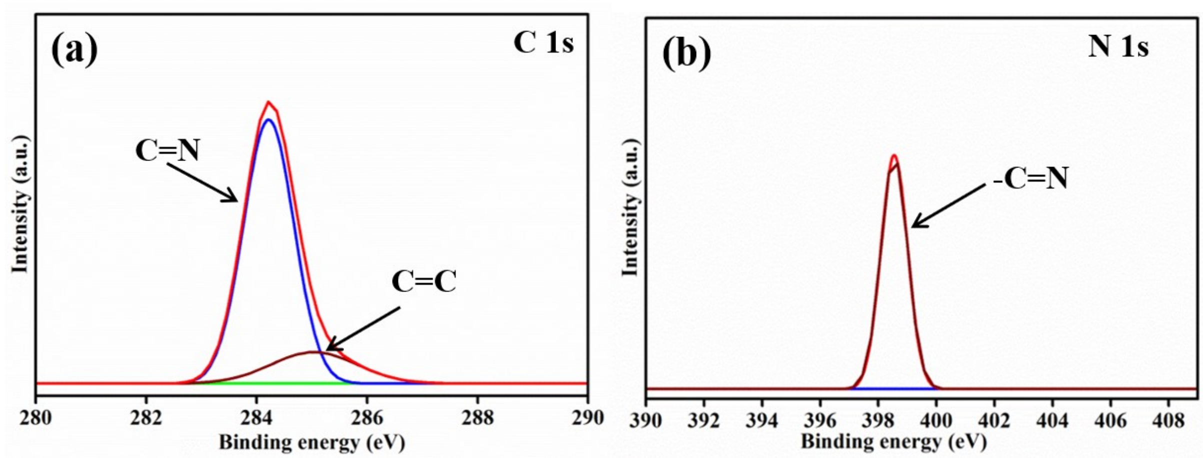


Figure S15. *XPS spectra of ETTA-TP COF (a) C 1s, and (b) N 1s.*

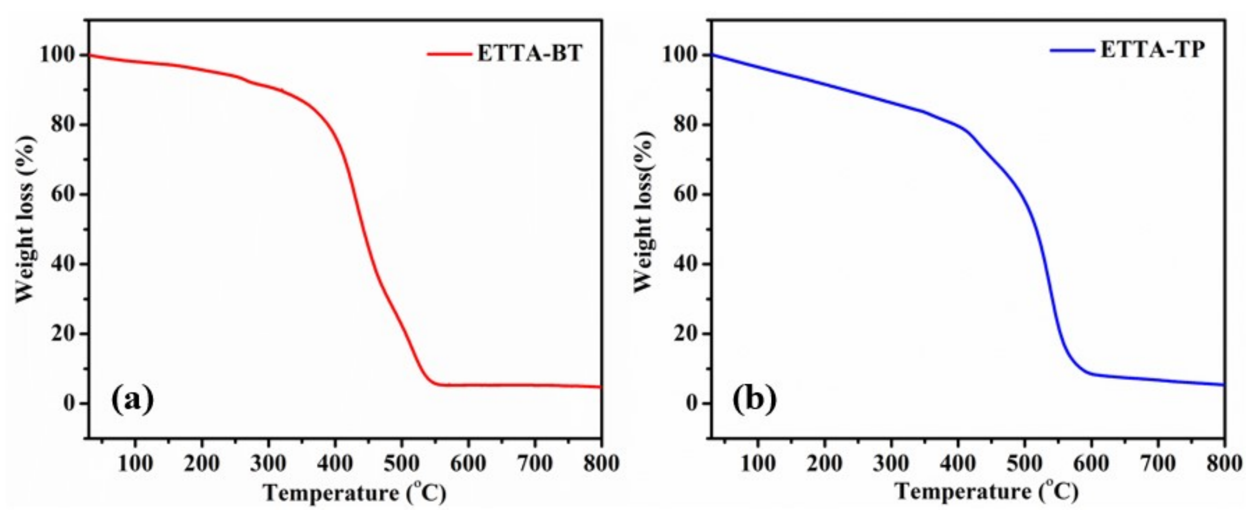


Figure S16. *TGA data of (a) ETTA-BT COF, and (b) ETTA-TP COF.*

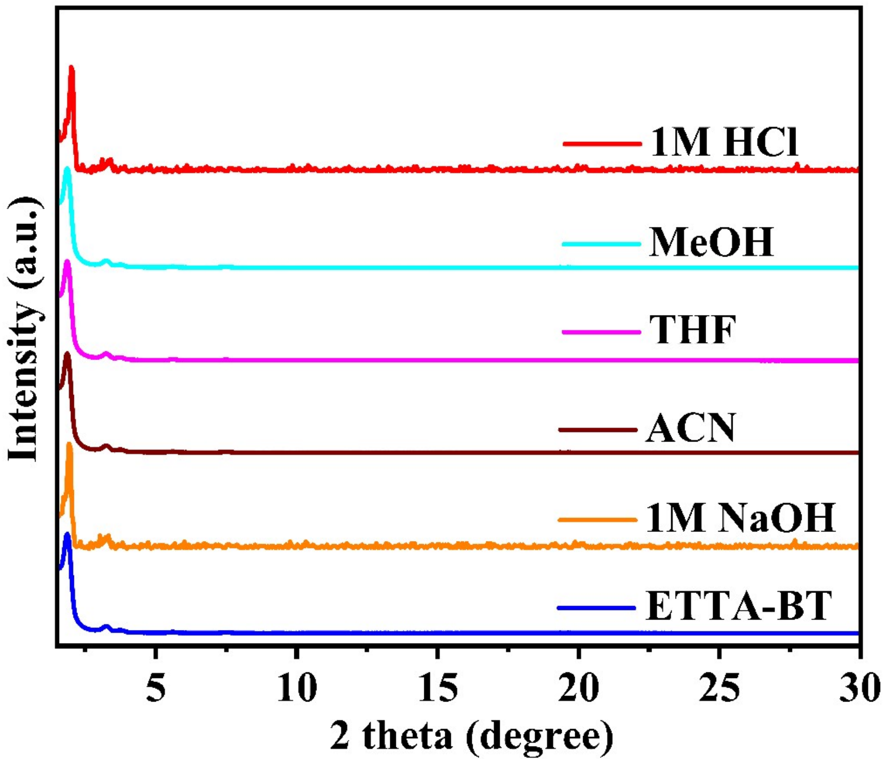


Figure S17. *XRD patterns of ETTA-BT COF after soaking in different solvents for 24 hours.*

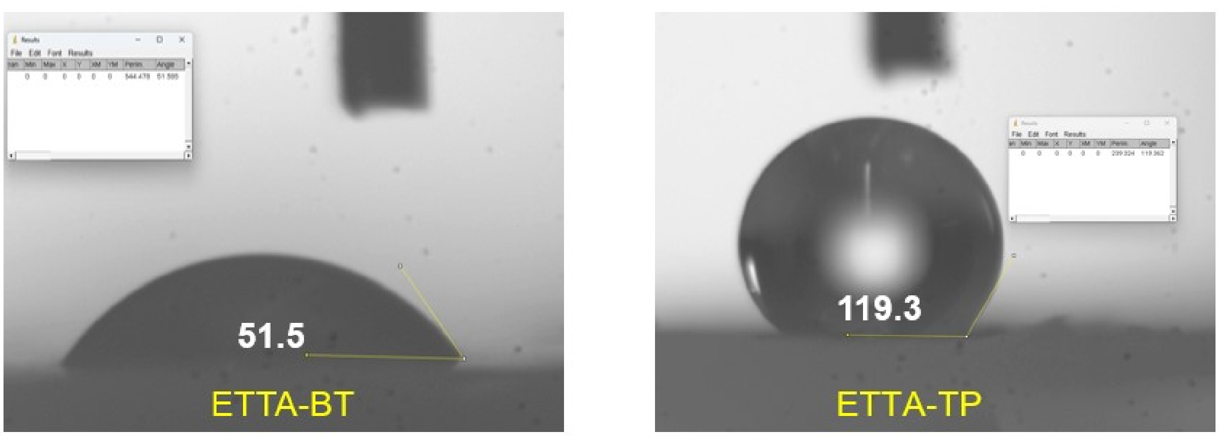


Figure S18*. Images of contact angle measurements of ETTA-BT and ETTA-TP COF.*

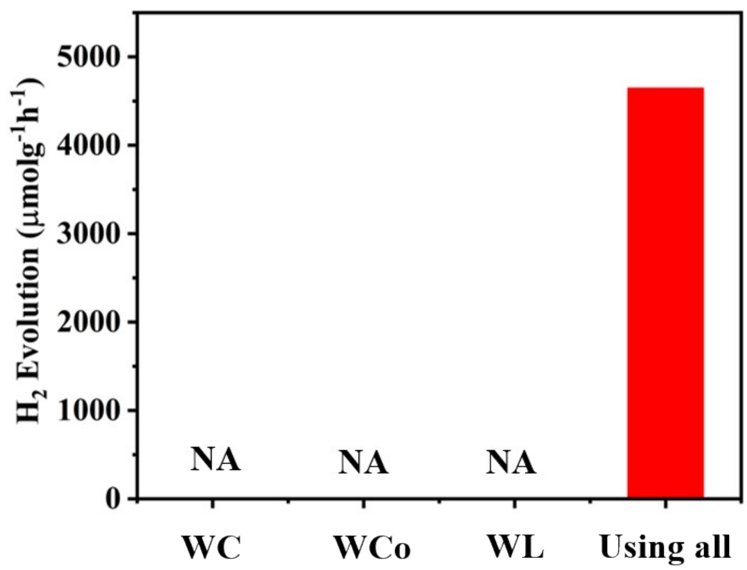


Figure S19. *Optimized conditions for photocatalytic hydrogen production without catalyst (WC), without co-catalyst (W-Co), without light (WL), and by using all.*

Table S3. The photocatalytic performance comparison of ETTA-BT COF with other representative COF-based photocatalysts.

Catalyst	Co-catalyst	SED	Solvent	Illumination	H_2 generation (μmol g^{-1} h^{-1})	AQY (%)	Reference
TP-BDDA COF	Pt	TEOA	Water	520 nm	324	1.8	S1
sp2c-COFERDN	Pt	TEOA	Water	> 495 nm	1240	0.48	S2
TFPT-COF	Pt	Ascorbic acid	Water	> 420 nm	230	-	S3
N_2–COF	Pt	PBS buffer	Water	> 450 nm	438	0.19	S4
TpPa–COF–NO_2	Pt	PBS buffer	Water	> 420 nm	220	-	S5
CTF-N	Pt	TEOA	Water	> 420 nm	538	4.07	S6
g-$C_{18}N_3$-COF	Pt	Ascorbic acid	Water	> 420 nm	292	1.06	S7
ZnPor-DETH-COF	Pt	TEOA	Water	> 400 nm	413	0.32	S8
COF-imide	Pt	TEOA	Water	> 420 nm	34	-	S9
BT-TAPT-COF	Pt	Ascorbic acid	Water	> 420 nm	949	0.19	S10
ETTA-BT	Pt	Ascorbic acid	Water /methanol	> 420 nm	890	0.26	This work

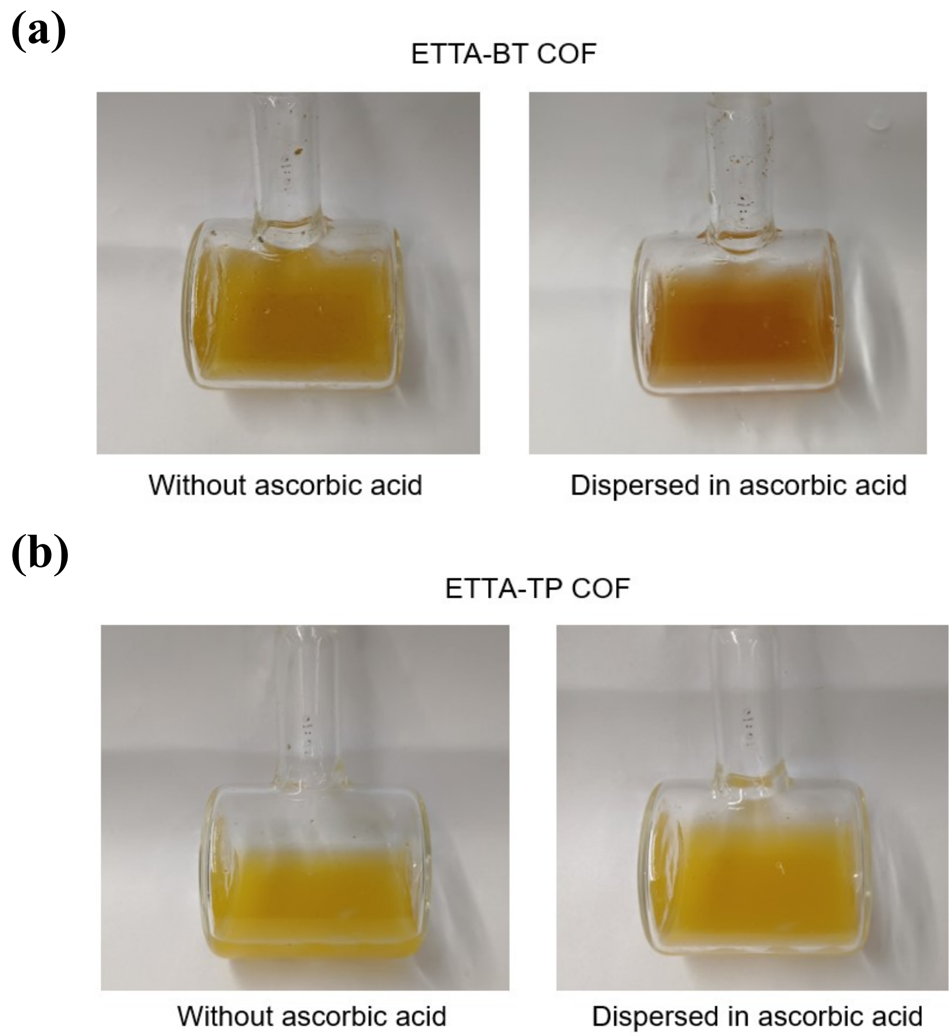


Figure S20. *Digital photographs of the protonation process of (a) ETTA-BT COF dispersion with/without ascorbic acid. (b) ETTA-TP COF dispersion with/without ascorbic acid, showing slight color change of ETTA-BT COF in the presence of ascorbic acid.*

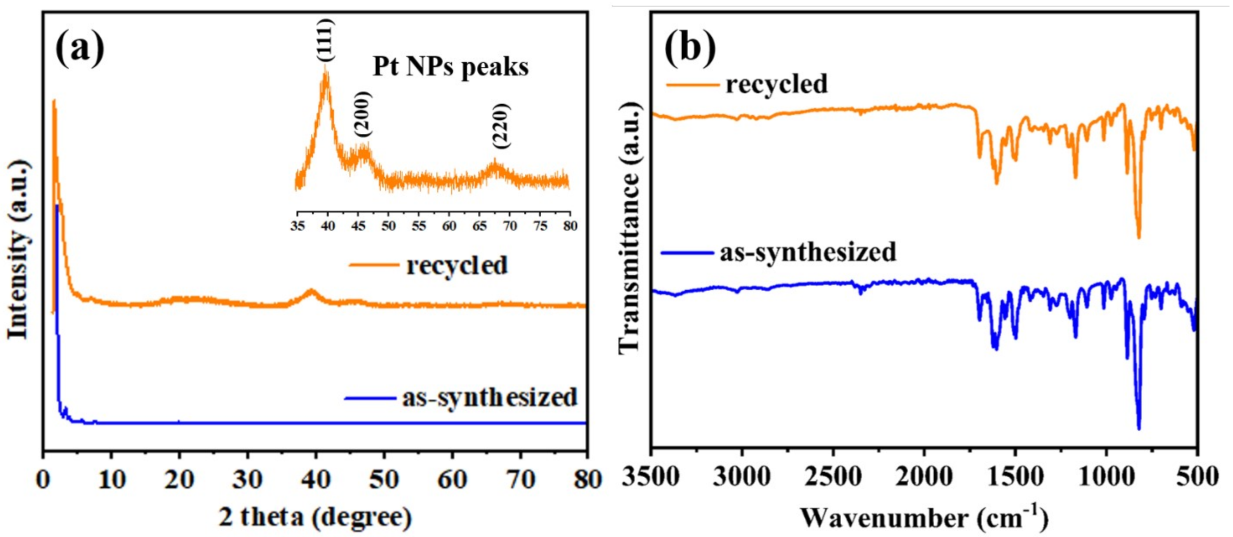


Figure S21. *(a) PXRD, and (b) FT-IR spectra of ETTA-BT COF after photocatalytic hydrogen evolution experiment.*

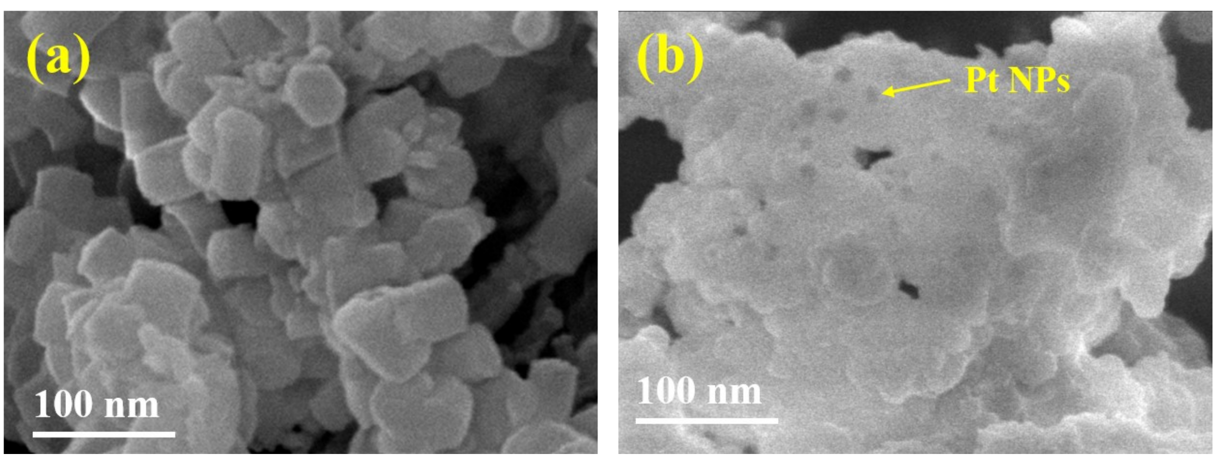


Figure S22. *SEM images of ETTA-BT COF (a) as-synthesized, and (b) recycled COF after hydrogen evolution activity.*

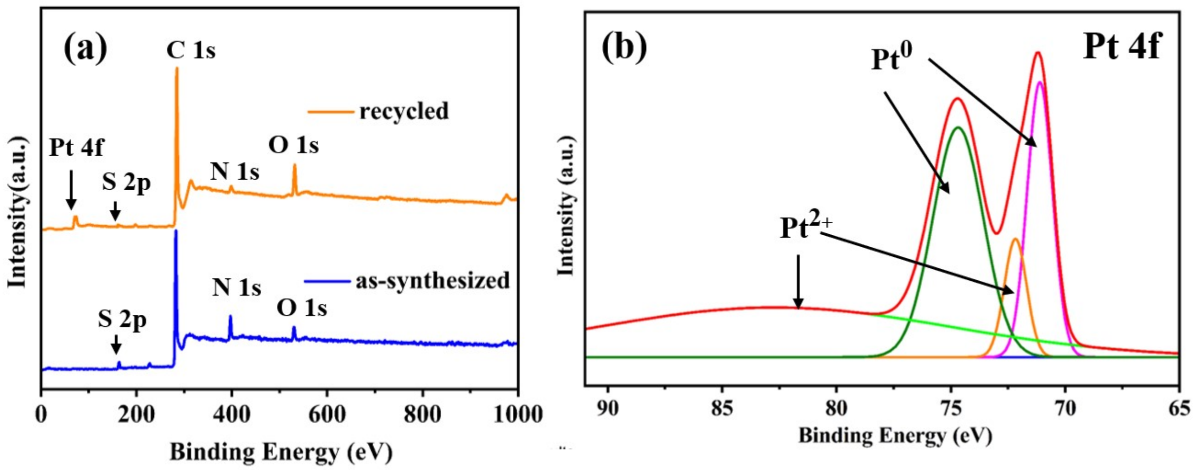


Figure S23. *(a) XPS survey spectra of ETTA-BT COF before and after photocatalysis. (b) High-resolution Pt 4f XPS spectra of ETTA-BT COF after photocatalysis.*

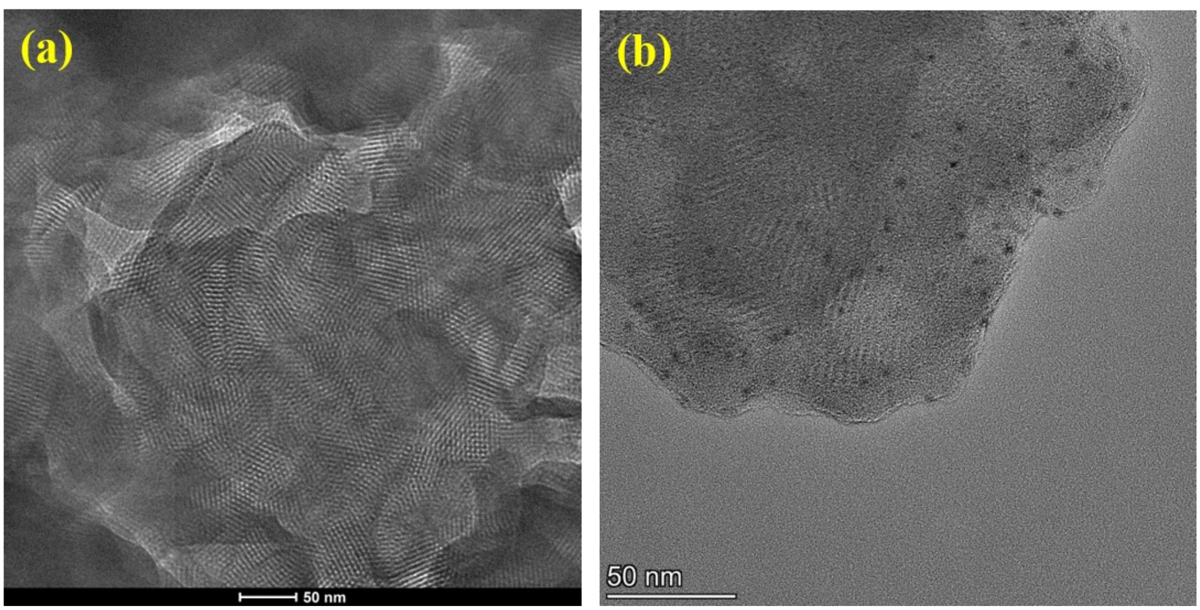


Figure S24. *TEM images (a) before photocatalysis, and (b) after photocatalytic hydrogen production.*

(a) (b)

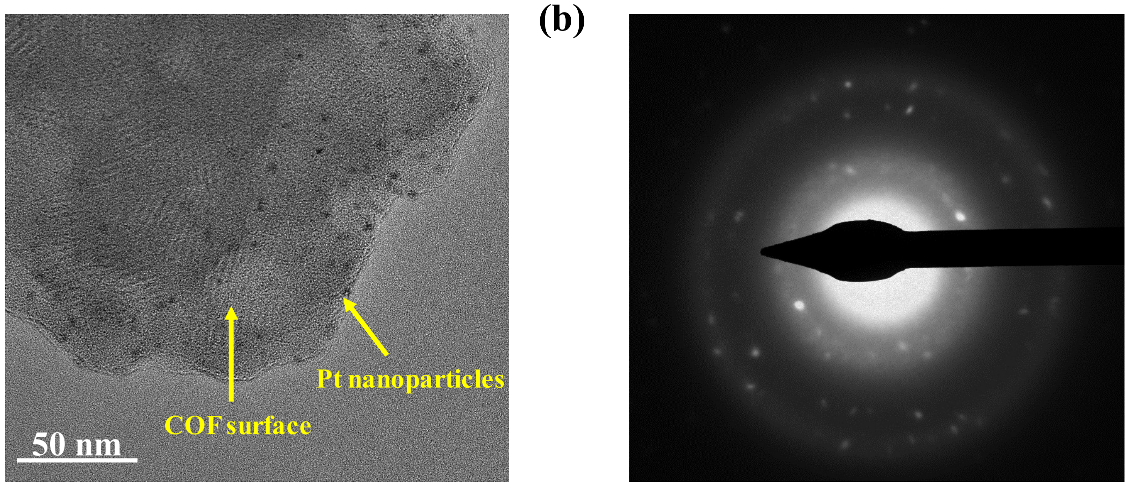


Figure S25. *(a) TEM image showing platinum nanoparticles deposited on* ETTA-BT COF *surface, and (b) corresponding SAED pattern after five cycles of photocatalytic reactions.*

Supplementary References

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