Construction of Dense H-bond Accept in the Channels of Covalent Organic Frameworks for Proton Conduction

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Experimental section

Materials: 4, 4', 4'', 4'''-(pyrene-1,3,6,8-tetrayl) tetra alkane (PyTTA), 2,5-bis (2-(2-methoxyethoxy) ethoxy-p-phenylenedicarboxylic acid (BMTP) and 2,5-dihydroxyterephthalaldehyde (DHTA) were purchased from Aladdin. Tetrahydrofuran (THF), N-butanol (BuOH), o-dichlorobenzene, (o-DCB) acetic acid (HAc), phosphoric acid crystal (PA) and methanol (MeOH) were from Sinopharm Chemical Reagent Co.,Ltd.

Synthesis of PyTTA-COFs: A mixture of o-DCB (0.5 mL), BuOH (0.5 mL), PyTTA (17.0 mg, 0.03 mmol), BMTP (22.2 mg, 0.06 mmol) or DHTA (9.97 mg, 0.06 mmol), and an aqueous acetic acid solution (3 M, 0.2 mL) was degassed in a Pyrex tube (10 mL) by three freeze-pump-thaw cycles. The tube was sealed and heated at 120 °C for 3 days. The precipitate was collected by centrifugation, washed with THF, and dried at 120 °C under vacuum overnight to give PyTTA-BMTP-COF (91.2%) and PyTTA-DHTA-COF (93.0%).

Synthesis of PA@PyTTA-COFs: PyTTA-COFs sample (50 mg) in vacuum vial (20 mL) preheated 30 min at 120 °C. Phosphoric acid crystal (100 mg) dissolved in anhydrous THF (3 mL) was injected into the vial to get a solution, which was stirred 3 h at room temperature. The solution was slowly evaporated 3 h under vacuum to remove THF at 70 °C to get PA@PyTTA-BMTP-COF and PA@PyTTA-DHTA-COF.

Synthesis of 0.5PA@PyTTA-COFs: PyTTA-COFs sample (50 mg) in vacuum vial (20 mL) preheated 30 min at 120 °C. Phosphoric acid crystal (50 mg) dissolved in anhydrous THF (2 mL) was injected into the vial to get a solution, which was stirred 3 h at room temperature. The solution was slowly evaporated 3 h under vacuum to remove THF at 70 °C to get 0.5PA@PyTTA-BMTP-COF and 0.5PA@PyTTA-DHTA-COF.

Synthesis of sample (to be tested): The powders (50 mg) of PA@PyTTA-BMTP-COF, PA@PyTTA-DHTA-COF, 0.5PA@PyTTA-BMTP-COF and 0.5PA@PyTTA-DHTA-COF were pressed 30 minutes into circular tabletting with a diameter of 1.0 cm under a pressure of 4 ton by oil press equipment.

Impedance Measurements: The tabletting was sandwiched between two electrodes. For the first test, preheated electrodes into 100 °C for 4 h to maintain stability, and the temperature rise test needs to be stable for 30 min. The proton conductivity was measured by the alternating-current impedance method (IMP) using an electrochemical workstation (CHI 760E, Shanghai C&H). It tested with a frequency range of 100 Hz-1000000 Hz under anhydrous condition from 100 to 150 °C. The conductivity was calculated using the equation of $\sigma = L/SR$ where σ is the conductivity (mS cm^{-1}), L is the sample thickness (cm), S is the sample area (cm^2) and R is the tested resistance (Ω). The activation energy (Ea) for the material conductivity was estimated from the equation of $\sigma T=\sigma_0 \exp(-Ea/(K_B T))$, where σ_0 is the pre-exponential factor, K_B is the Boltzmann constant, and T is the tested temperature.

Characterization: Powder X-ray diffraction (PXRD) data were recorded on an Ultima IV diffractometer with Cu Kα radiation by depositing powder on glass substrate, from 2ϑ = 3° up to 30° with 0.02° increment. Fourier transform infrared (FT IR) spectra were obtained from a Nicolet Magna 550 spectrometer. Solid-state ^{13}C CM/MAS NMR (^{13}C NMR) spectra were recorded on Bruker AVANCE NEO 400 WB spectrometer. Nitrogen sorption isotherms were measured at 77 K with a TriStar II Micromeritics. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha XPS spectrometer using Al Kα X-ray source for radiation. Thermogravimetric analysis (TGA) measurements were performed on a Mettler-Toledo model TGA/SDTA851e under N_2, by heating to 800 °C at a rate of 10 °C min^{-1}. High-resolution transmission electron microscope images were obtained by transmission electron microscopy (TEM, FEI Tecnai G2) installed with energy dispersive spectrometer (EDS, Oxford). The morphology was measured by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPPHIRE).

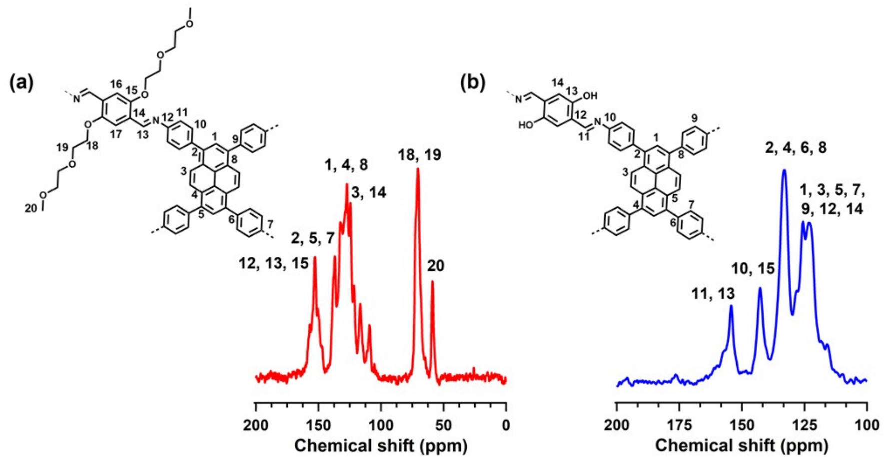

Figure S1. The ^{13}C NMR spectrum of (a) PyTTA-BMTP-COF and (b) PyTTA-DHAT-COF.

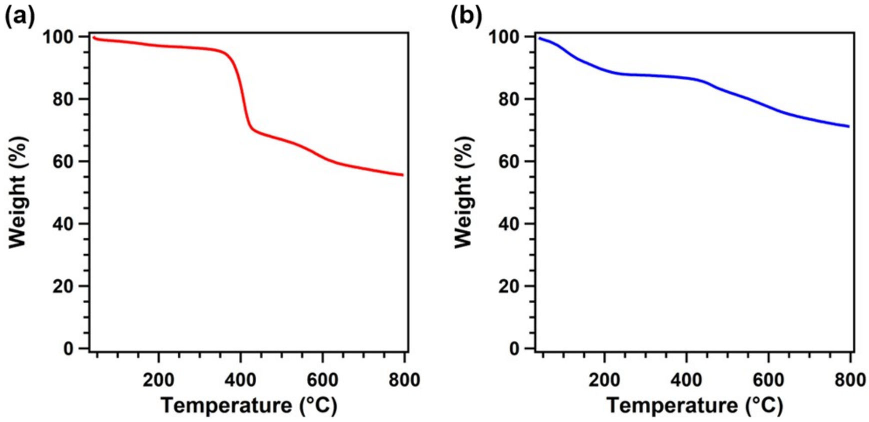

Figure S2. TGA profiles for (a) PyTTA-BMTP-COF and (b) PyTTA-DHAT-COF from 40 to 800 °C under N_2.

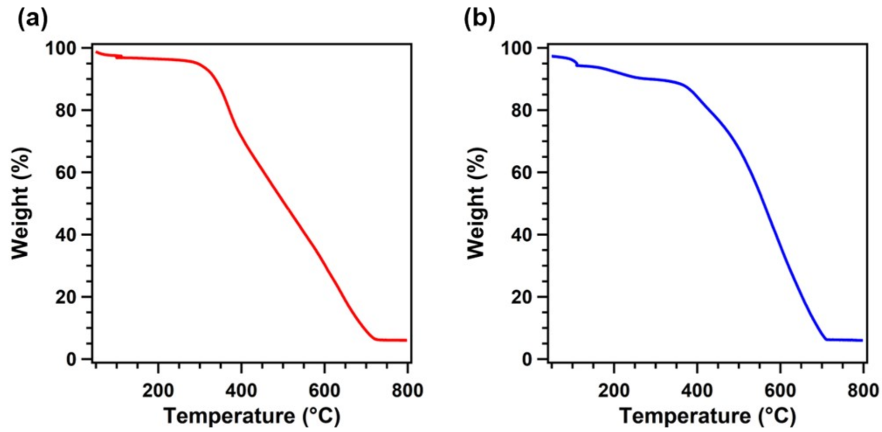

Figure S3. TGA curves of (a) PyTTA-BMTP-COF and (b) PyTTA-DHTA-COF from 40 to 800 °C under air.

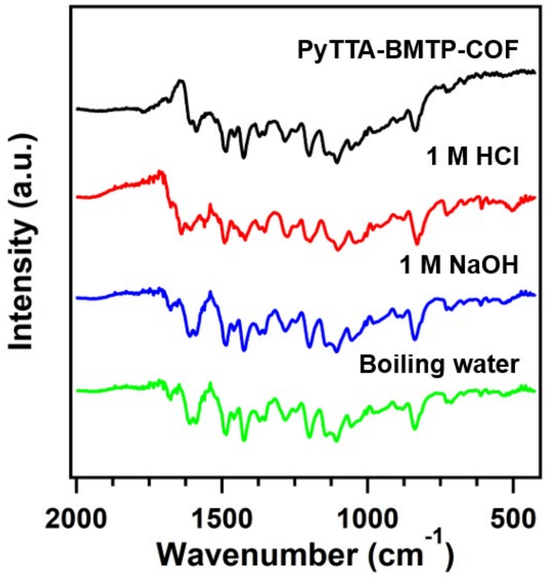

Figure S4. The FT IR spectra of PyTTA-BMTP-COF in 1 M HCl, 1 M NaOH and boiling water for one week.

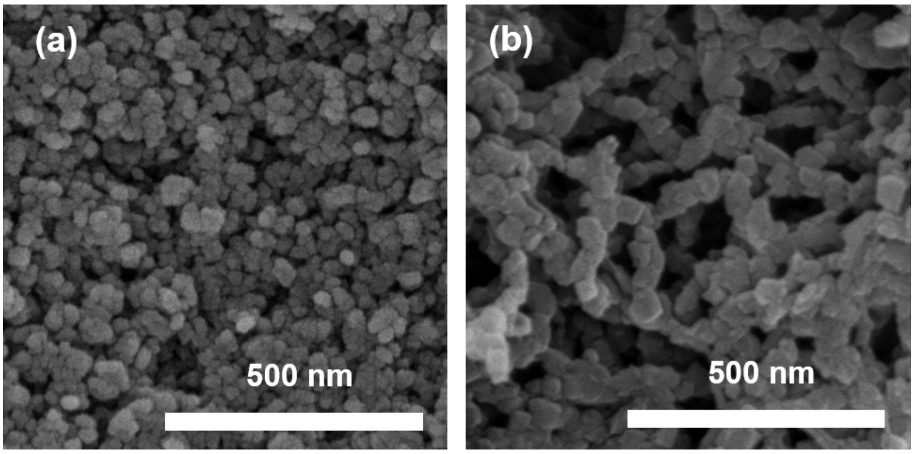

Figure S5. SEM images of (a) PyTTA-BMTP-COF and (b) PyTTA-DHAT-COF.

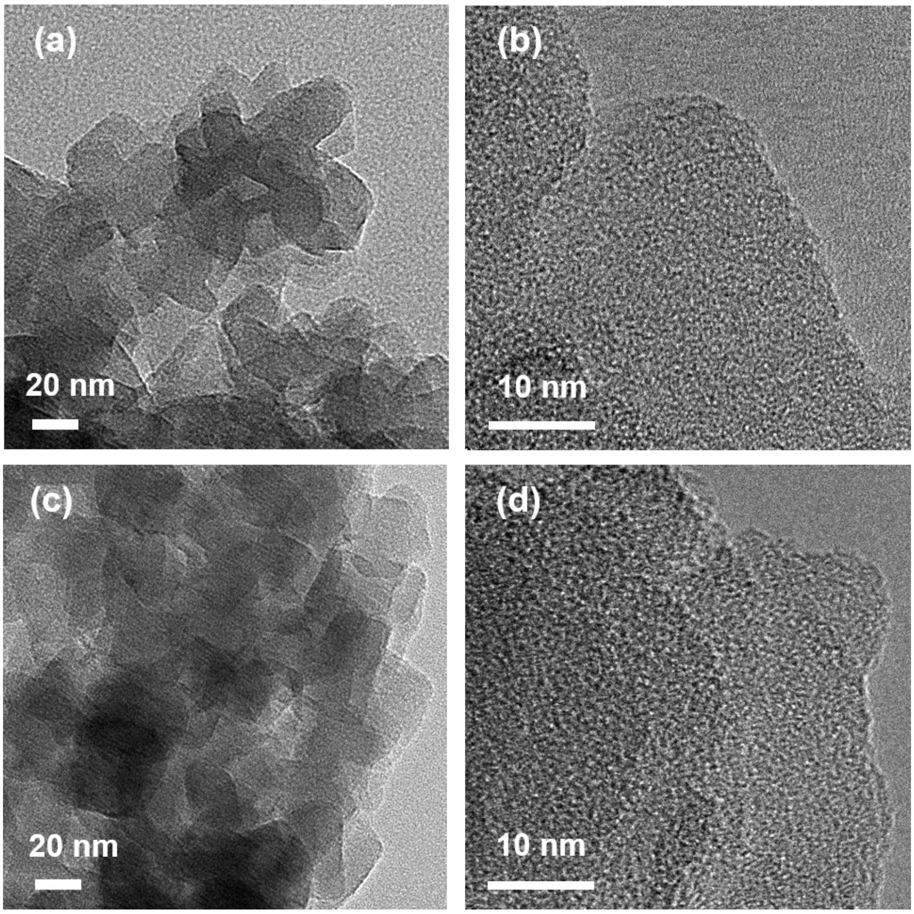

Figure S6. (a) TEM and (b) HR-TEM images of PyTTA-BMTP-COF, (c) TEM and (d) HR-TEM images PyTTA-DHAT-COF.

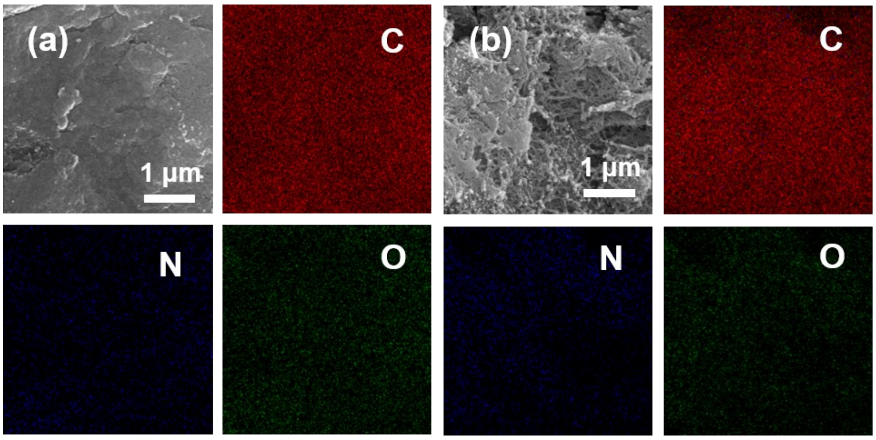

Figure S7. EDX images of (a) PyTTA-BMTP-COF and (b) PyTTA-DHAT-COF.

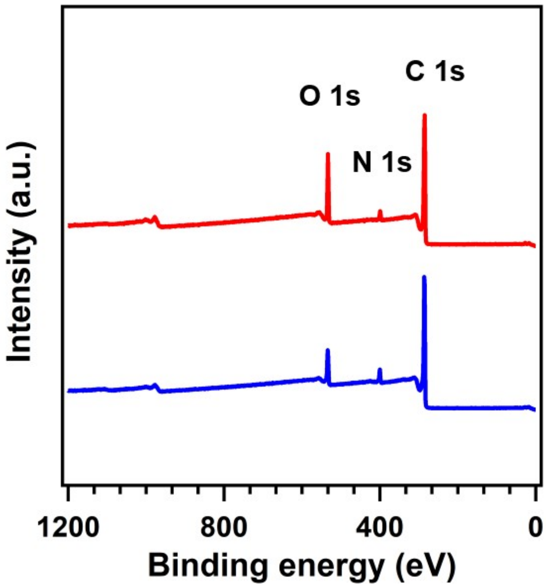

Figure S8. XPS spectra of PyTTA-BMTP-COF (red curve) and PyTTA-DHAT-COF (blue curve).

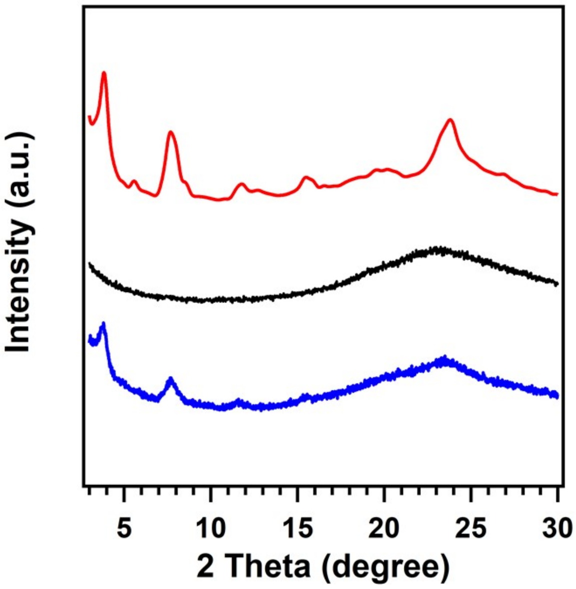

Figure S9. PXRD profile of PyTTA-BMTP-COF (red curve), PA@PyTTA-DHAT-COF (black curve) and PA@PyTTA-DHAT-COF after washing (blue curve).

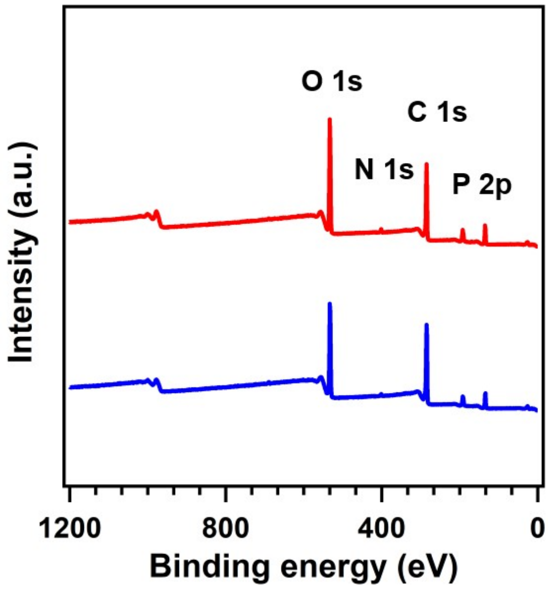

Figure S10. XPS spectra of PA@PyTTA-BMTP-COF (red curve) and PA@PyTTA-DHAT-COF (blue curve).

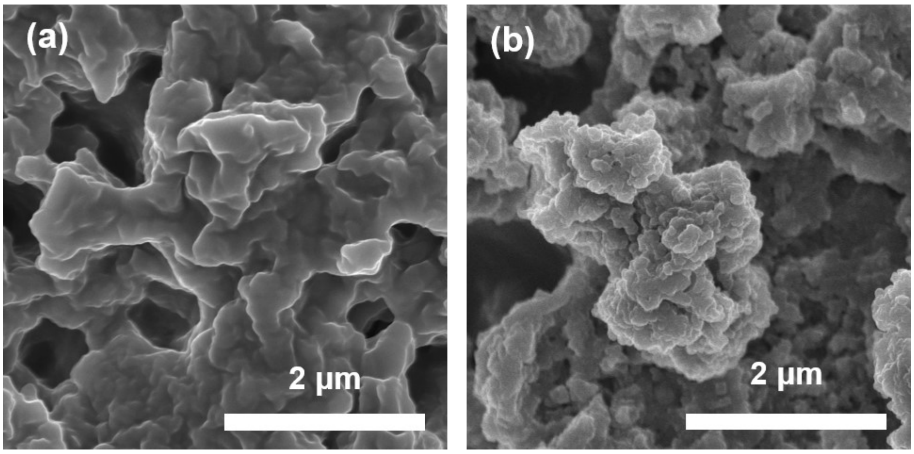

Figure S11. SEM images of (a) PA@PyTTA-BMTP-COF and (b) PA@PyTTA-DHAT-COF.

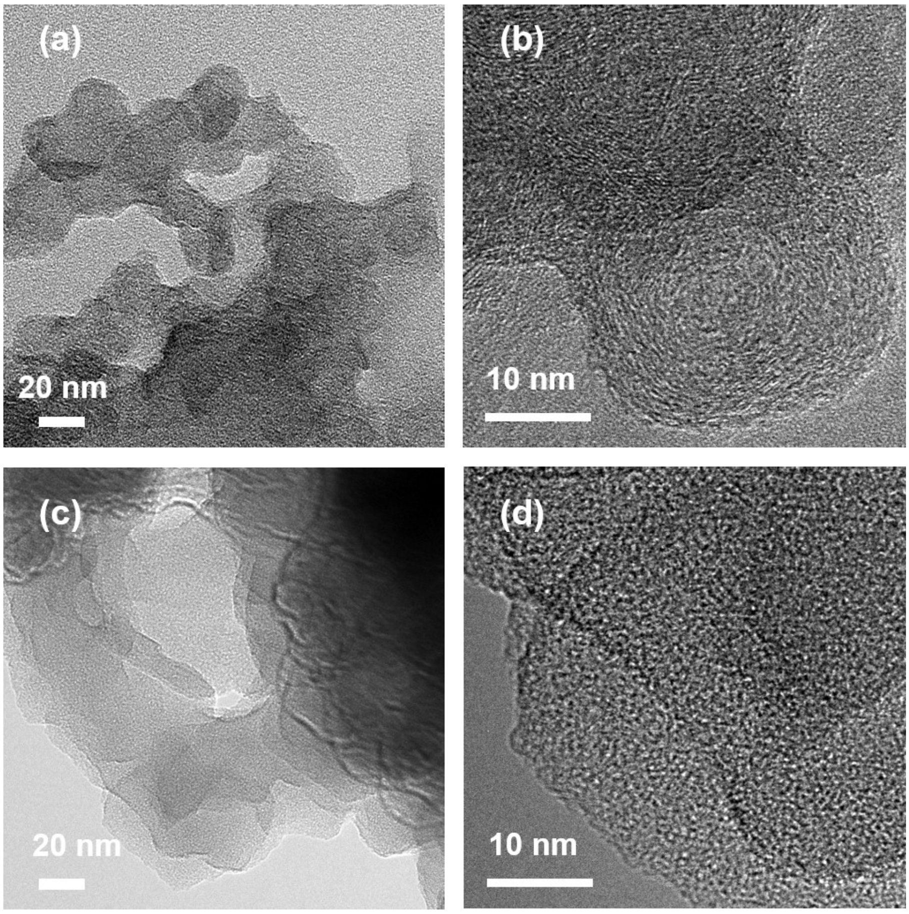

Figure S12. (a) TEM and (b) HR-TEM images of PA@PyTTA-BMTP-COF, (c) TEM and (d) HR-TEM images PA@PyTTA-DHAT-COF.

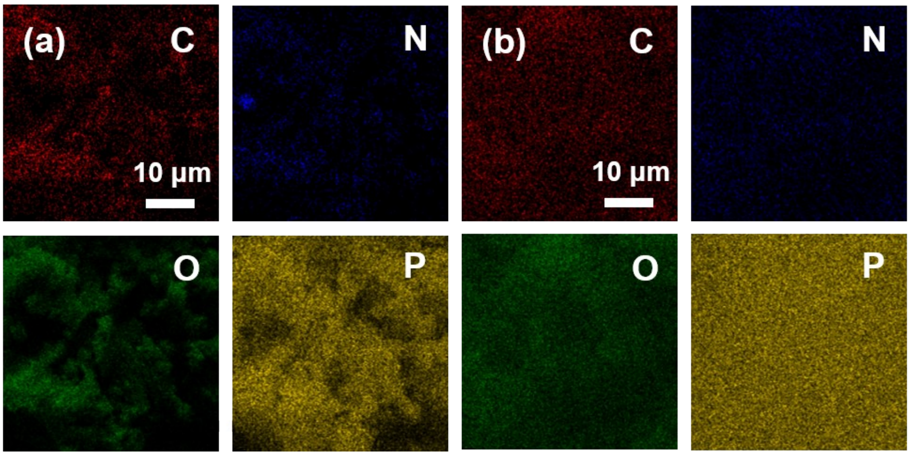

Figure S13. EDX images of (a) PA@PyTTA-BMTP-COF and (b) PA@PyTTA-DHAT-COF.

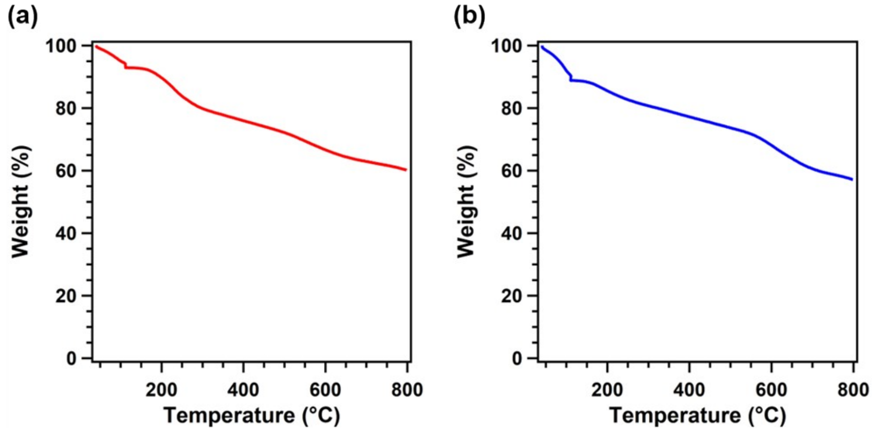

Figure S14. TGA profiles for (a) PA@PyTTA-BMTP-COF and (b) PA@PyTTA-DHAT-COF from 40 to 800 °C under N_2.

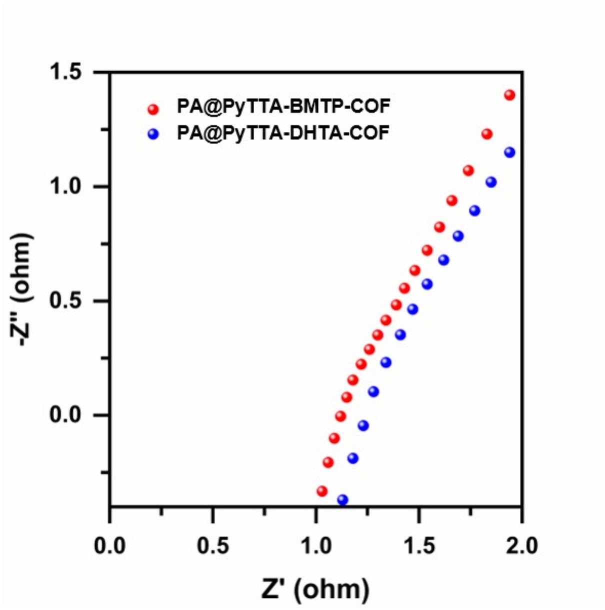

Figure S15. Nyquist plots of PA@PyTTA-BMTP-COF (red) and PA@PyTTA-DHTA-COF (blue) at 90 °C under 90% RH.

Table S1. Atomistic coordinates of AA stacking model for PyTTA-BMTP-COF optimized by using CASTEP-method.
Space group: *P1;*
a = 24.0373 Å, *b* = 24.4164 Å, *c* = 3.5865 Å;
α = *β* =*90.0000˚, γ* = 84.4770˚.

	Atom	x/a	y/b	z/c
N1	N	0.84222	-1.56729	-0.4319
C2	C	0.92769	-1.52188	-0.40542
C3	C	1.022	-1.5621	-0.52945
C4	C	1.04335	-1.51224	-0.44956
C5	C	0.94903	-1.47203	-0.32541
C6	C	0.86672	-1.52302	-0.37584
C7	C	1.10429	-1.5111	-0.48023
C8	C	1.49111	-1.95937	-0.57278
C9	C	1.42582	-2.02915	-0.54901
C10	C	1.46889	-2.07045	-0.61694
C11	C	1.53383	-2.0006	-0.65155
C12	C	1.50836	-1.90353	-0.52433
C13	C	1.4541	-2.12757	-0.60952
C14	C	1.0111	-1.23346	0.07314
O15	O	0.97965	-1.27814	0.0313
C16	C	1.01853	-1.32166	-0.0696
C17	C	0.98853	-1.37205	-0.15127
O18	O	1.02826	-1.41616	-0.25993
C19	C	1.00663	-1.46624	-0.34484
C20	C	0.95984	-1.80062	-0.92894
O21	O	0.99133	-1.75598	-0.88662
C22	C	0.95248	-1.71245	-0.78549
C23	C	0.98251	-1.66208	-0.70369
O24	O	0.94279	-1.61797	-0.59488
C25	C	0.96442	-1.56789	-0.50998
C26	C	1.74853	-2.1604	-1.03756
O27	O	1.71379	-2.11187	-0.98799
C28	C	1.66133	-2.12927	-0.91515
C29	C	1.62017	-2.0798	-0.83471
O30	O	1.56669	-2.09778	-0.75994
C31	C	1.52366	-2.05625	-0.67936
C32	C	1.4355	-1.97371	-0.53644
O33	O	1.38935	-1.93565	-0.46663
C34	C	1.38123	-1.89285	-0.73465
C35	C	1.33212	-1.85288	-0.62145
O36	O	1.3331	-1.80432	-0.82451
C37	C	1.28875	-1.76955	-0.68255
C38	C	1.58614	-1.63018	-0.3475

C39	C	1.60438	-1.57771	-0.37913
C40	C	1.56361	-1.53203	-0.41468
C41	C	1.50597	-1.54007	-0.41305
C42	C	1.48905	-1.59383	-0.37369
C43	C	1.52972	-1.63969	-0.34342
C44	C	1.46507	-1.49421	-0.4559
C45	C	1.40743	-1.50228	-0.45331
C46	C	1.39212	-1.55566	-0.4095
C47	C	1.43195	-1.60037	-0.37356
C48	C	1.57892	-1.47866	-0.45925
C49	C	1.5391	-1.43399	-0.4987
C50	C	1.48199	-1.44051	-0.49962
C51	C	1.4413	-1.39475	-0.53857
C52	C	1.38488	-1.40432	-0.53026
C53	C	1.36665	-1.45664	-0.48972
C54	C	1.51643	-1.69826	-0.32771
C55	C	1.30492	-1.46043	-0.47954
C56	C	1.4544	-1.33628	-0.57969
C57	C	1.66612	-1.57387	-0.38566
C58	C	1.46375	-1.71279	-0.21709
C59	C	1.45153	-1.76754	-0.2232
C60	C	1.49188	-1.80904	-0.33823
C61	C	1.54515	-1.79536	-0.44015
C62	C	1.55721	-1.74057	-0.43352
C63	C	1.26863	-1.41346	-0.39393
C64	C	1.21085	-1.41588	-0.37958
C65	C	1.18806	-1.46529	-0.45128
C66	C	1.22372	-1.51228	-0.54196
C67	C	1.28143	-1.50966	-0.55703
C68	C	1.70254	-1.62076	-0.47098
C69	C	1.76032	-1.61828	-0.48253
C70	C	1.7472	-1.52197	-0.31759
C71	C	1.68948	-1.52466	-0.30526
C72	C	1.50804	-1.32248	-0.67376
C73	C	1.51941	-1.26763	-0.70338
C74	C	1.42317	-1.23828	-0.55412
C75	C	1.41203	-1.29317	-0.52389
N76	N	1.47668	-1.86406	-0.36943
N77	N	1.12883	-1.46681	-0.4257
C78	C	1.78299	-1.56888	-0.40824
C79	C	1.47719	-1.22522	-0.6423
N80	N	1.49063	-2.16946	-0.66072
C81	C	0.80177	0.85591	-0.03756
O82	O	0.83063	0.79817	-0.03756

C83	C	0.8883	0.81464	-0.03756
C84	C	0.97004	0.81442	0.87796
O85	O	1.01125	0.85097	0.87796
C86	C	0.97019	0.89426	0.87796
C87	C	1.00088	0.15258	0.07106
O88	O	0.96082	0.1135	0.07106
C89	C	0.99699	0.06775	0.07106
C90	C	0.28154	0.28247	0.1708
O91	O	0.23676	0.3049	0.36016
C92	C	0.23069	0.35698	0.20985

Table S2. Atomistic coordinates of AB stacking model for PyTTA-BMTP-COF optimized by using CASTEP-method.

Space group: *P1;*

a = 24.1073 Å, *b* = 24.5783 Å, *c* = 6.7459 Å;

α = β = γ = 90.0000°.

	Atom	x/a	y/b	z/c
N1	N	0.81361	0.45149	0.19626
C2	C	0.90416	0.48928	0.27102
C3	C	-0.00805	0.44258	0.25165
C4	C	0.02075	0.49192	0.27193
C5	C	0.93298	0.53845	0.29346
C6	C	0.84325	0.4916	0.26433
C7	C	0.08166	0.49045	0.26249
C8	C	0.46946	0.05314	0.21289
C9	C	0.4105	0.97348	0.24914
C10	C	0.4563	0.93958	0.23452
C11	C	0.51532	1.01932	0.20064
C12	C	0.48058	0.11166	0.19592
C13	C	0.4445	0.88101	0.24173
C14	C	0.04138	0.77521	0.3426
O15	O	1.00014	0.73524	0.35697
C16	C	0.02896	0.68656	0.34317
C17	C	0.98907	0.63869	0.32702
O18	O	0.0206	0.59028	0.31348
C19	C	-0.00884	0.54072	0.29503
C20	C	0.88642	0.21242	0.07535
O21	O	0.92511	0.24693	0.16627
C22	C	0.89608	0.29476	0.19828
C23	C	0.93583	0.3428	0.21378
O24	O	0.90411	0.39079	0.23605
C25	C	0.93363	0.4403	0.25208
C26	C	0.74575	0.90398	0.1478
O27	O	0.70574	0.94387	0.17204
C28	C	0.65525	0.91557	0.17723
C29	C	0.60866	0.95605	0.18866
O30	O	0.55645	0.92841	0.20116
C31	C	0.50995	0.9624	0.21259
C32	C	0.41604	0.03036	0.23946
O33	O	0.37008	0.06468	0.25917
C34	C	0.31722	0.03825	0.26738
C35	C	0.27261	0.0797	0.3093
O36	O	0.27112	0.11844	0.15868
C37	C	0.27347	0.16825	0.25795
C38	C	0.55407	0.3875	0.17159

C39	C	0.57593	0.44028	0.17775
C40	C	0.53877	0.4842	0.19131
C41	C	0.48085	0.47377	0.20209
C42	C	0.46014	0.41946	0.19773
C43	C	0.49732	0.37567	0.18139
C44	C	0.44343	0.51781	0.2173
C45	C	0.38561	0.50709	0.22944
C46	C	0.36648	0.45321	0.22562
C47	C	0.40291	0.41038	0.2086
C48	C	0.5579	0.53819	0.19202
C49	C	0.52126	0.5812	0.2066
C50	C	0.46398	0.57223	0.22036
C51	C	0.42644	0.61599	0.23652
C52	C	0.36975	0.60356	0.25073
C53	C	0.34835	0.55061	0.24773
C54	C	0.48047	0.31696	0.17972
C55	C	0.28701	0.5437	0.26528
C56	C	0.4425	0.67512	0.23878
C57	C	0.63755	0.4461	0.17562
C58	C	0.42849	0.29849	0.24884
C59	C	0.41589	0.24285	0.25848
C60	C	0.45518	0.2048	0.20015
C61	C	0.50683	0.22293	0.129
C62	C	0.51914	0.27823	0.11891
C63	C	0.25605	0.58465	0.35686
C64	C	0.19848	0.58031	0.3707
C65	C	0.17068	0.53485	0.29389
C66	C	0.20092	0.49369	0.20127
C67	C	0.25859	0.4983	0.18655
C68	C	0.6696	0.40504	0.08995
C69	C	0.72736	0.40753	0.09636
C70	C	0.72295	0.49243	0.27585
C71	C	0.66498	0.48973	0.2697
C72	C	0.49798	0.69364	0.23927
C73	C	0.511	0.74929	0.23994
C74	C	0.41322	0.76961	0.24084
C75	C	0.40051	0.71425	0.23993
N76	N	0.44272	0.14804	0.21896
N77	N	0.11164	0.53273	0.30669
C78	C	0.75436	0.45112	0.18884
C79	C	0.46866	0.78757	0.24075
N80	N	0.48251	0.84437	0.23763
C81	C	0.80272	0.92889	0.18484
O82	O	0.84295	0.88904	0.16721

C83	C	0.89218	0.91511	0.22353
C84	C	1.01614	0.83118	0.35266
O85	O	0.05821	0.87046	0.33913
C86	C	1.03069	0.91937	0.31379
C87	C	-0.10907	0.15547	0.15975
O88	O	0.85054	0.12223	0.0727
C89	C	0.85844	0.07112	0.15591
C90	C	0.27107	0.21443	0.1095
O91	O	0.27382	0.26394	0.21044
C92	C	0.25516	0.30206	0.07337
N93	N	0.36812	-0.0475	0.8108
C94	C	0.45811	-0.00999	0.72539
C95	C	-0.45459	-0.05785	0.7112
C96	C	-0.42539	-0.00862	0.69447
C97	C	0.48725	0.03917	0.70768
C98	C	0.39741	-0.00698	0.74435
C99	C	-0.36437	-0.01099	0.68496
C100	C	0.02211	-0.44818	0.79421
C101	C	-0.03965	0.47332	0.77869
C102	C	0.00545	0.43875	0.75336
C103	C	0.06699	0.51731	0.76825
C104	C	0.03546	-0.38988	0.81245
C105	C	-0.00685	0.38016	0.73771
C106	C	-0.40683	0.27617	0.7017
O107	O	0.55339	0.23539	0.6693
C108	C	-0.4169	0.18717	0.68017
C109	C	0.54344	0.1388	0.68148
O110	O	-0.42488	0.09035	0.68169
C111	C	-0.45461	0.04083	0.69295
C112	C	0.44123	-0.2957	0.73845
O113	O	0.48101	-0.25404	0.73966
C114	C	0.45032	-0.20631	0.74397
C115	C	0.4892	-0.15734	0.73718
O116	O	0.45729	-0.10904	0.73865
C117	C	0.4872	-0.05954	0.72646
C118	C	0.29285	0.39275	0.67651
O119	O	0.2553	0.4353	0.68961
C120	C	0.20311	0.40986	0.68498
C121	C	0.15861	0.45176	0.72102
O122	O	0.10522	0.42601	0.7198
C123	C	0.05984	0.46067	0.74874
C124	C	-0.03219	-0.47044	0.79902
O125	O	-0.0779	-0.43941	0.85256
C126	C	-0.10052	-0.40966	0.69245

C127	C	-0.14774	-0.37562	0.76922
O128	O	-0.15892	-0.3338	0.63608
C129	C	-0.16983	-0.28925	0.75697
C130	C	0.10978	-0.11134	0.85724
C131	C	0.1307	-0.05819	0.85132
C132	C	0.09285	-0.01509	0.82975
C133	C	0.03543	-0.02673	0.80502
C134	C	0.01587	-0.08149	0.80683
C135	C	0.05346	-0.1245	0.83821
C136	C	-0.0023	0.01653	0.77367
C137	C	-0.05927	0.00464	0.73746
C138	C	-0.077	-0.04971	0.73653
C139	C	-0.04037	-0.09175	0.7713
C140	C	0.11082	0.03929	0.83203
C141	C	0.07378	0.08149	0.80556
C142	C	0.01717	0.07124	0.77547
C143	C	-0.02024	0.11418	0.73966
C144	C	-0.07568	0.10083	0.70151
C145	C	-0.09669	0.0475	0.70042
C146	C	0.03792	-0.18367	0.84292
C147	C	-0.1581	0.04048	0.67097
C148	C	-0.005	0.17339	0.74264
C149	C	0.19232	-0.05141	0.85595
C150	C	-0.01719	-0.20237	0.86298
C151	C	-0.02988	-0.2581	0.86353
C152	C	0.01236	-0.29616	0.84519
C153	C	0.0675	-0.27797	0.82785
C154	C	0.07996	-0.22252	0.82732
C155	C	-0.19002	0.08594	0.61992
C156	C	-0.24768	0.08213	0.60745
C157	C	-0.27501	0.03281	0.64595
C158	C	-0.24392	-0.01307	0.69505
C159	C	-0.1861	-0.00903	0.7077
C160	C	0.22492	-0.09287	0.93682
C161	C	0.28264	-0.09063	0.92368
C162	C	0.27715	-0.00477	0.75091
C163	C	0.21927	-0.00726	0.76318
C164	C	0.04154	0.19347	0.84608
C165	C	0.05305	0.24937	0.85534
C166	C	-0.02875	0.26682	0.65984
C167	C	-0.03983	0.21104	0.64957
N168	N	-0.00163	-0.35292	0.83726
N169	N	-0.33423	0.03182	0.64714
C170	C	0.30906	-0.04692	0.82955

C171	C	0.01778	0.28639	0.76368
N172	N	0.02948	0.34351	0.77978
C173	C	0.35094	0.41381	0.71907
O174	O	0.38791	0.37063	0.71413
C175	C	0.4402	0.39525	0.69885
C176	C	0.56883	0.33102	0.65222
O177	O	-0.39063	0.37145	0.67445
C178	C	0.58012	0.41998	0.67435
C179	C	-0.5304	-0.35038	0.73579
O180	O	0.42957	-0.39191	0.73356
C181	C	0.45962	-0.43961	0.71134
C182	C	-0.16078	-0.237	0.64215
O183	O	-0.16861	-0.19282	0.7683
C184	C	-0.18227	-0.15	0.64282

Table S3. Atomistic coordinates of AA stacking model for PyTTA-DHTA-COF optimized by using CASTEP-method.
Space group: *P1;*
a = 24.5960 Å, *b* = 24.0958 Å, *c* = 3.5171 Å;
α = β = γ = 90.0000˚.

	Atom	x/a	y/b	z/c
C1	C	1.49638	-2.94188	-0.49504
C2	C	1.45335	-3.03509	-0.45342
C3	C	1.49584	-2.88084	-0.49455
N4	N	1.54832	-3.14488	-0.55756
C5	C	1.9444	-2.48902	-0.49274
C6	C	1.96031	-2.54381	-0.54303
C7	C	2.01556	-2.55417	-0.54969
C8	C	1.88721	-2.4743	-0.48232
O9	O	1.3991	-2.95703	-0.39708
C10	C	1.44925	-2.97753	-0.44805
O11	O	2.07732	-2.41248	-0.41418
C12	C	1.38868	-2.59768	-0.47403
C13	C	1.44107	-2.6171	-0.46213
C14	C	1.48608	-2.5774	-0.46632
C15	C	1.47734	-2.51988	-0.49454
C16	C	1.42353	-2.50193	-0.51209
C17	C	1.37837	-2.54135	-0.49545
C18	C	1.46046	-2.40644	-0.55971
C19	C	1.41637	-2.44512	-0.54932
C20	C	1.31992	-2.52701	-0.49711
C21	C	1.55454	-2.32112	-0.55042
C22	C	1.30435	-2.47277	-0.42903
C23	C	1.24954	-2.46067	-0.42401
C24	C	1.22373	-2.5572	-0.55022
C25	C	1.27859	-2.56907	-0.55614
C26	C	1.60142	-2.28602	-0.61591
C27	C	1.59894	-2.22826	-0.61892
C28	C	1.54951	-2.20419	-0.55616
C29	C	1.50244	-2.23861	-0.48968
C30	C	1.50515	-2.29631	-0.48596
C31	C	1.79109	-2.49728	-0.5157
N32	N	1.8469	-2.51092	-0.52491
H33	H	0.02381	0.42397	0.17056
H34	H	0.02479	0.41599	0.69012
H35	H	0.11148	0.5745	0.76478
H36	H	0.53624	0.1439	0.45765
H37	H	0.87901	0.57124	0.56533
H38	H	0.40383	0.08415	0.74444

H39	H	0.35158	0.37162	0.53369
H40	H	0.4523	0.63942	0.40974
H41	H	0.37315	0.56921	0.42864
H42	H	0.33669	0.5623	0.62338
H43	H	0.23781	0.58372	0.62951
H44	H	0.19094	0.40805	0.40084
H45	H	0.29048	0.3866	0.39057
H46	H	0.6423	0.69538	0.33232
H47	H	0.6374	0.79943	0.32721
H48	H	0.4618	0.78051	0.56154
H49	H	0.46685	0.67587	0.57009
H50	H	0.42481	0.94731	0.31509
H51	H	0.43832	0.94651	0.82891

Table S4. Atomistic coordinates of AB stacking model for PyTTA-DHTA-COF optimized by using CASTEP-method.
Space group: *P1;*
a = 24.5987 Å, *b* = 23.9210 Å, *c* = 6.8241 Å;
α = β = γ = 90.0000°.

	Atom	x/a	y/b	z/c
C1	C	0.48708	0.04362	0.24299
C2	C	0.45983	0.94807	0.38855
C3	C	0.4835	0.10146	0.22581
N4	N	0.53811	0.83761	0.17254
C5	C	0.93612	0.49305	0.24865
C6	C	0.95264	0.43791	0.25947
C7	C	0.01138	0.42484	0.26202
C8	C	0.8817	0.50643	0.24649
O9	O	0.418	0.03311	0.49375
C10	C	0.45512	0.01007	0.37331
O11	O	0.07286	0.57381	0.23194
C12	C	0.38149	0.38664	0.26989
C13	C	0.43375	0.36701	0.27226
C14	C	0.47906	0.40598	0.26384
C15	C	0.47106	0.46397	0.25294
C16	C	0.41742	0.48291	0.24871
C17	C	0.37171	0.44361	0.25729
C18	C	0.45581	0.57883	0.22901
C19	C	0.41114	0.54051	0.23597
C20	C	0.31328	0.45853	0.2538
C21	C	0.54921	0.66149	0.21434
C22	C	0.29813	0.51422	0.24972
C23	C	0.24342	0.52681	0.24727
C24	C	0.21676	0.42804	0.25315
C25	C	0.2715	0.41568	0.25538
C26	C	0.5837	0.69386	0.08926
C27	C	0.5797	0.75177	0.07672
C28	C	0.54147	0.77826	0.18984
C29	C	0.50729	0.74615	0.31705
C30	C	0.51127	0.68826	0.32932
C31	C	0.78556	0.48326	0.25103
N32	N	0.84126	0.46914	0.25304
C33	C	0.50088	0.92352	0.25668
C34	C	0.52814	0.01907	0.11111
C35	C	0.50447	0.86568	0.27391
N36	N	0.44994	0.12955	0.3275
C37	C	0.05187	0.4741	0.25211
C38	C	0.03535	0.52924	0.24135

C39	C	0.97661	0.5423	0.23876
C40	C	0.10629	0.46071	0.25415
O41	O	0.56998	0.93403	0.00594
C42	C	0.53286	0.95707	0.12639
O43	O	0.91513	0.39334	0.26896
C44	C	0.60649	0.5805	0.22989
C45	C	0.55423	0.60013	0.22745
C46	C	0.50892	0.56115	0.23582
C47	C	0.51692	0.50316	0.24671
C48	C	0.57056	0.48423	0.25096
C49	C	0.61627	0.52352	0.24246
C50	C	0.53217	0.3883	0.27064
C51	C	0.57684	0.42662	0.26372
C52	C	0.67469	0.5086	0.24606
C53	C	0.43878	0.30565	0.28542
C54	C	0.68985	0.45291	0.25019
C55	C	0.74456	0.44033	0.25281
C56	C	0.77122	0.53911	0.24695
C57	C	0.71648	0.55146	0.24455
C58	C	0.40441	0.27332	0.41097
C59	C	0.40843	0.21541	0.4236
C60	C	0.44657	0.18889	0.31013
C61	C	0.48063	0.22098	0.18248
C62	C	0.47662	0.27886	0.17012
C63	C	0.20242	0.48388	0.24918
N64	N	0.14672	0.49801	0.24738
C65	C	-0.01001	0.04514	0.74334
C66	C	-0.03729	0.94959	0.88884
C67	C	-0.0136	0.10298	0.72611
N68	N	0.04093	0.83911	0.6726
C69	C	0.43899	0.49457	0.74786
C70	C	0.45551	0.43943	0.75862
C71	C	-0.48575	0.42636	0.76123
C72	C	0.38457	0.50795	0.74583
O73	O	-0.07917	0.03463	0.99385
C74	C	-0.04202	0.01159	0.87354
O75	O	-0.42427	0.57532	0.73099
C76	C	-0.11563	0.38817	0.77006
C77	C	-0.06337	0.36853	0.77249
C78	C	-0.01806	0.40751	0.76414
C79	C	-0.02606	0.4655	0.75328
C80	C	-0.0797	0.48444	0.74902
C81	C	-0.12541	0.44514	0.75751
C82	C	-0.04131	0.58036	0.72938

C83	C	-0.08598	0.54204	0.73629
C84	C	-0.18383	0.46006	0.75393
C85	C	0.05207	0.66301	0.71462
C86	C	-0.19899	0.51575	0.74979
C87	C	-0.2537	0.52834	0.74717
C88	C	-0.28036	0.42956	0.75305
C89	C	-0.22562	0.4172	0.75545
C90	C	0.08646	0.69535	0.58912
C91	C	0.08244	0.75326	0.5765
C92	C	0.04429	0.77977	0.68995
C93	C	0.01022	0.74769	0.81756
C94	C	0.01423	0.6898	0.8299
C95	C	0.28844	0.48479	0.75081
N96	N	0.34414	0.47066	0.75261
C97	C	0.00378	0.92505	0.75706
C98	C	0.03106	0.0206	0.61157
C99	C	0.00736	0.86721	0.77424
N100	N	-0.04725	0.13106	0.82744
C101	C	-0.44526	0.47562	0.75134
C102	C	-0.46178	0.53076	0.74051
C103	C	0.47948	0.54382	0.73795
C104	C	-0.39084	0.46223	0.75351
O105	O	0.07292	0.93556	0.50653
C106	C	0.03577	0.9586	0.62684
O107	O	0.41799	0.39486	0.76801
C108	C	0.10937	0.58203	0.73014
C109	C	0.05711	0.60166	0.72777
C110	C	0.01179	0.56268	0.73618
C111	C	0.0198	0.50469	0.74706
C112	C	0.07344	0.48576	0.75128
C113	C	0.11915	0.52505	0.74272
C114	C	0.03505	0.38983	0.77094
C115	C	0.07972	0.42815	0.76401
C116	C	0.17757	0.51013	0.7462
C117	C	-0.05834	0.30717	0.7856
C118	C	0.19273	0.45444	0.75028
C119	C	0.24744	0.44185	0.75273
C120	C	0.2741	0.54063	0.74684
C121	C	0.21936	0.55299	0.74461
C122	C	-0.09284	0.2748	0.91068
C123	C	-0.08884	0.21689	0.92322
C124	C	-0.0506	0.1904	0.81012
C125	C	-0.01643	0.22252	0.68291
C126	C	-0.02041	0.28041	0.67063

C127	C	-0.2947	0.4854	0.74897
N128	N	-0.3504	0.49952	0.74694
H129	H	0.41821	0.92647	0.35628
H130	H	0.47194	0.93691	0.54433
H131	H	0.51199	0.12398	0.11577
H132	H	0.01905	0.39602	0.13317
H133	H	0.02059	0.40178	0.40325
H134	H	0.87363	0.55281	0.2385
H135	H	0.43961	0.06203	0.59896
H136	H	0.05795	0.60933	0.31713
H137	H	0.34437	0.35581	0.27843
H138	H	0.44864	0.62535	0.21757
H139	H	0.36815	0.55578	0.2313
H140	H	0.33076	0.55015	0.24836
H141	H	0.23211	0.57232	0.24369
H142	H	0.18367	0.39256	0.25456
H143	H	0.28299	0.37023	0.25854
H144	H	0.6153	0.67293	-0.00318
H145	H	0.60771	0.77766	-0.02615
H146	H	0.47615	0.76732	0.41081
H147	H	0.48358	0.6624	0.43333
H148	H	0.51756	0.02948	-0.04686
H149	H	0.56899	0.04159	0.14842
H150	H	0.4759	0.84314	0.38366
H151	H	0.96866	0.56673	0.09927
H152	H	0.96768	0.56982	0.36987
H153	H	0.11436	0.41434	0.26223
H154	H	0.61165	0.95049	0.04603
H155	H	0.87995	0.40477	0.35928
H156	H	0.64361	0.61133	0.22143
H157	H	0.53934	0.34178	0.28205
H158	H	0.61983	0.41135	0.26841
H159	H	0.65722	0.41699	0.25147
H160	H	0.75588	0.39482	0.25642
H161	H	0.8043	0.57459	0.24559
H162	H	0.70498	0.59691	0.24132
H163	H	0.37288	0.29426	0.50371
H164	H	0.38051	0.18954	0.52684
H165	H	0.51169	0.19978	0.08844
H166	H	0.50423	0.3047	0.06577
H167	H	0.3765	0.55433	0.73772
H168	H	0.11799	0.67441	0.49641
H169	H	0.11036	0.77913	0.4733
H170	H	-0.02085	0.76888	0.91158

H171	H	-0.01339	0.66396	0.93422
H172	H	0.02052	0.03101	0.45357
H173	H	0.07191	0.04311	0.64899
H174	H	-0.02115	0.84469	0.88422
H175	H	0.47153	0.56825	0.59846
H176	H	0.47056	0.57135	0.86907
H177	H	0.11459	0.95203	0.54672
H178	H	0.3828	0.40628	0.85828
H179	H	0.14649	0.61286	0.72163
H180	H	0.04222	0.34331	0.78237
H181	H	0.12271	0.41288	0.76868
H182	H	0.1601	0.41852	0.75166
H183	H	0.25875	0.39635	0.75631
H184	H	0.30719	0.57611	0.74542
H185	H	0.20787	0.59844	0.74144
H186	H	0.9211	0.92798	0.85652
H187	H	0.9748	0.93845	1.04465
H188	H	1.01498	0.12552	0.61639
H189	H	0.52193	0.39754	0.63241
H190	H	0.52344	0.4033	0.90248
H191	H	0.94241	0.06356	1.09908
H192	H	0.56084	0.61085	0.81617
H193	H	0.84725	0.35734	0.7785
H194	H	0.95152	0.62689	0.71797
H195	H	0.87103	0.55731	0.7316
H196	H	0.83364	0.55168	0.74851
H197	H	0.73498	0.57384	0.74355
H198	H	0.68656	0.39408	0.75442
H199	H	0.78588	0.37175	0.7587
H200	H	0.61723	0.41585	0.76151
H201	H	0.87556	0.29573	1.0031
H202	H	0.88315	0.191	1.02609
H203	H	1.01472	0.20134	0.58916
H204	H	1.00728	0.30626	0.56663

Table S5. Elemental analysis of PyTTA-BMTP-COF and PyTTA-DHTA-COF.

Materials		C (wt.%)	H (wt.%)	N (wt.%)
PyTTA-BMTP-COF	theoretical	76.90	5.90	3.88
	analysis	72.22	6.29	4.08
PyTTA-DHTA-COF	theoretical	84.06	4.35	5.41
	analysis	79.56	4.93	5.97

Table S6. Summary of the anhydrous proton conductors based on COFs.

Materials	σ (mS cm^{-1})	T (K)	Ea (eV)	Ref.
PA@PyTTA-BMTP-COF	**26.00**	**413**	**0.22**	**This work**
PA@PyTTA-DHTA-COF	**9.20**	**413**	**0.078**	**This work**
H_3PO_4@TpBpy-MC	2.50	393	0.11	1
H_3PO_4@Tp-Azo-COF	6.7×10^{-2}	340	0.11	2
H_3PO_4@COF-F6-H	42.00	413	0.16	3
phytic@TpPa-(SO_3H-Py)	5.0×10^{-2}	393	0.16	4
phytic@TpPa-SO_3H	7.5×10^{-2}	393	0.10	4
im@XJCOF-1	43.80	413	0.21	5
PIL-TB-COF	2.21	393	0.30	6
PA@EB-COF	9.66	433	0.35	7
Tra@EB-COF	3.25	433	0.18	7
F6-[dema]HSO_4-1.5	13.3	413	0.34	8
H_3PO_4@TPB-DABI-COF	97.10	393	0.23	9
Im@Py-TT-COF-50	3.08	403	0.31	10
im@TPB-DMTP-COF	4.37	403	0.38	11
Tri@TPB-DMTP-COF	1.10	403	0.21	11
H@TPT-COF	12.7	433	0.17	12
H_3PO_4@TPB-DMeTP-COF	191	433	0.34	13
H_3PO_4@CMP-F6-60%	4.39	393	0.35	14

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