Electronic Supplementary Information

High-density Sulfonic Acid-grafted Covalent Organic Framework with Efficient Anhydrous Proton Conduction

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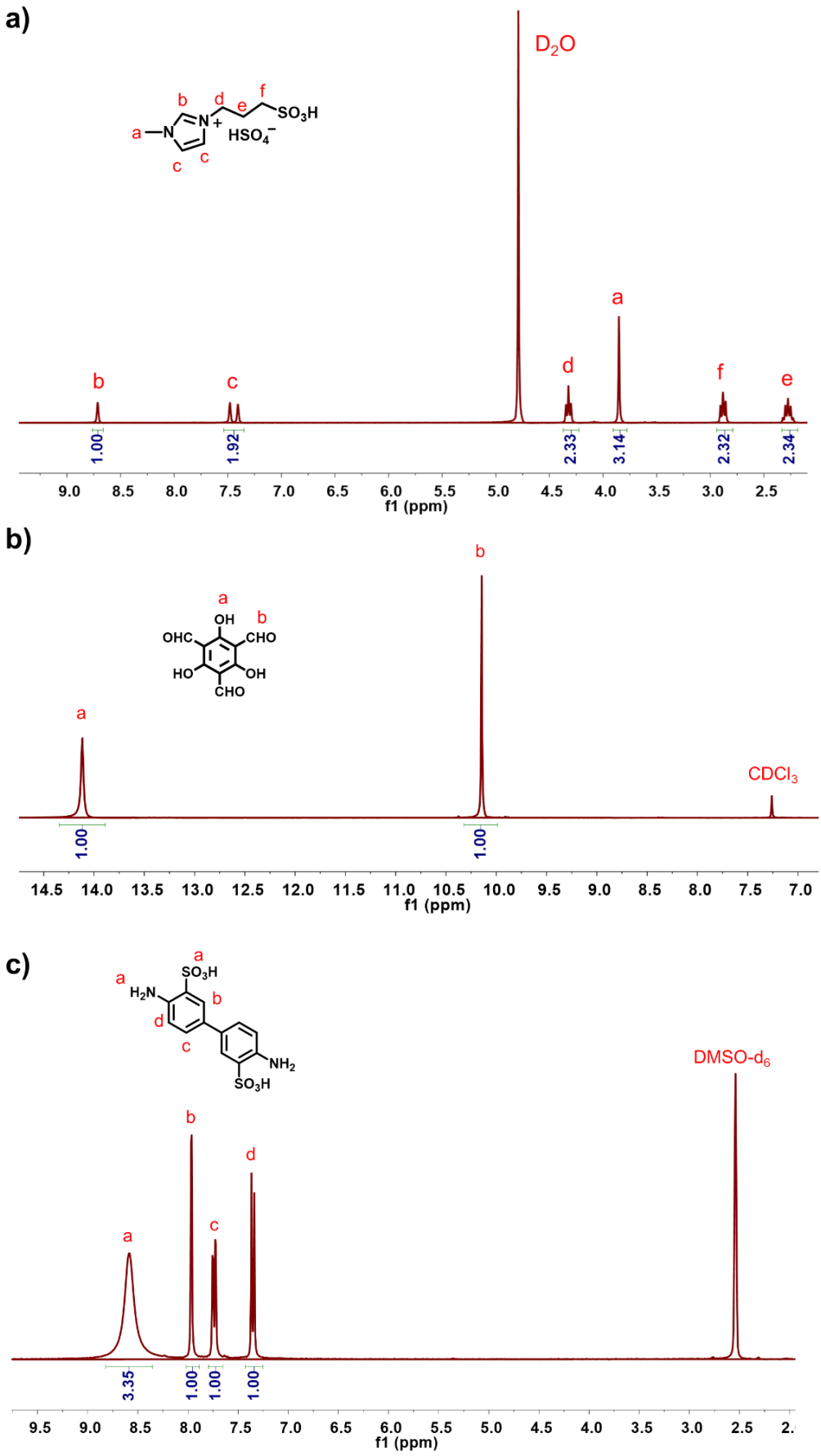

Figure S1. ^{1}H NMR of spectrum of (a) [PSMIm][HSO_4], (b) Tp and (c) BD-(SO_3H)$_2$.

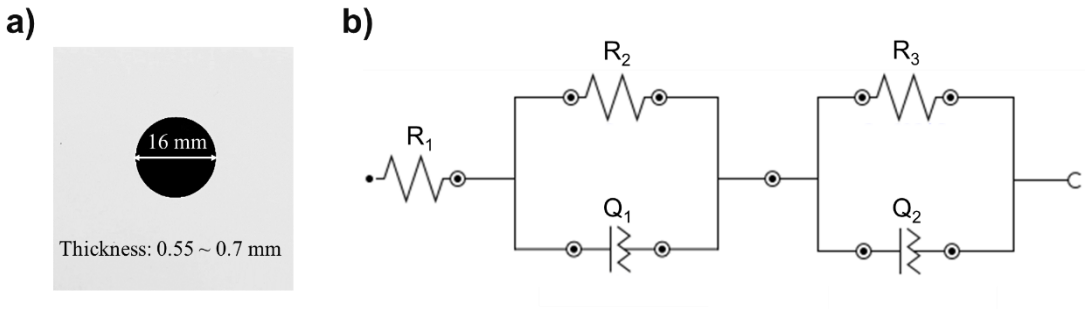

Figure S2. (a) Digital image of the TB-COF pallet for proton conductivity measurements. (b) Equivalent circuit model representation for the proton conduction in COFs wherein R_1, R_2, R_3 represent resistors and Q_1, Q_2 represent imperfect capacitors in the circuit.

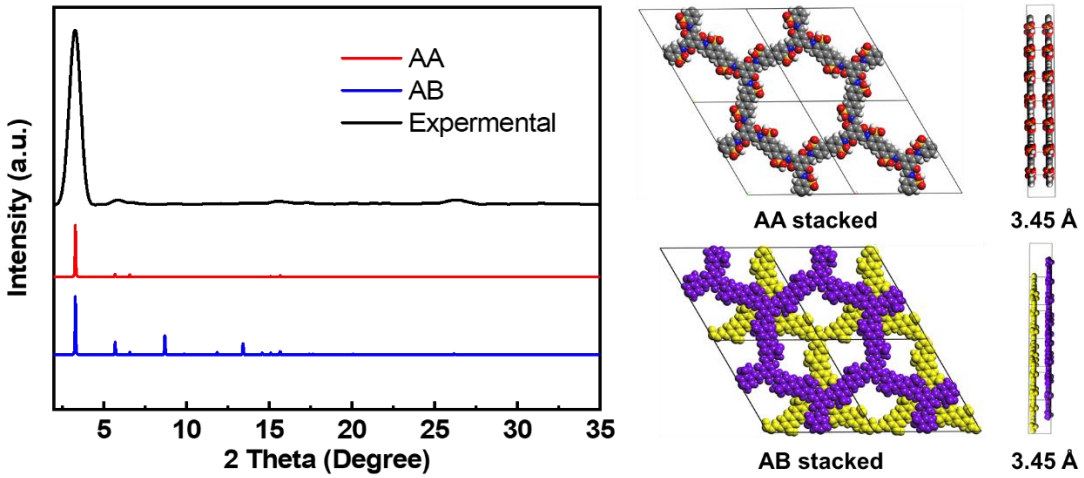

Figure S3. Experimental PXRD spectra of TB-COF and simulated PXRD of TB-COF with AA and AB stacking models.

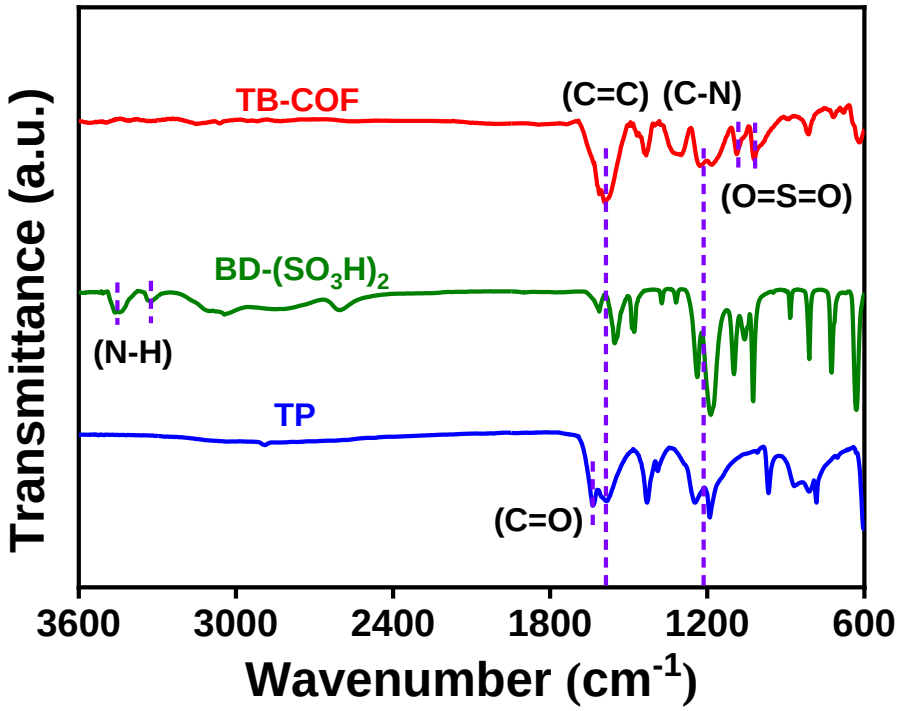

Figure S4. FTIR spectra of TB-COF and corresponding monomers.

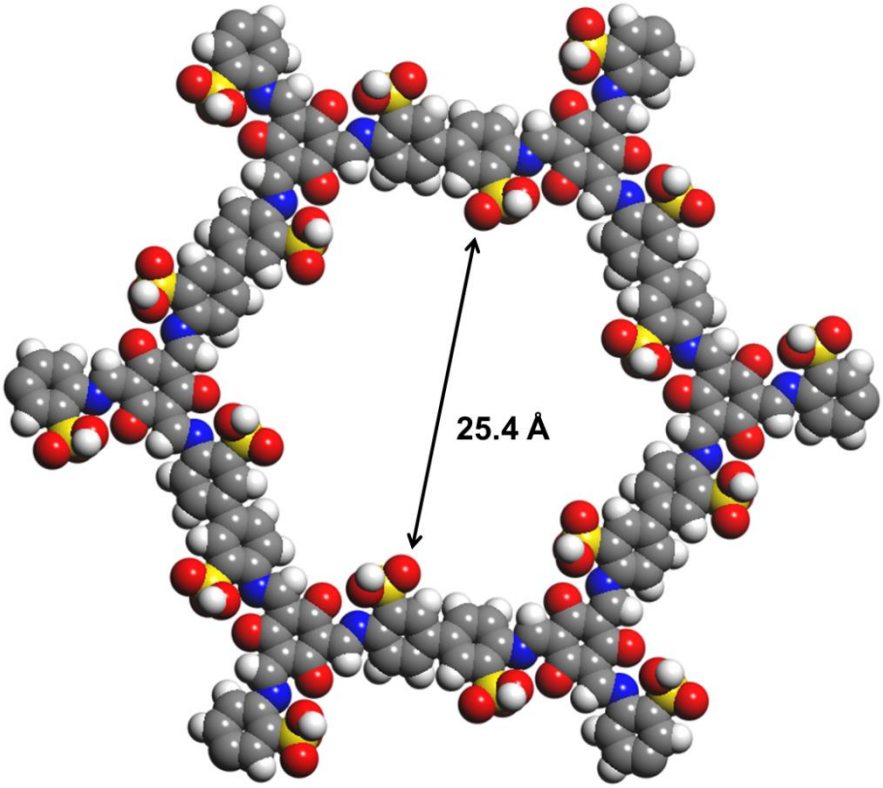

Figure S5. DFT-optimized TB-COF, which shows the values of pore diameter.

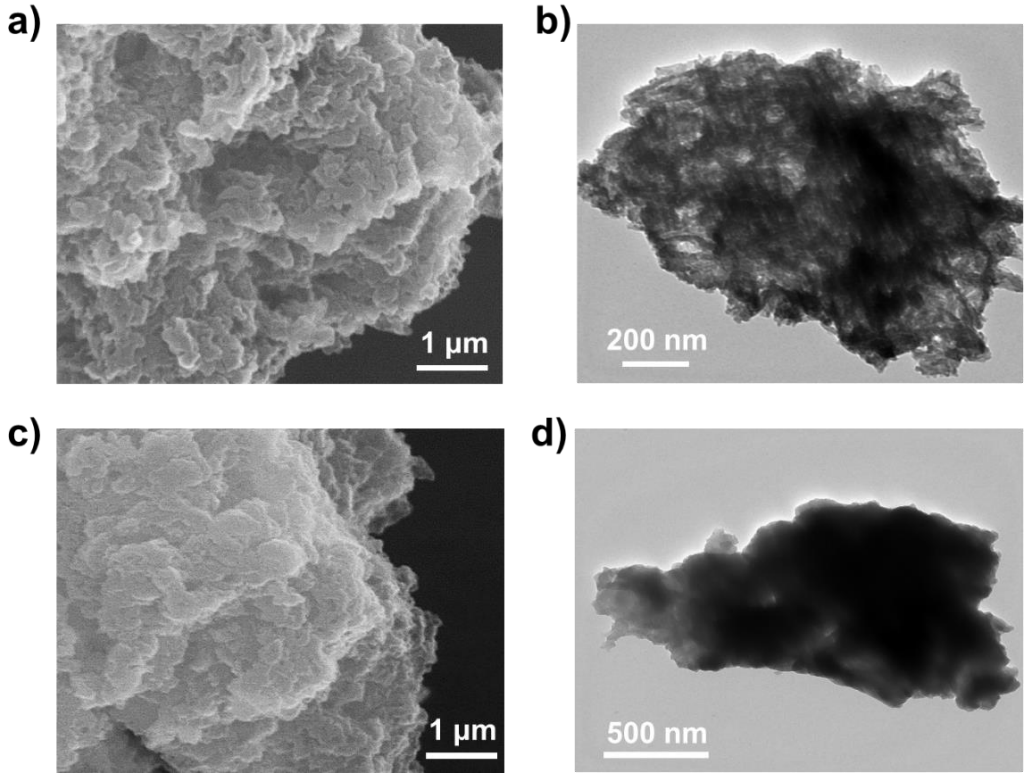

Figure S6. (a) SEM images of TB-COF. (b) TEM images of TB-COF. (c) SEM images of PIL-TB-COF. (d) TEM images of PIL-TB-COF.

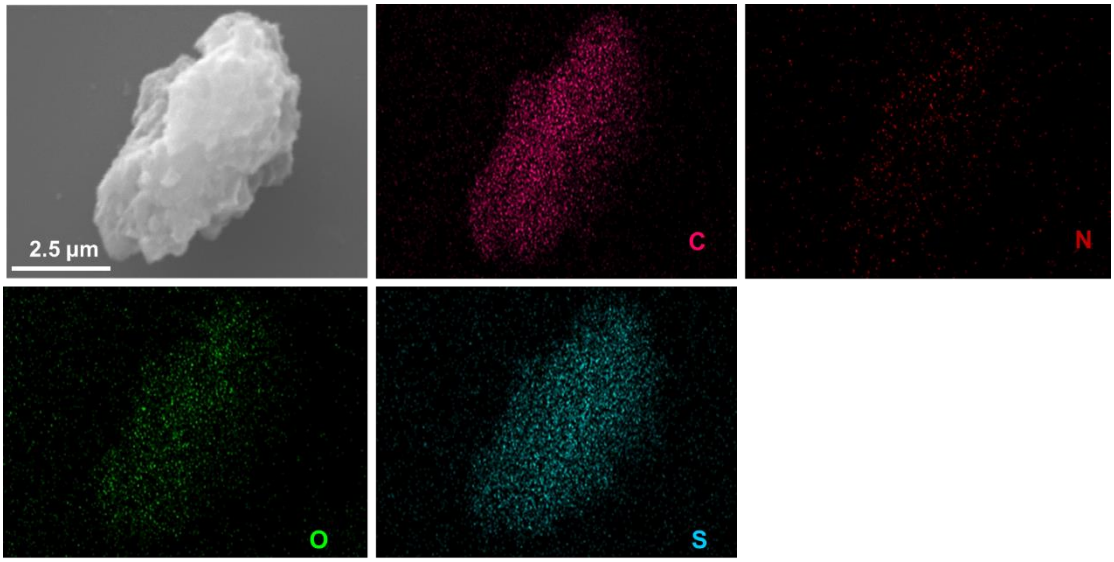

Figure S7. EDS mapping images of TB-COF.

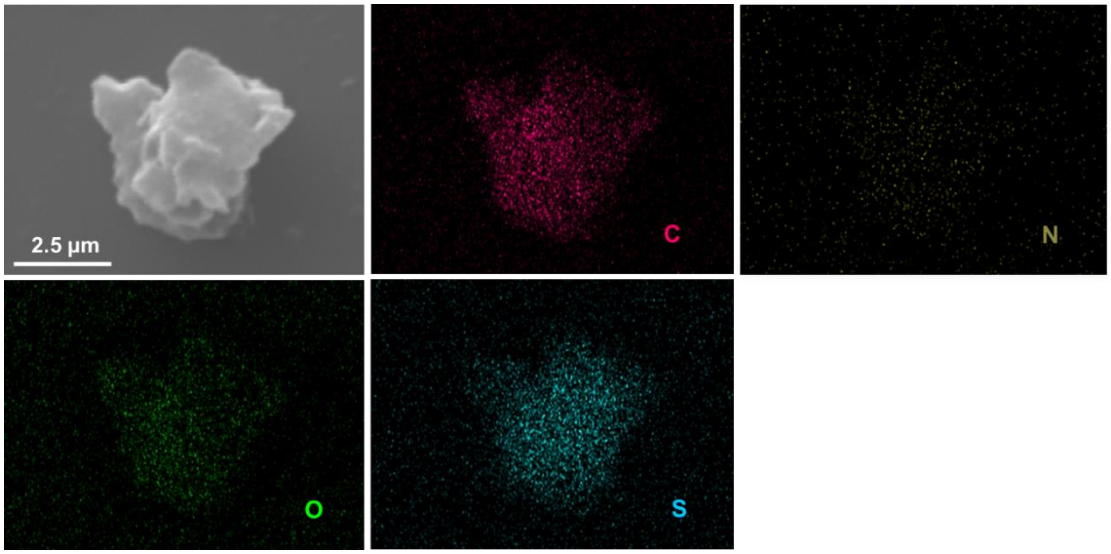

Figure S8. EDS mapping images of PIL-TB-COF.

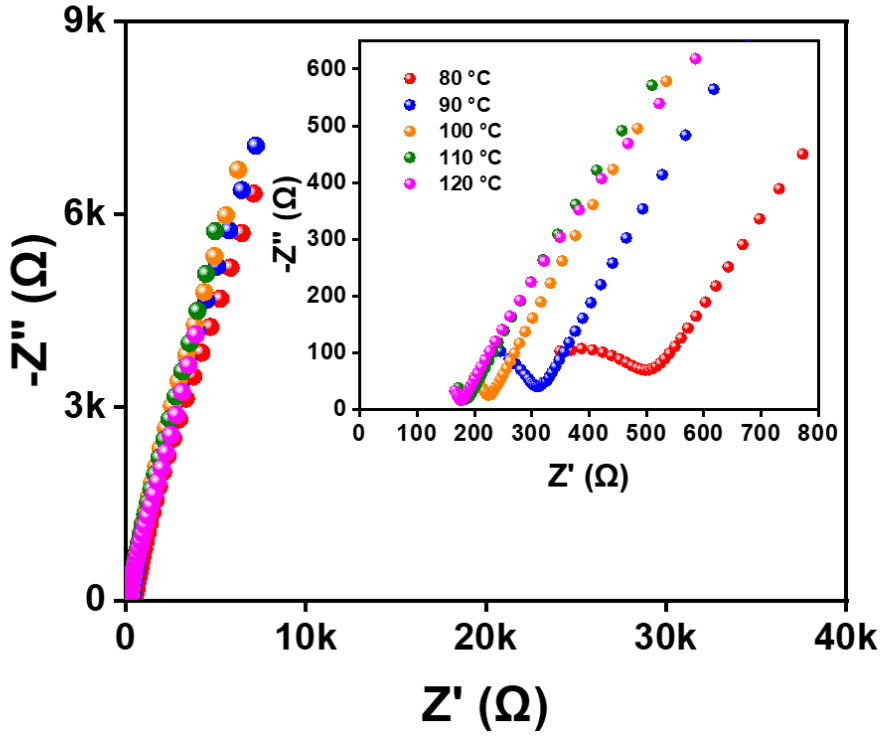

Figure S9. Nyquist plots of TB-COF measured at different temperatures under anhydrous conditions.

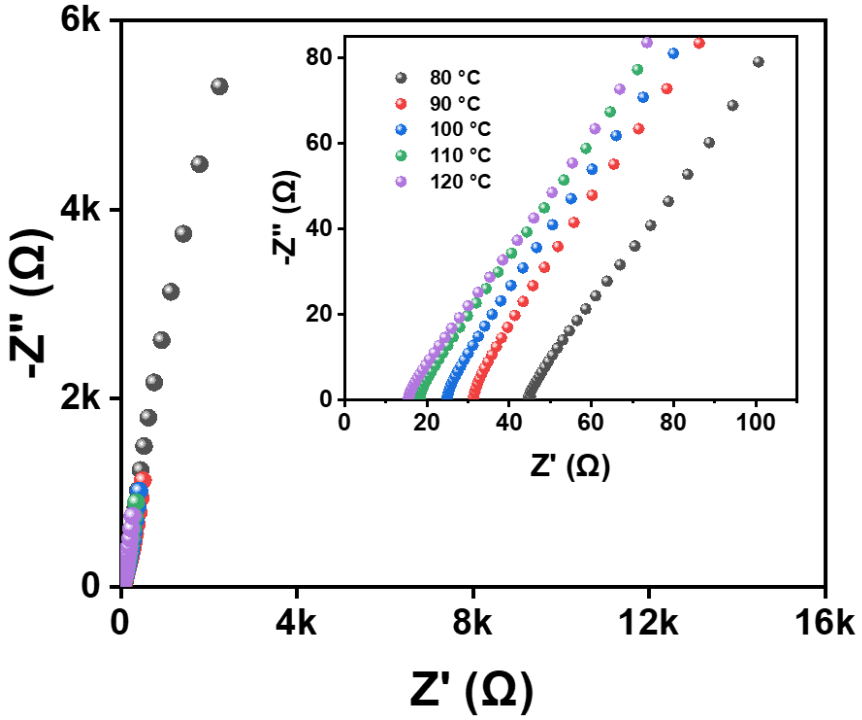

Figure S10. Nyquist plots of PIL-TB-COF measured at different temperatures under anhydrous conditions.

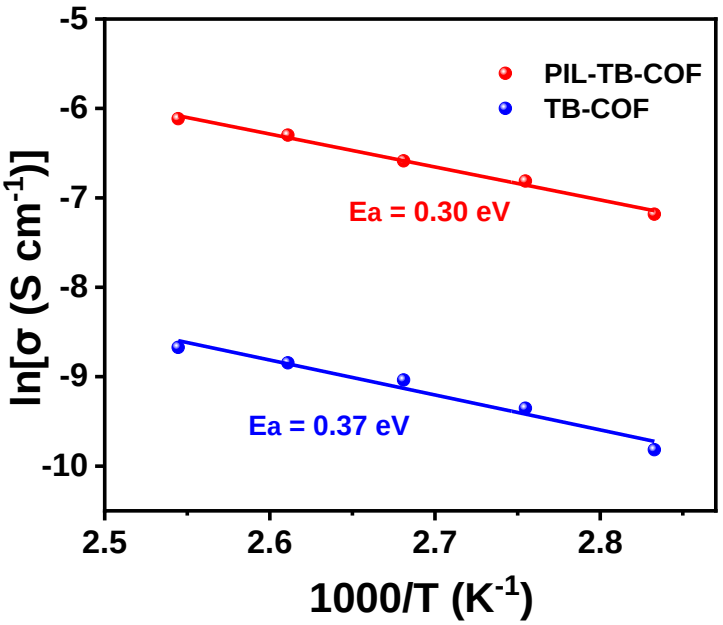

Figure S11. Arrhenius plots for TB-COF (blue) and PIL-TB-COF (red).

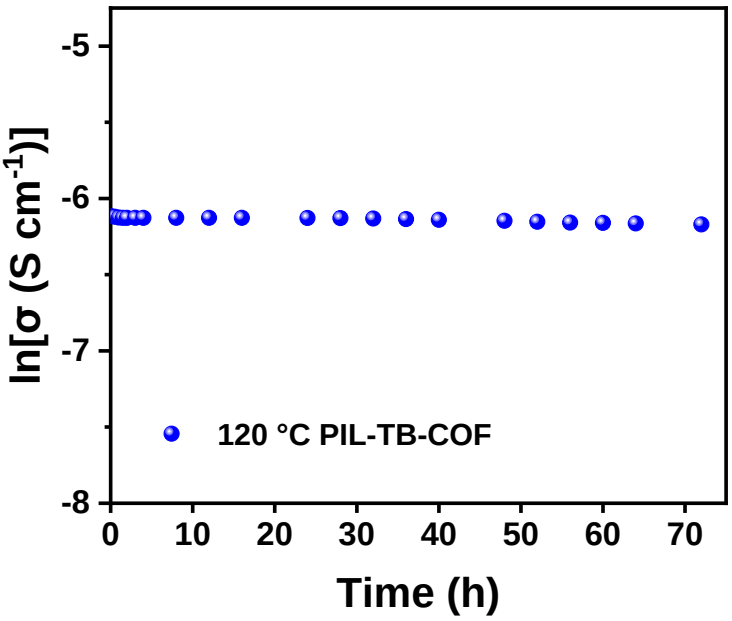

Figure S12. Long-period proton conductivity test for PIL-TB-COF at 120 ℃.

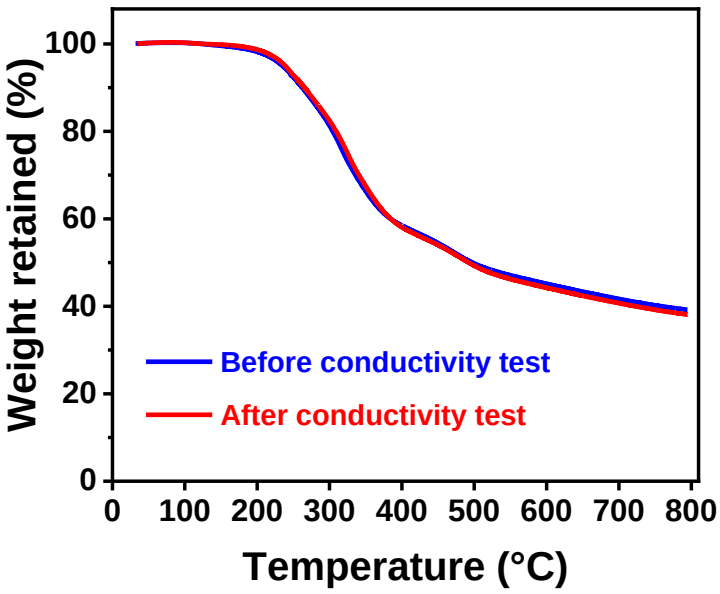

Figure S13. TGA curves of PIL-TB-COF before and after conductivity test.

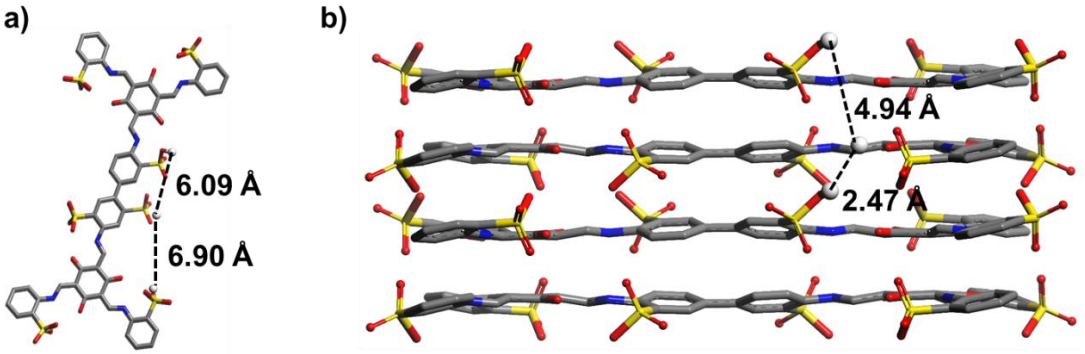

Figure S14. H-ion hopping distances in the (a) planar and (b) axial pathways in TB-COF.

Table S1. Structural parameters for the unit cell of TB-COF.

	TB-COF
Empirical formula	$C_{108}H_{60}N_{12}O_{48}S_{12}$
Symmetry	Hexagonal
Space group	*P*622
a (Å)	31.041254
b (Å)	31.041254
c (Å)	6.802055
α (deg.)	90
β (deg.)	90
γ (deg.)	120

Table S2. Atomic coordinates for the unit cell of TB-COF.

Atom list	*x*	*y*	*z*
O1	15.10188	-0.27275	1.913059
C2	11.30339	10.799	1.780671
C3	12.7488	10.87465	2.074842
C4	13.57424	9.702482	2.006182
C5	13.01224	8.382189	1.687127
C6	11.57374	8.296091	1.407781
C7	10.7486	9.467259	1.452401
N8	10.41777	11.88618	1.900078
C9	8.337356	14.1057	1.963332
C10	7.462941	15.36235	2.006657
C11	6.028378	15.11467	1.776741
H12	13.18912	11.87565	2.432501
H13	14.68975	9.797221	2.259265
H14	11.07907	7.294705	1.140157
S15	8.932954	9.201367	1.330632
H16	5.779516	14.03353	1.426597
O17	8.428527	10.31871	0.212026
O18	8.354261	9.56549	2.661341
O19	8.706831	7.838362	0.737702
H20	8.026105	9.810132	-0.5902

O21	19.56772	-2.30584	1.913059
C22	11.87855	19.90995	1.780671
C23	11.09033	21.12388	2.074842
C24	11.69274	22.42482	2.006182
C25	13.11715	22.59826	1.687127
C26	13.91096	21.39553	1.407781
C27	13.30927	20.09536	1.452401
N28	11.37984	18.59939	1.900078
C29	10.49788	15.68794	1.963332
C30	9.8468	14.30235	2.006657
C31	10.77858	13.18382	1.776741
H32	10.00328	21.00471	2.432501
H33	11.05294	23.34351	2.259265
H34	15.02552	21.46783	1.140157
S35	14.44736	18.65591	1.330632
H36	11.8393	13.50887	1.426597
O37	13.73192	17.66039	0.212026
O38	14.42137	17.97268	2.661341
O39	15.74082	19.14158	0.737702
H40	14.37358	17.56617	-0.5902
C41	3.700661	15.85258	1.780671
C42	3.043469	14.56299	2.074842

C43	1.615619	14.43422	2.006182
C44	0.753214	15.58108	1.687127
C45	1.3979	16.8699	1.407781
C46	2.824733	16.99891	1.452401
N47	5.084994	16.07596	1.900078
C48	8.047364	16.76789	1.963332
C49	9.572859	16.89683	2.006657
C50	10.07565	18.26304	1.776741
H51	3.690203	13.68117	2.432501
H52	1.139914	13.4208	2.259265
H53	0.778012	17.799	1.140157
S54	3.502286	18.70425	1.330632
H55	9.263782	19.01913	1.426597
O56	4.722149	18.58243	0.212026
O57	4.106972	19.02335	2.661341
O58	2.434951	19.58158	0.737702
H59	4.482916	19.18522	-0.5902
O60	19.09551	2.578234	1.913059
O61	11.78069	15.79314	1.913059
C62	15.57918	4.721388	1.780671
C63	14.13378	4.645741	2.074842
C64	13.30833	5.817908	2.006182

C65	13.87033	7.138201	1.687127
C66	15.30883	7.224299	1.407781
C67	16.13397	6.053131	1.452401
N68	16.4648	3.63421	1.900078
C69	18.54522	1.414687	1.963332
C70	19.41963	0.158041	2.006657
C71	20.85419	0.405719	1.776741
H72	13.69346	3.64474	2.432501
H73	12.19283	5.72317	2.259265
H74	15.80351	8.225685	1.140157
S75	17.94962	6.319023	1.330632
H76	21.10306	1.486858	1.426597
O77	18.45404	5.201677	0.212026
O78	18.52831	5.9549	2.661341
O79	18.17574	7.682028	0.737702
H80	18.85647	5.710258	-0.5902
C81	15.00402	-4.38956	1.780671
C82	15.79224	-5.60349	2.074842
C83	15.18984	-6.90443	2.006182
C84	13.76543	-7.07787	1.687127
C85	12.97161	-5.87514	1.407781
C86	13.5733	-4.57497	1.452401

N87	15.50274	-3.079	1.900078
C88	16.38469	-0.16755	1.963332
C89	17.03577	1.218044	2.006657
C90	16.104	2.336572	1.776741
H91	16.87929	-5.48432	2.432501
H92	15.82963	-7.82312	2.259265
H93	11.85705	-5.94744	1.140157
S94	12.43521	-3.13552	1.330632
H95	15.04327	2.011524	1.426597
O96	13.15065	-2.14	0.212026
O97	12.4612	-2.45229	2.661341
O98	11.14175	-3.62119	0.737702
H99	12.50899	-2.04578	-0.5902
O100	7.314852	17.82623	1.913059
O101	7.787059	12.94216	1.913059
C102	23.18191	-0.33219	1.780671
C103	23.8391	0.957396	2.074842
C104	25.26695	1.086171	2.006182
C105	26.12936	-0.06069	1.687127
C106	25.48467	-1.34951	1.407781
C107	24.05784	-1.47852	1.452401
N108	21.79758	-0.55557	1.900078

C109	18.83521	-1.2475	1.963332
C110	17.30971	-1.37644	2.006657
C111	16.80693	-2.74265	1.776741
H112	23.19237	1.839223	2.432501
H113	25.74266	2.099593	2.259265
H114	26.10456	-2.27861	1.140157
S115	23.38029	-3.18386	1.330632
H116	17.61879	-3.49874	1.426597
O117	22.16042	-3.06204	0.212026
O118	22.7756	-3.50296	2.661341
O119	24.44762	-4.06119	0.737702
H120	22.39966	-3.66483	-0.5902
O121	7.314852	13.21479	4.88906
C122	15.00402	4.389318	5.021448
C123	15.79224	5.603255	4.727277
C124	15.18984	6.904197	4.795937
C125	13.76543	7.077633	5.114992
C126	12.97161	5.874906	5.394338
C127	13.5733	4.574728	5.349719
N128	15.50274	3.078761	4.902041
C129	16.38469	0.167308	4.838787
C130	17.03577	-1.21828	4.795462

C131	16.104	-2.33681	5.025378
H132	16.87929	5.484081	4.369618
H133	15.82963	7.822881	4.542854
H134	11.85705	5.947198	5.661962
S135	12.43521	3.13528	5.471487
H136	15.04327	-2.01176	5.375522
O137	13.15065	2.13976	6.590093
O138	12.4612	2.452055	4.140778
O139	11.14175	3.620954	6.064417
H140	12.50899	2.045543	7.392321
O141	7.787059	18.09886	4.88906
C142	23.18191	0.331952	5.021448
C143	23.8391	-0.95763	4.727277
C144	25.26695	-1.08641	4.795937
C145	26.12936	0.060449	5.114992
C146	25.48467	1.349275	5.394338
C147	24.05784	1.478285	5.349719
N148	21.79758	0.55533	4.902041
C149	18.83521	1.24726	4.838787
C150	17.30971	1.376204	4.795462
C151	16.80693	2.742409	5.025378
H152	23.19237	-1.83946	4.369618

H153	25.74266	-2.09983	4.542854
H154	26.10456	2.278369	5.661962
S155	23.38029	3.183625	5.471487
H156	17.61879	3.4985	5.375522
O157	22.16042	3.061799	6.590093
O158	22.7756	3.502727	4.140778
O159	24.44762	4.060956	6.064417
H160	22.39966	3.664597	7.392321
C161	15.57918	-4.72163	5.021448
C162	14.13378	-4.64598	4.727277
C163	13.30833	-5.81815	4.795937
C164	13.87033	-7.13844	5.114992
C165	15.30883	-7.22454	5.394338
C166	16.13397	-6.05337	5.349719
N167	16.4648	-3.63445	4.902041
C168	18.54522	-1.41492	4.838787
C169	19.41963	-0.15828	4.795462
C170	20.85419	-0.40596	5.025378
H171	13.69346	-3.64498	4.369618
H172	12.19283	-5.72341	4.542854
H173	15.80351	-8.22592	5.661962
S174	17.94962	-6.31926	5.471487

H175	21.10306	-1.4871	5.375522
O176	18.45404	-5.20191	6.590093
O177	18.52831	-5.95514	4.140778
O178	18.17574	-7.68227	6.064417
H179	18.85647	-5.7105	7.392321
O180	11.78069	15.24788	4.88906
O181	19.56772	2.305605	4.88906
C182	11.87855	11.13107	5.021448
C183	11.09033	9.917135	4.727277
C184	11.69274	8.616193	4.795937
C185	13.11715	8.442757	5.114992
C186	13.91096	9.645484	5.394338
C187	13.30927	10.94566	5.349719
N188	11.37984	12.44163	4.902041
C189	10.49788	15.35308	4.838787
C190	9.8468	16.73867	4.795462
C191	10.77858	17.8572	5.025378
H192	10.00328	10.03631	4.369618
H193	11.05294	7.697509	4.542854
H194	15.02552	9.573192	5.661962
S195	14.44736	12.38511	5.471487
H196	11.8393	17.53215	5.375522

O197	13.73192	13.38063	6.590093
O198	14.42137	13.06834	4.140778
O199	15.74082	11.89944	6.064417
H200	14.37358	13.47485	7.392321
C201	3.700661	15.18844	5.021448
C202	3.043469	16.47802	4.727277
C203	1.615619	16.6068	4.795937
C204	0.753214	15.45994	5.114992
C205	1.3979	14.17112	5.394338
C206	2.824733	14.04211	5.349719
N207	5.084994	14.96506	4.902041
C208	8.047364	14.27313	4.838787
C209	9.572859	14.14419	4.795462
C210	10.07565	12.77798	5.025378
H211	3.690203	17.35985	4.369618
H212	1.139914	17.62022	4.542854
H213	0.778012	13.24202	5.661962
S214	3.502286	12.33677	5.471487
H215	9.263782	12.02189	5.375522
O216	4.722149	12.45859	6.590093
O217	4.106972	12.01766	4.140778
O218	2.434951	11.45943	6.064417

H219	4.482916	11.85579	7.392321
O220	19.09551	-2.57847	4.88906
O221	15.10188	0.27251	4.88906
C222	11.30339	20.24202	5.021448
C223	12.7488	20.16637	4.727277
C224	13.57424	21.33854	4.795937
C225	13.01224	22.65883	5.114992
C226	11.57374	22.74493	5.394338
C227	10.7486	21.57376	5.349719
N228	10.41777	19.15484	4.902041
C229	8.337356	16.93531	4.838787
C230	7.462941	15.67867	4.795462
C231	6.028378	15.92635	5.025378
H232	13.18912	19.16537	4.369618
H233	14.68975	21.2438	4.542854
H234	11.07907	23.74631	5.661962
S235	8.932954	21.83965	5.471487
H236	5.779516	17.00749	5.375522
O237	8.428527	20.7223	6.590093
O238	8.354261	21.47553	4.140778
O239	8.706831	23.20266	6.064417
H240	8.026105	21.23089	7.392321

Table S3. Element analysis results for TB-COF.

TB-COF (formula)		C (wt%)	N (wt%)	H (wt%)	S (wt%)
$C_{108}H_{60}N_{12}O_{48}S_{12}$	Calcd.	48.43	6.29	2.24	14.35
	Found.	48.59	5.41	3.61	13.96

Table S4. Comparison of proton conductivity with reported COFs materials in anhydrous conditions.

Material	Temperature (℃)	Proton conductivity (S cm^{-1})	References
COF-F6	140	3.63×10^{-11}	J. Am. Chem. Soc., 2020, **142**, 14357–14364.
TPB-DMeTP-COF	160	9.6×10^{-11}	Nat. Commun., 2020, **11**, 8–15.
TpPa-SO_3H	120	1.7×10^{-5}	Chem. Mater., 2016, **28**, 1489–1494.
TB-COF	120	1.52×10^{-4}	This work
Phytic@TpPa-(SO_3H-Py)	120	5×10^{-4}	Chem. Mater. 2016, **28**, 1489-1494.
PA@Tp-Azo	67	6.7×10^{-5}	J. Am. Chem. Soc., 2014, **136**, 6570–6573.
Tri@TPB-DMTP-COF	130	1.10×10^{-3}	Nat. Mater., 2016, **15**, 722–726.
Im@TPB-DMTP-COF	130	4.37×10^{-3}	
PA@TpBpy-ST	120	1.98×10^{-3}	J. Mater. Chem. A, 2016, **4**, 2682–2690.
PA@TpBpy-MC	120	2.5×10^{-3}	
PA@EB-COF	130	5.88×10^{-3}	J. Mater. Chem. A, 2020, **8**, 13702–13709.
Tra@EB-COF	130	2.31×10^{-3}	
H_3PO_4@TPB-DMeTP-COF	120	7.59×10^{-2}	Nat. Commun., 2020, **11**, 8–15.
H_3PO_4@COF-F6	140	4.2×10^{-2}	J. Am. Chem. Soc., 2020, **142**, 14357–14364.
H_3PO_4@TPB-DABI-COF	120	9.71×10^{-2}	Angew. Chemie - Int. Ed., 2021, **60**, 12918–12923.
F6-[dema]HSO_4-1.5	140	1.33×10^{-2}	ACS Appl. Mater. Interfaces, 2021, **13**, 37172–37178.
Im@ Py-TT-COF-50	130	03.08×10^{-3}	ACS Appl. Mater. Interfaces, 2020, **12**, 22910–22916.
PIL-TB-COF	120	2.21×10^{-3}	This work