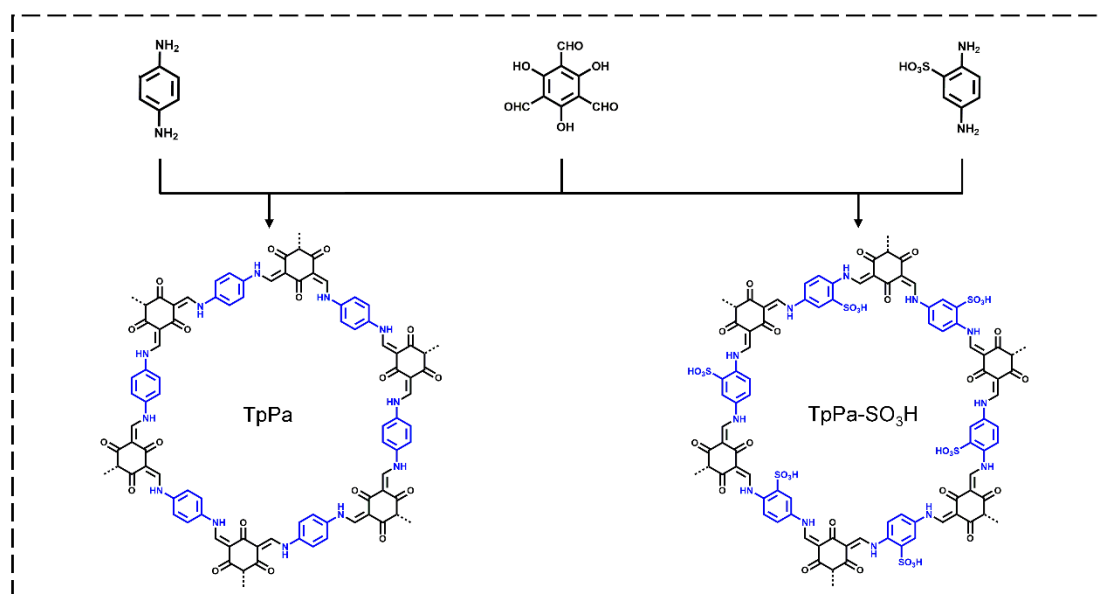


Supporting Information

Proton conduction properties of intrinsically sulfonated covalent organic framework composites

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Scheme S1. Synthesis of TpPa and TpPa-SO₃H.

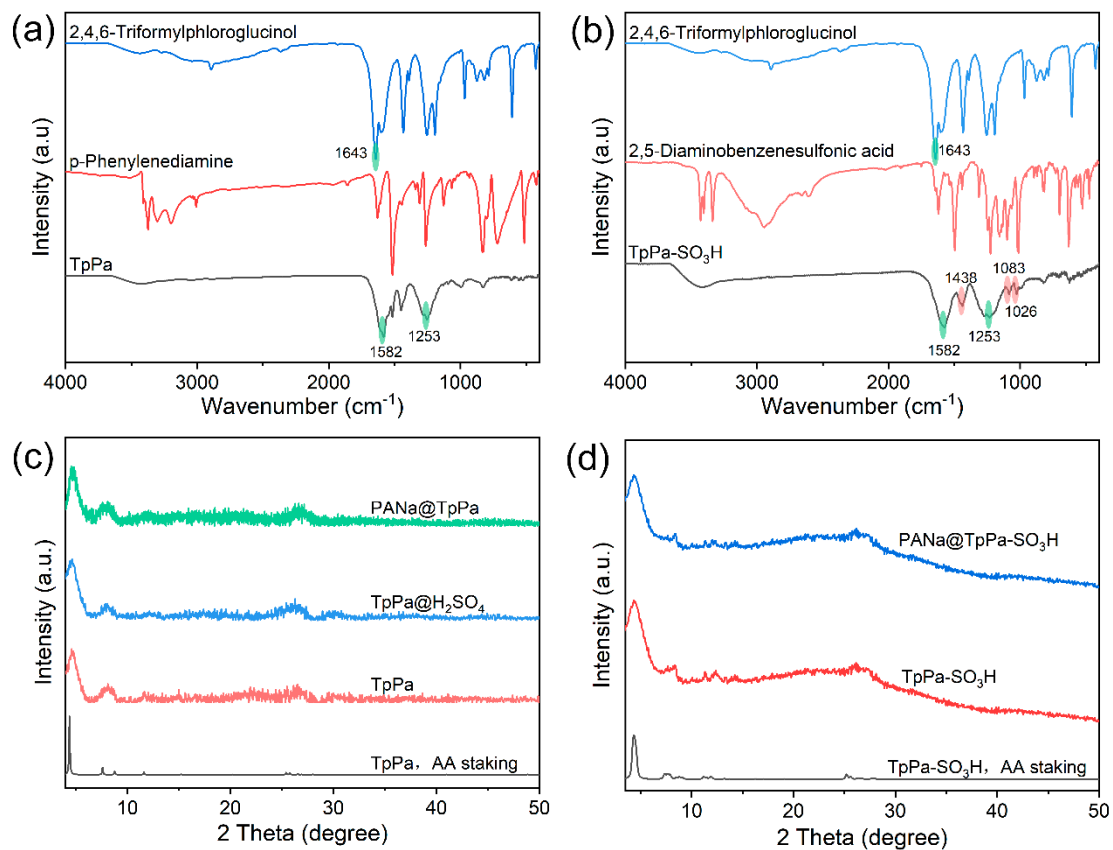


Figure S1. FT-IR spectra of (a) TpPa, p-phenylenediamine and 2,4,6-triformylphloroglucinol, (b) TpPa-SO₃H, 2,5-diaminobenzenesulfonic acid and 2,4,6-triformylphloroglucinol, PXRD patterns of (c) TpPa, TpPa@H₂SO₄ and PANA@TpPa (d) TpPa-SO₃H and PANA@TpPa-SO₃H.

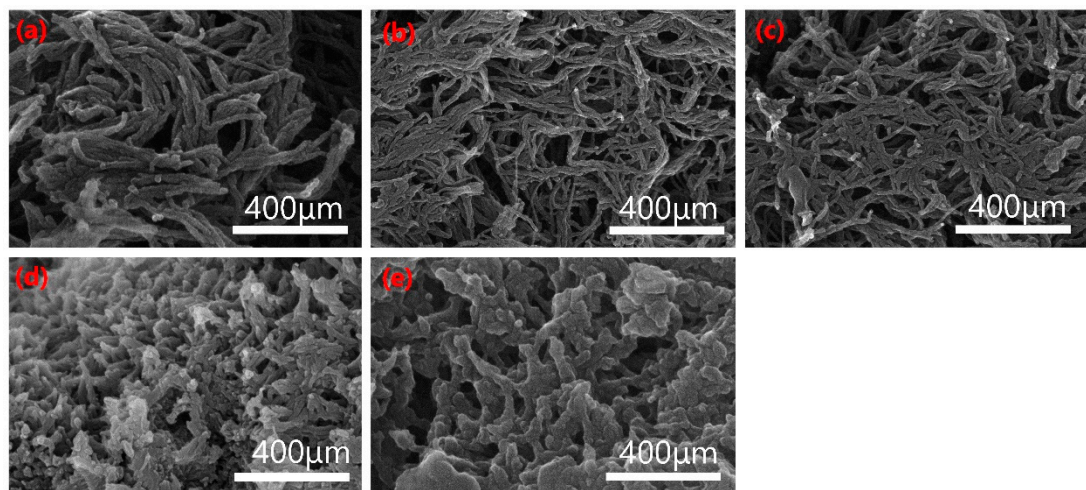


Figure S2. SEM image comparison of (a) TpPa, (b) TpPa@H₂SO₄, (c) TpPa-SO₃H, (d) PANA@TpPa and (e) PANA@TpPa-SO₃H.

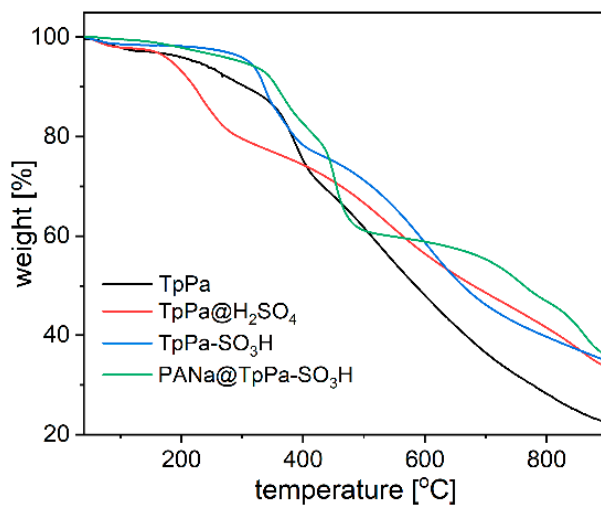


Figure S3. Thermal gravimetric analysis of TpPa, TpPa@H₂SO₄, TpPa-SO₃H and PANA@TpPa-SO₃H.

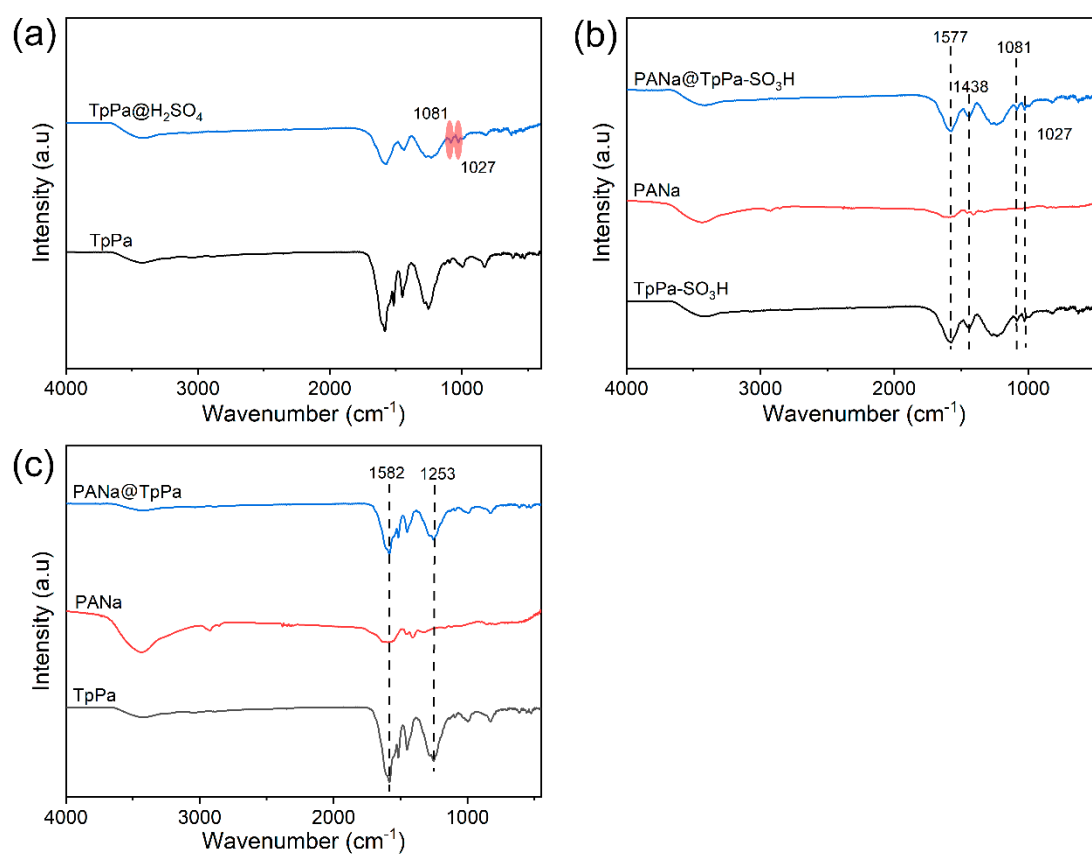


Figure S4. FT-IR spectra of (a) TpPa and TpPa@H₂SO₄; (b) TpPa-SO₃H, PANA and PANA@TpPa-SO₃H, (c) TpPa, PANA and PANA@TpPa.

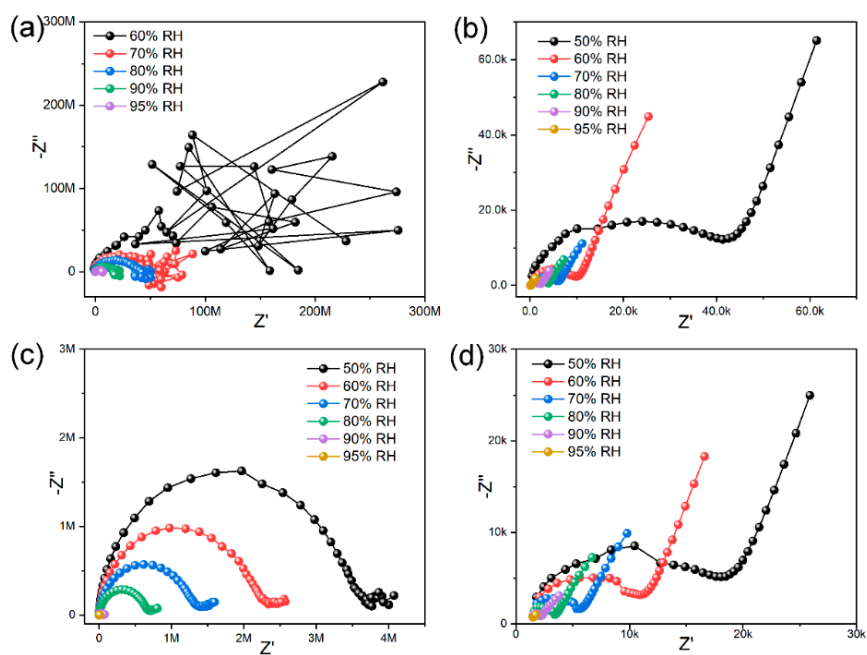


Figure S5. Humidity-dependent proton conductivities at 80 °C: Nyquist plots of (a) TpPa, (b) TpPa@H₂SO₄, (c) TpPa-SO₃H and (d) PANa@TpPa-SO₃H.

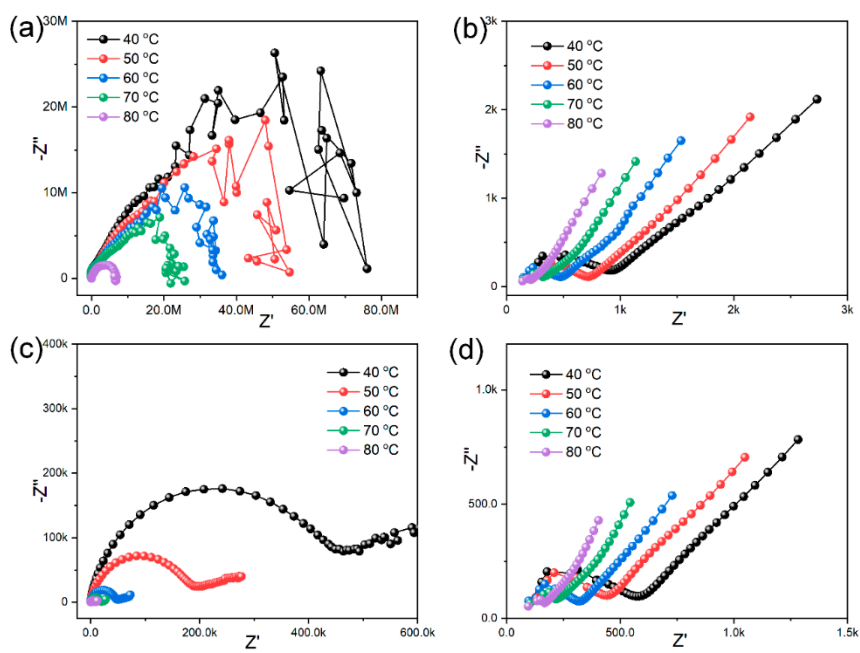


Figure S6. Temperature-dependent Nyquist plots of (a) TpPa, (b) TpPa@H₂SO₄, (c) TpPa-SO₃H and (d) PANa@TpPa-SO₃H.

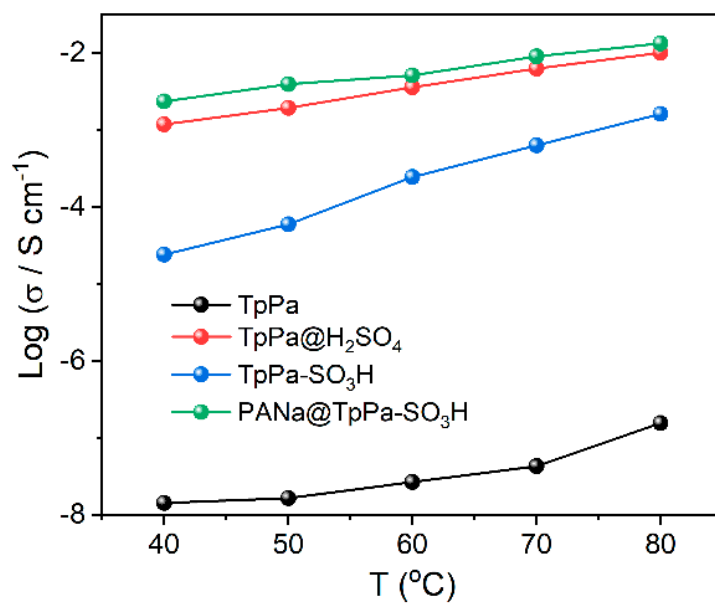


Figure S7. Temperature-dependent Log-scaled proton conductivities of TpPa, TpPa@H₂SO₄, TpPa-SO₃H and PANA@TpPa-SO₃H.

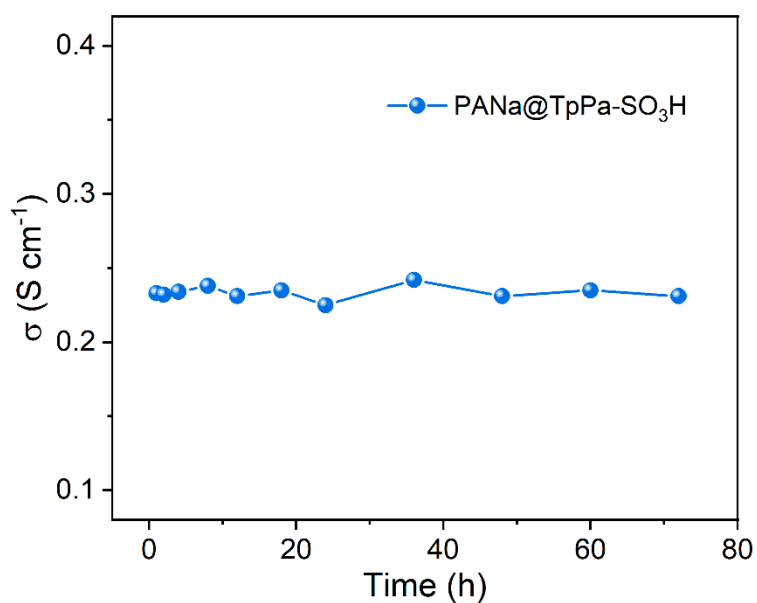


Figure S8. The time-dependent proton conductivities of PANA@TpPa-SO₃H at 80 °C under 95% RH.

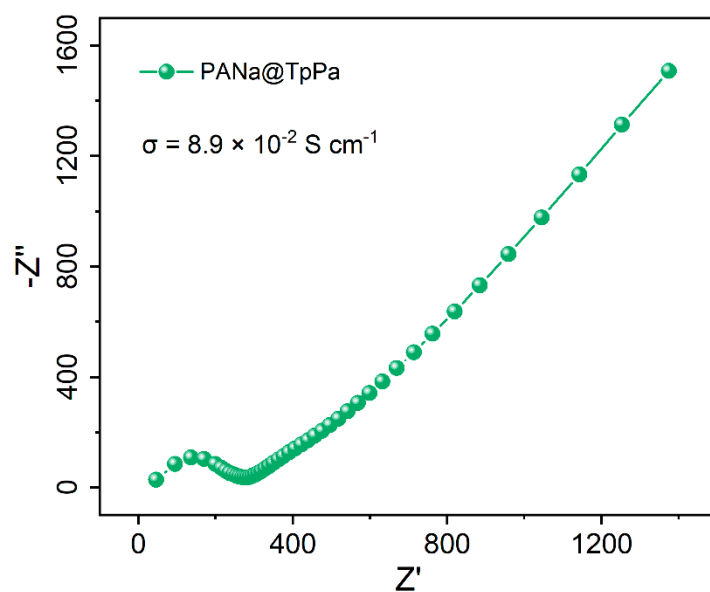


Figure S9. Nyquist plots of PANA@TpPa at 80 °C under 95% RH.

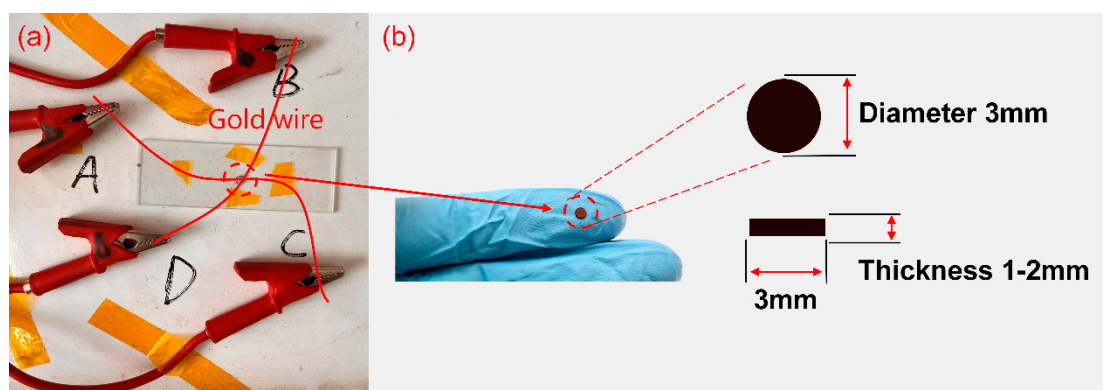


Figure S10. Proton conduction measurement diagram (a), diameter and thickness of sample particles (b).

Table S1. Comparison of proton conductivities in reported materials.

	Compound Name	Conductivity (S cm ⁻¹)	Conditions	References
1	SCOF[1]	5.40×10^{-1}	80 °C, 100% RH	<i>Angew. Chem. Int. Ed.</i> 2021
2	IPC-COF[2]	3.80×10^{-1}	80 °C, 35% RH	<i>Adv. Mater.</i> 2020
3	PANa@TpPa-SO ₃ H	2.33×10^{-1}	80 °C, 95% RH	This work
4	H ₃ PO ₄ @NKCOF-1[3]	1.13×10^{-1}	80 °C, 98% RH	<i>Angew. Chem. Int. Ed.</i> 2020
5	PIL _{0.5} @m-TpPa-SO ₃ H[4]	1.02×10^{-1}	90 °C, 100% RH	<i>Adv. Funct. Mater.</i> 2023
6	ZUT-COF-SO ₃ H[5]	8.65×10^{-2}	80 °C, 98% RH	<i>J. Mater. Chem. A</i> , 2023
7	H ₃ PO ₄ @PyPz-COF[6]	8.10×10^{-2}	80 °C, 98% RH	<i>Small</i> 2023
8	H ₃ PO ₄ @NKCOF-10[7]	6.97×10^{-2}	25 °C, 90% RH	<i>Nat. Commun.</i> 2021
9	im@XJCOF-1[8]	4.38×10^{-2}	140 °C, Anhydrous	<i>ACS Nano</i> 2021
10	COF-F6-H[9]	4.20×10^{-2}	140 °C, Anhydrous	<i>J. Am. Chem. Soc.</i> 2020
11	PA@EB-COF[10]	2.77×10^{-2}	180 °C, Anhydrous	<i>J. Mater. Chem. A</i> , 2020
12	PCF-1-SO ₃ H[11]	2.60×10^{-2}	30 °C, 95% RH	<i>J. Mater. Chem. A</i> , 2017
13	TpPa-SO ₃ H	1.62×10^{-2}	80 °C, 95% RH	This work
14	NUS-10@PVDF-50[12]	1.58×10^{-2}	80 °C, 97% RH	<i>ACS Appl. Mater. Interfaces</i> 2016
15	H@TPT-COF[13]	1.27×10^{-2}	160 °C, anhydrous	<i>Angew. Chem. Int. Ed.</i> 2022
16	CuCl ₂ @TpTta-10[14]	8.81×10^{-3}	100 °C, 98% RH	<i>ACS Appl. Mater. Interfaces</i> 2022
17	aza-COF-2H[15]	4.80×10^{-3}	50 °C, 97% RH	<i>Chem. Mater.</i> 2018
18	EB-COF: PW ₁₂ [16]	3.32×10^{-3}	25 °C, 97% RH	<i>J. Am. Chem. Soc.</i> 2016
19	phytic@TpPa-(SO ₃ H-Py)[17]	5.00×10^{-4}	120 °C, Anhydrous	<i>Chem. Mater.</i> 2016
20	TpPa	1.56×10^{-7}	80 °C, 95% RH	This work

Table S2. Fractional atomic coordinates for the unit cell of TpPa.

Space group		P6/M	
Unit cell		$a = b = 23.3 \text{ \AA}, c = 3.5 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	
atoms	x	y	z
C1	0.30486	0.71075	0.5
C2	0.25918	0.63762	0.5
C3	0.38469	0.57717	0.5
N4	0.45324	0.59306	0.5
C5	0.47517	0.54499	0.5
C6	0.54348	0.56834	0.5
C7	0.57022	0.5251	0.5
O8	0.46591	0.71976	0.5
H9	0.57779	0.62123	0.5
H10	0.50883	0.35776	0.5
H11	0.65263	0.47464	0.5
H12	0.3753	0.45244	0.5

Table S3. Fractional atomic coordinates for the unit cell of TpPa-SO₃H.

Space group		P1	
Unit cell		$a = b = 23.3 \text{ \AA}, c = 3.8 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	
atoms	x	y	z
O1	1.27851	0.52156	0.88261
O2	1.34551	0.52156	0.9924
O3	1.30686	0.52156	0.84134
O4	0.59901	0.52156	0.66582
O5	0.60073	0.52156	0.58066
O6	0.49914	0.52156	0.65039
O7	1.11957	0.52156	1.33211
O8	1.14524	0.52156	1.42818
O9	1.02138	0.52156	1.281
H10	0.63363	0.52156	0.66113
H11	1.1671	0.52156	1.37102
H12	1.26255	0.52156	0.83385
H13	1.40081	0.50702	1.32267
H14	0.93982	0.49899	0.51874
H15	0.62153	0.49238	1.05159
C16	0.71791	0.5	-0.71063
C17	0.64679	0.5	-0.75033
C18	0.60698	0.5	-0.7133
C19	0.63669	0.5	-0.6387

C20	0.70822	0.5	-0.60216
C21	0.75028	0.5	-0.63635
C22	0.60317	0.5	-0.60132
N23	0.53377	0.5	-0.62712
C24	0.49712	0.5	-0.58876
C25	0.52834	0.5	-0.51851
C26	0.49381	0.5	-0.48047
C27	0.42535	0.5	-0.51306
C28	0.39472	0.5	-0.58268
C29	0.42821	0.5	-0.62069
N30	0.3838	0.5	-0.48008
C31	0.4028	0.5	-0.40905
C32	0.36166	0.5	-0.37992
C33	0.28981	0.5	-0.4171
C34	0.2478	0.5	-0.38233
C35	0.28014	0.5	-0.30843
C36	0.35123	0.5	-0.26861
C37	0.39089	0.5	-0.30585
S38	0.5279	0.5	-0.41114
O39	0.73355	0.5	-0.54145
O40	0.74981	0.5	-0.74118
O41	0.54913	0.5	-0.74474
O42	0.44915	0.5	-0.27582
O43	0.24684	0.5	-0.27902
C44	0.81564	0.5	-0.59753
N45	0.86388	0.5	-0.62212
C46	0.62285	0.5	-0.8185
N47	0.5554	0.5	-0.8664
C48	0.37504	0.5	-0.20065
N49	0.4425	0.5	-0.15306
C50	0.18168	0.5	-0.41325
N51	0.14092	0.5	-0.48453
O52	0.26497	0.5	-0.47716
C53	0.93342	0.5	-0.58345
C54	0.46859	0.5	-0.08084
C55	0.07096	0.5	-0.51801
C56	0.43125	0.5	-0.04466
C57	0.53582	0.5	-0.04447
C58	0.03484	0.5	-0.48135
C59	0.03617	0.5	-0.58915
C60	0.96717	0.5	-0.51273
C61	0.96949	0.5	-0.61949
C62	0.52938	0.5	-0.93861

C63	0.46215	0.5	-0.97498
C64	0.56672	0.5	-0.97476
S65	0.36411	0.5	-0.07652
S66	0.06366	0.5	-0.63351
H67	0.63143	0.5	-0.54794
H68	0.5068	0.5	-0.6778
H69	0.57984	0.5	-0.4917
H70	0.34278	0.5	-0.60934
H71	0.33542	0.5	-0.51334
H72	0.45371	0.5	-0.3756
H73	0.83178	0.5	-0.54427
H74	0.84921	0.5	-0.67308
H75	0.65821	0.5	-0.83751
H76	0.52029	0.5	-0.84973
H77	0.33953	0.5	-0.18179
H78	0.47731	0.5	-0.17022
H79	0.15825	0.5	-0.38113
H80	0.16284	0.5	-0.51544
H81	0.56506	0.5	-0.07084
H82	0.05802	0.5	-0.42791
H83	0.94571	0.5	-0.67336
H84	0.4329	0.5	-0.94863

Table S4. Humidity-dependent proton conductivity (S cm^{-1}) of TpPa, TpPa@H₂SO₄, TpPa-SO₃H and PANa@TpPa-SO₃H.

Conditions	TpPa	TpPa@H ₂ SO ₄	TpPa-SO ₃ H	PANa@TpPa-SO ₃ H
80°C, 50%RH		2.68×10^{-4}	3.65×10^{-5}	6.46×10^{-4}
80°C, 60%RH	5.44×10^{-9}	1.02×10^{-3}	4.92×10^{-5}	1.28×10^{-3}
80°C, 70%RH	1.84×10^{-8}	2.69×10^{-3}	8.14×10^{-5}	2.86×10^{-3}
80°C, 80%RH	2.74×10^{-8}	5.38×10^{-3}	1.59×10^{-4}	5.81×10^{-3}
80°C, 90%RH	5.54×10^{-8}	1.39×10^{-2}	2.06×10^{-3}	7.54×10^{-2}
80°C, 95%RH	1.56×10^{-7}	1.33×10^{-1}	1.62×10^{-2}	2.33×10^{-1}

Table S5. Temperature-dependent proton conductivity (S cm^{-1}) of TpPa, TpPa@H₂SO₄, TpPa-SO₃H and PANA@TpPa-SO₃H.

Conditions	TpPa	TpPa@H ₂ SO ₄	TpPa-SO ₃ H	PANA@TpPa-SO ₃ H
40°C, 95%RH	1.43×10^{-8}	1.55×10^{-2}	2.41×10^{-4}	2.35×10^{-2}
50°C, 95%RH	1.65×10^{-8}	2.53×10^{-2}	5.95×10^{-4}	3.95×10^{-2}
60°C, 95%RH	2.68×10^{-8}	4.71×10^{-2}	2.46×10^{-3}	5.14×10^{-2}
70°C, 95%RH	4.30×10^{-8}	8.26×10^{-2}	6.32×10^{-3}	9.05×10^{-2}
80°C, 95%RH	1.56×10^{-7}	1.33×10^{-1}	1.62×10^{-2}	2.33×10^{-1}

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