Supplementary Information (SI) for CrystEngComm.

Supporting Information for

Thiadiazole-based 3D Covalent Organic Framework for Efficient Anhydrous Proton Conduction

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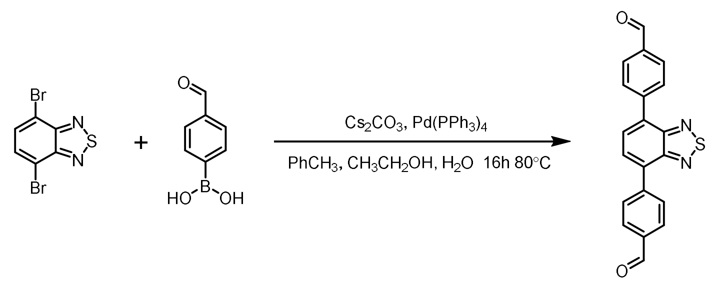
1 Synthesis Section

All chemicals and solvents used in the syntheses are of reagent grade and used without further purification. 4,7-dibromobenzo[c][1,2,5]thiadiazole, 4-bromobenzaldehyde, 4,4',4'',4'''-methanetetrayltetraaniline, 4-bromobenzaldehyde, 4,7-dibromobenzothiadiazole, dichlorobenzene, n-butanol, dichloromethane, chloroform, toluene, sodium iodide, isopropanol and p-benzoquinone were purchased from J&K Chemical Co. Ltd. (Beijing, China). Ethanol, acetic acid were obtained from DIBAI Chemistry Reagent Co. Ltd. (Beijing, China). 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde was synthesized following published procedures.

Cesium carbonate (10.86 g, 33 mmol) was dissolved in 17 mL of water under a nitrogen atmosphere. 4,7-dibromobenzo[c][1,2,5]thiadiazole (2 g, 6.8 mmol) and 4-bromobenzaldehyde (2.5 g, 13.6 mmol) were dissolved in 50 mL of toluene and 34 mL of ethanol under a nitrogen atmosphere. The cesium carbonate solution and tetrakis (triphenylphosphorus) palladium (0.38 g, 0.33 mmol) were added to the reaction flask. The reaction was placed at 80°C to reflux for 16 hours, and quenched with ice water. The resulting product was extracted with chloroform, analyzed by dichloromethane thin-layer chromatography and purified by dichloromethane column chromatography to give the 4,4'-(benzothiadiazole-4,7-diyl) dibenzaldehyde as a light-yellow solid (1.8 g, 5.2 mmol, 76.9%)[1]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2H), 8.08 (d, J = 8.5 Hz, 4H), 8.18 (d, J = 8.0 Hz, 4H), 10.14(s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 191.87, 153.80, 142.98, 136.08, 133.04, 130.04, 129.97, 128.73.



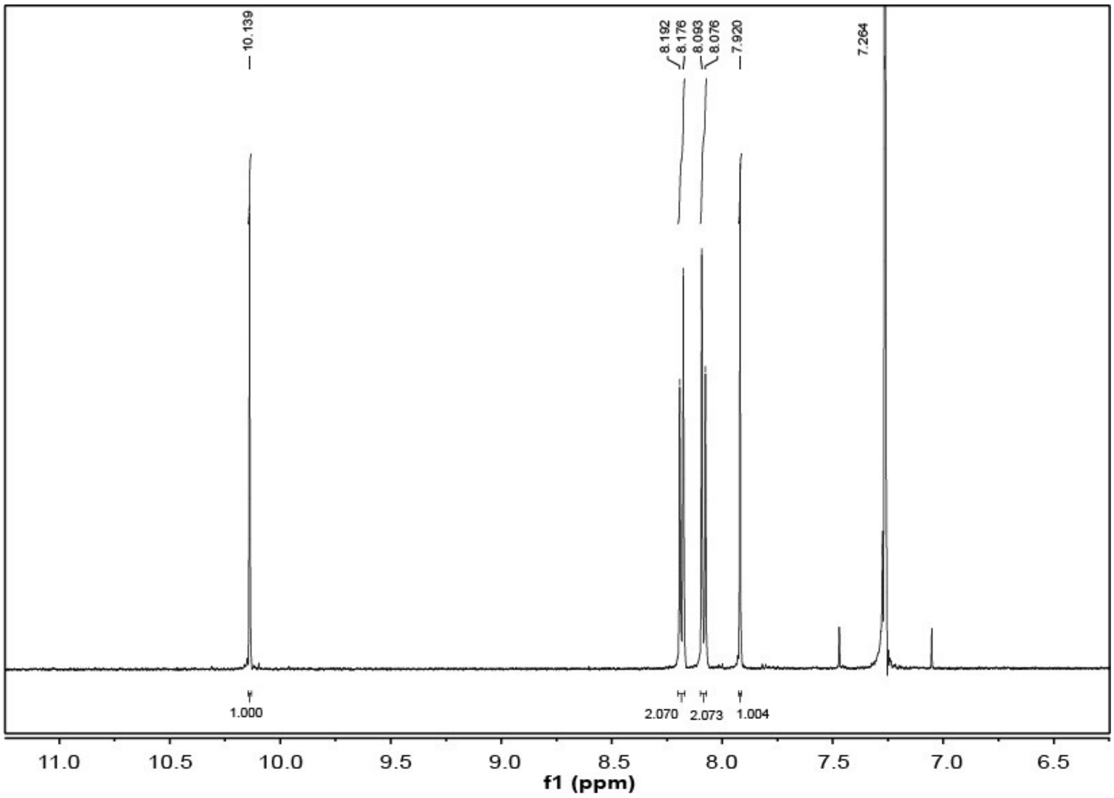


Figure S1. ^{1}H-NMR spectrum of **BT-BA** in $CDCl_3$.

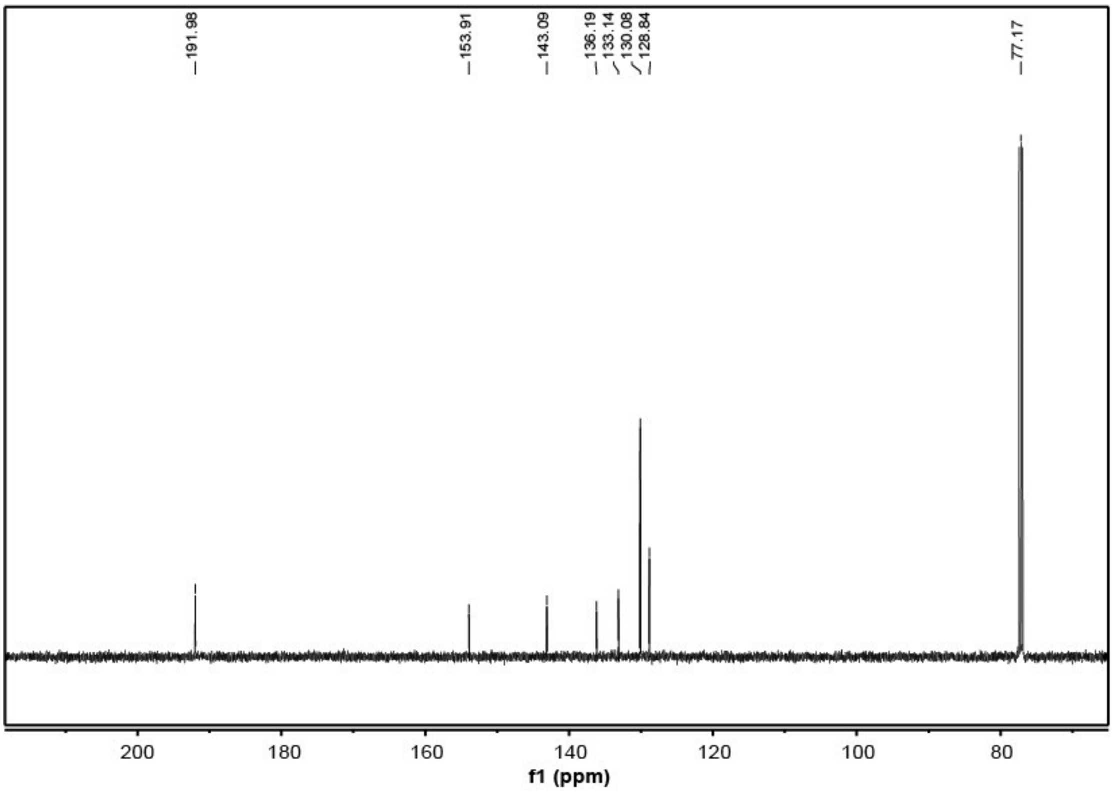
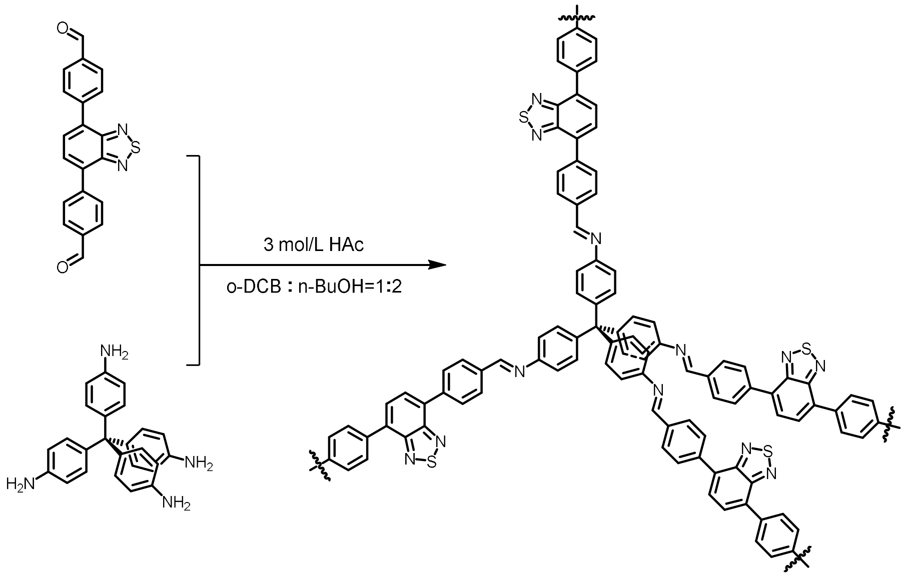


Figure S2. ^{13}C-NMR spectrum of **BT-BA** in $CDCl_3$.

NUST-28 was synthesized in *o*-dichlorobenzene: 1,4 *n*-Butanol = 1:2 with 3 mol/L acetic acid as a catalyst at 120 °C for 6 days. The precursors 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dibenzaldehyde (34 mg, 0.10 mmol) and 4,4',4'',4'''-methanetetrayltetraaniline(19 mg, 0.05 mmol) were dissolved in a ternary solvent mixture of 1,2-dichlorobenzene / 1-butanol / 3 M acetic acid (6/9/2 by vol.; 1.7 mL). The reaction mixture was sonicated for 15 min, bubbled with N_2 for another 15 min, and then heated at 120 °C for 6 days. After being cooled to room temperature, the precipitate was washed with acetone and THF, and then dried under vacuum at 120 °C for 10 h. Finally, NUST-28 was obtained as yellow powders, (47mg, 87% yield).



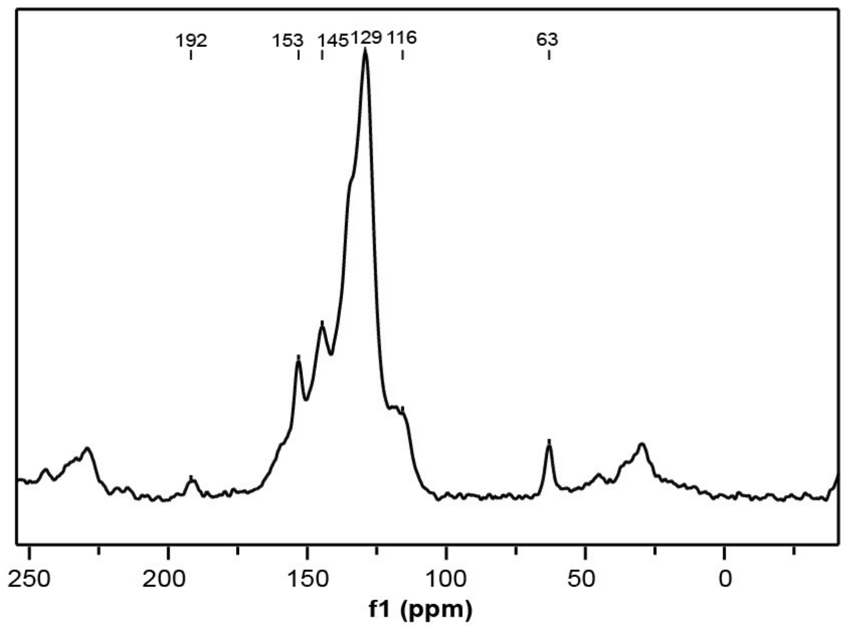


Figure S3. Solid-state ^{13}C-NMR spectrum of NUST-28.

2 Characterization Section

2.1 Characterizations of COF and reactants

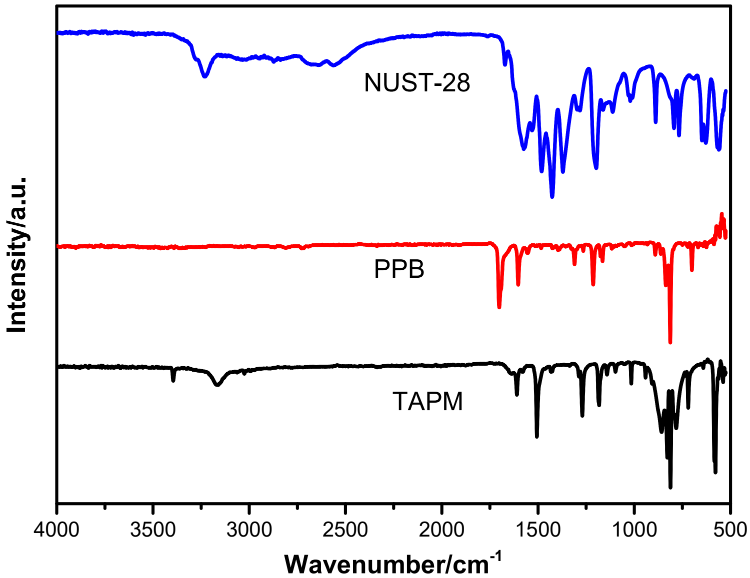


Figure S4. FT-IR spectra of NUST-28 and reactants.

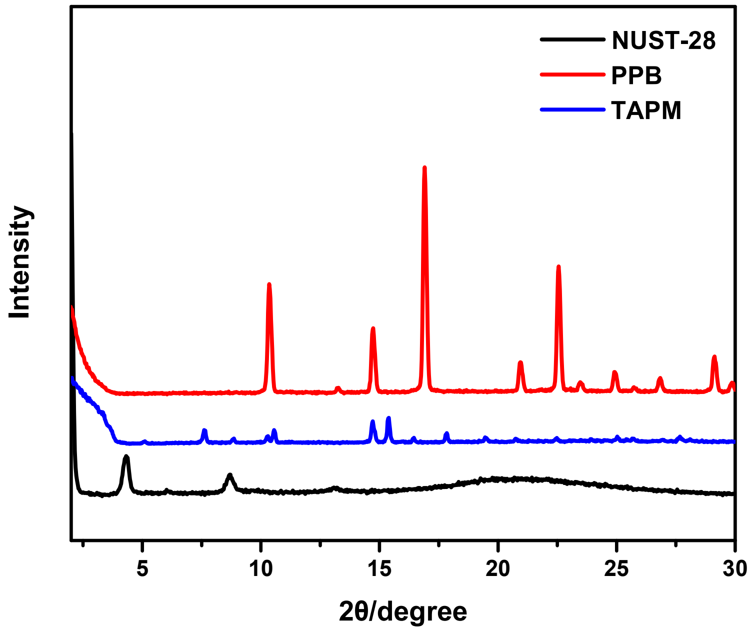


Figure S5. Powder X-ray diffraction patterns of NUST-28 and reactants.

2.2 Stability test of NUST-28

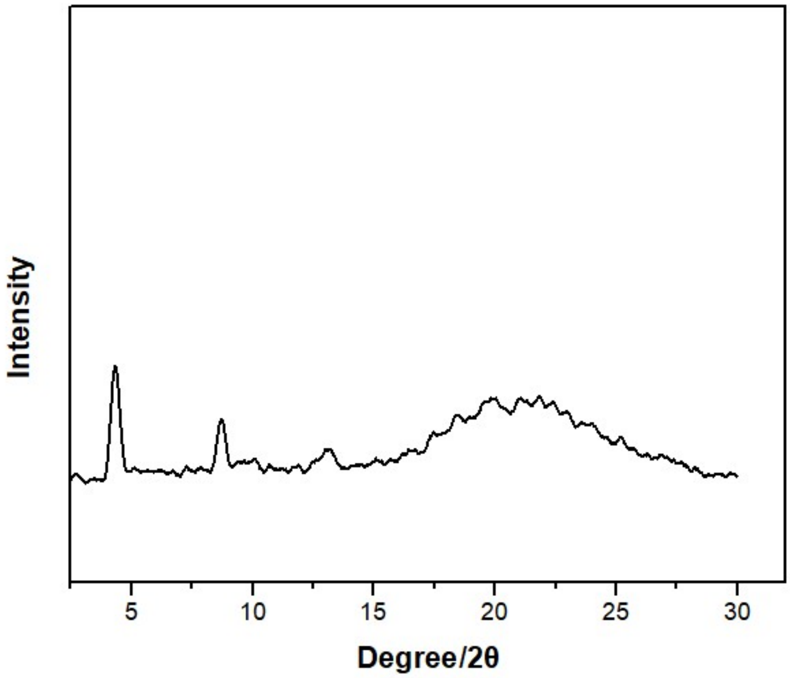


Figure S6. The powder X-ray diffraction pattern of NUST-28 in 1M acetic acid solution.

2.3 Surface morphology characteristics of A

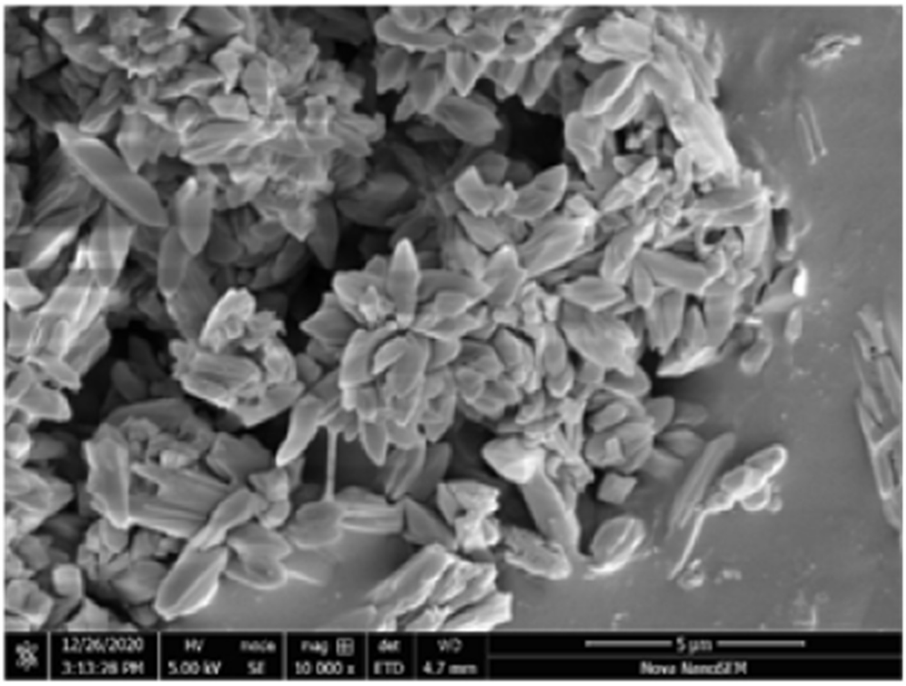


Figure S7. SEM image of NUST-28 powder.

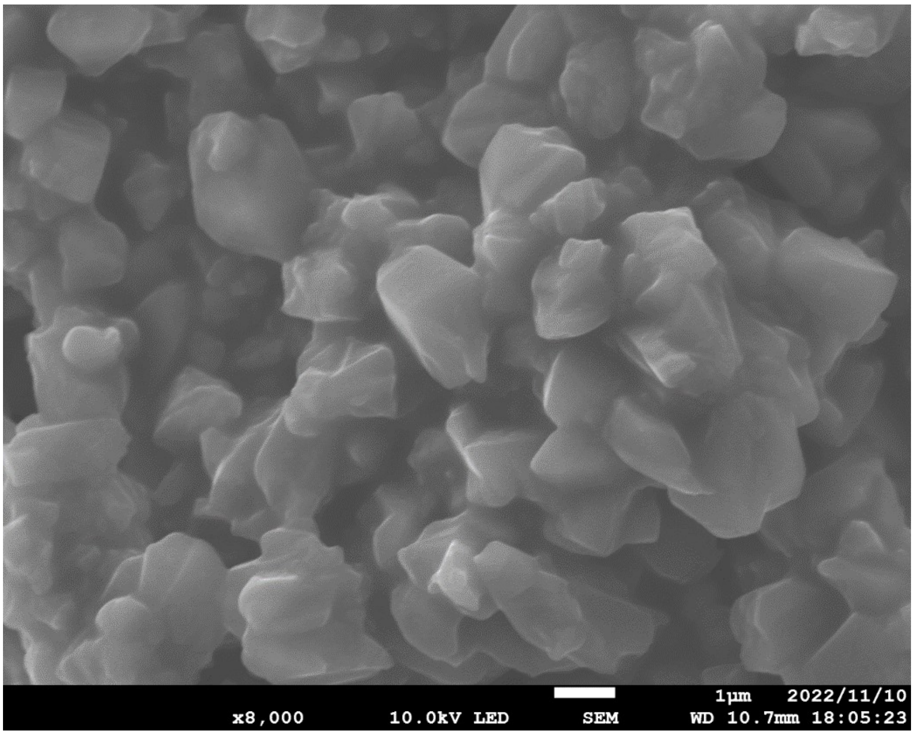


Figure S8. SEM image of phosphoric acid doped NUST-28.

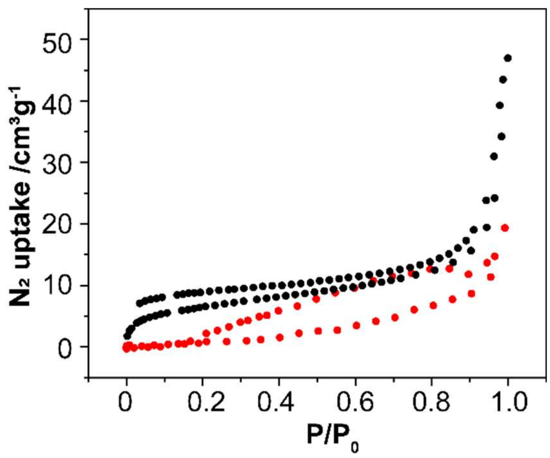


Figure S9. Nitrogen adsorption isotherms spectra of NUST-28 powder (black) and NUST-28 powder doped with phosphoric acid (red).

Figure S10. Photo of COF in water (left) and 85% phosphoric acid solution (right).

2.4 Atomic coordinates of COF

Table S1. Fractional atomic coordinates for simulated NUST-28 powders.

Space group: *P*2$_1$				
3D hexagonal; a = 55.1876 Å b = 62.1305 Å, c = 70.3214 Å; α =90°, β = 90.542°, γ = 90°				
Atom	element	X	Y	Z
C1	C	0.41316	0.33061	0.38967
C2	C	0.38892	0.33806	0.38925
C3	C	0.37909	0.34911	0.40485
C4	C	0.39327	0.35307	0.42133
C5	C	0.41759	0.34599	0.4216
C6	C	0.42743	0.33504	0.40599
C7	C	0.38348	0.36368	0.43725
C8	C	0.42226	0.31845	0.37442
N9	N	0.44513	0.31059	0.37476
C10	C	0.45699	0.29716	0.36288
C11	C	0.39526	0.38149	0.44584
C12	C	0.38573	0.39157	0.4618
C13	C	0.26911	0.46187	0.53657
C14	C	0.25627	0.47673	0.5477
C15	C	0.26368	0.48199	0.56657
C16	C	0.28375	0.47026	0.57402
C17	C	0.29672	0.4554	0.56294
C18	C	-0.08736	0.8298	0.38987
C19	C	-0.11198	0.83621	0.38984
C20	C	-0.12182	0.84729	0.4054
C21	C	-0.1073	0.85231	0.42147

C22	C	-0.08262	0.84626	0.42134
C23	C	-0.07276	0.83527	0.40576
C24	C	-0.11713	0.86299	0.43734
C25	C	-0.07822	0.8176	0.37467
N26	N	-0.05497	0.81068	0.37457
C27	C	-0.04306	0.79731	0.36267
C28	C	-0.10604	0.88153	0.44523
C29	C	-0.11559	0.89175	0.46112
C30	C	-0.23097	0.96195	0.53644
C31	C	-0.24385	0.97676	0.54758
C32	C	-0.23651	0.98198	0.56647
C33	C	-0.21646	0.97022	0.57394
C34	C	-0.20346	0.9554	0.56286
C35	C	0.41577	0.83218	0.88723
C36	C	0.39939	0.84927	0.8837
C37	C	0.39	0.86158	0.89876
C38	C	0.39638	0.85702	0.91792
C39	C	0.41191	0.83928	0.92136
C40	C	0.42176	0.82728	0.90633
C41	C	0.38748	0.86959	0.93322
C42	C	0.42552	0.82035	0.87201
N43	N	0.44698	0.80993	0.87388
C44	C	0.45926	0.79691	0.86186
C45	C	0.40245	0.87664	0.94851
C46	C	0.39319	0.88839	0.96375
C47	C	0.26774	0.9552	1.04158
C48	C	0.25431	0.96901	1.0533
C49	C	0.26548	0.98224	1.06737
C50	C	0.29084	0.97954	1.06993
C51	C	0.30451	0.96634	1.05783
C52	C	-0.08667	0.32939	0.88787
C53	C	-0.1043	0.34556	0.8847
C54	C	-0.11383	0.35754	0.8999
C55	C	-0.10644	0.35352	0.91895
C56	C	-0.08954	0.33668	0.92204
C57	C	-0.07958	0.32502	0.90684
C58	C	-0.11524	0.36604	0.93437
C59	C	-0.07674	0.31806	0.87245
N60	N	-0.05463	0.30872	0.87389
C61	C	-0.04208	0.29611	0.86172
C62	C	-0.09992	0.37194	0.94982
C63	C	-0.10856	0.38441	0.96504

C64	C	-0.23124	0.45477	1.04229
C65	C	-0.24476	0.46885	1.05371
C66	C	-0.23366	0.48216	1.06776
C67	C	-0.20835	0.4793	1.07064
C68	C	-0.19464	0.46575	1.05886
C69	C	0.41662	0.67101	0.76502
C70	C	0.3929	0.6623	0.76522
C71	C	0.38328	0.65133	0.74931
C72	C	0.39726	0.64866	0.73272
C73	C	0.42096	0.6572	0.7325
C74	C	0.43049	0.66819	0.74838
C75	C	0.38793	0.63767	0.71669
C76	C	0.42567	0.68256	0.78083
N77	N	0.44815	0.6913	0.78075
C78	C	0.46016	0.70415	0.79321
C79	C	0.39948	0.61921	0.70929
C80	C	0.39018	0.60837	0.69345
C81	C	0.26926	0.5405	0.61631
C82	C	0.25584	0.5251	0.60605
C83	C	0.2657	0.51383	0.59032
C84	C	0.28959	0.51972	0.58499
C85	C	0.30315	0.53509	0.59528
C86	C	-0.08215	0.17009	0.76466
C87	C	-0.10488	0.15956	0.76562
C88	C	-0.11473	0.14873	0.74973
C89	C	-0.10195	0.14805	0.73241
C90	C	-0.07925	0.15841	0.73138
C91	C	-0.0695	0.1693	0.74725
C92	C	-0.11156	0.13718	0.71645
C93	C	-0.07291	0.18134	0.78057
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C95	C	-0.03935	0.20435	0.79246
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C105	C	0.3835	0.14881	0.25123

C106	C	0.39629	0.14723	0.23394
C107	C	0.4196	0.15659	0.23307
C108	C	0.42983	0.16724	0.24887
C109	C	0.38603	0.13669	0.21796
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C208	C	0.35867	0.60407	0.66837
C209	C	0.33395	0.59808	0.6683
C210	C	0.32374	0.58623	0.65317
C211	C	0.36875	0.61532	0.68405
C212	C	0.32841	0.56697	0.62271
N213	N	0.3054	0.55932	0.62294
C214	C	0.2933	0.5454	0.61138
C215	C	0.35727	0.63399	0.69128
C216	C	0.3666	0.64489	0.70735
C217	C	0.48293	0.71172	0.78734
C218	C	0.49591	0.72668	0.79843
C219	C	0.48682	0.73453	0.81597
C220	C	0.46468	0.72541	0.82228
C221	C	0.45135	0.7108	0.81105
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C223	C	-0.13787	0.08688	0.63691
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C225	C	-0.14151	0.10391	0.66824
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C227	C	-0.1764	0.0859	0.65315
C228	C	-0.13128	0.11502	0.68395
C229	C	-0.17189	0.06719	0.6224
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C242	C	0.35436	0.10489	0.16994
C243	C	0.3351	0.09044	0.17308
C244	C	0.32424	0.07934	0.1578
C245	C	0.36501	0.11568	0.18548
C246	C	0.32184	0.07123	0.12351
N247	N	0.3029	0.05772	0.12599
C248	C	0.29064	0.0446	0.11395
C249	C	0.35174	0.13119	0.19579
C250	C	0.36213	0.14154	0.21174
C251	C	0.48268	0.21079	0.28888
C252	C	0.49497	0.22603	0.30015
C253	C	0.48504	0.23407	0.31733
C254	C	0.46286	0.2247	0.32324
C255	C	0.45021	0.2098	0.31181
C256	C	-0.16755	0.58276	0.13927
C257	C	-0.14784	0.59697	0.13642
C258	C	-0.13693	0.60795	0.15177
C259	C	-0.14569	0.6051	0.17041
C260	C	-0.16536	0.59103	0.17336
C261	C	-0.17614	0.58	0.15801
C262	C	-0.13507	0.61583	0.18601
C263	C	-0.17792	0.5716	0.12377
N264	N	-0.19684	0.55808	0.12617
C265	C	-0.20895	0.54491	0.11409
C266	C	-0.14877	0.63039	0.19704
C267	C	-0.13834	0.64078	0.21294
C268	C	-0.01764	0.71243	0.288
C269	C	-0.00534	0.7276	0.29931
C270	C	-0.01439	0.73439	0.31721
C271	C	-0.03562	0.72384	0.32369
C272	C	-0.04825	0.70892	0.31229
C273	C	-0.50121	0.25042	0.32955

C274	C	0.00092	0.25051	0.82811
C275	C	0.24994	0.99797	0.0788
C276	C	0.24992	0.49794	0.57906
N277	N	0.39959	0.40807	0.46762
S278	S	0.42422	0.41198	0.45404
N279	N	0.41582	0.39103	0.44023
N280	N	0.09644	0.58954	0.46754
S281	S	0.07153	0.58656	0.4537
N282	N	0.08019	0.60791	0.44062
N283	N	-0.40318	0.08952	0.46683
S284	S	-0.42758	0.08629	0.45249
N285	N	-0.41899	0.10796	0.43981

3 Performance of Proton conductivities

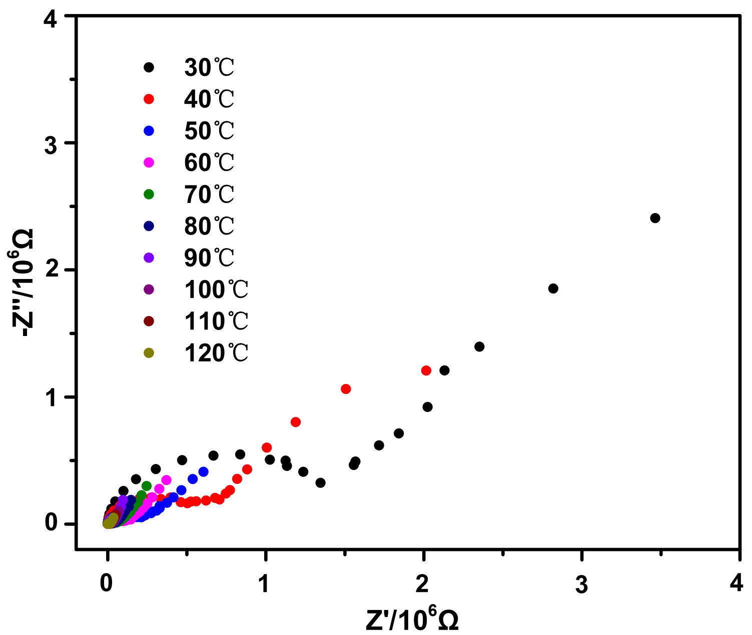

Figure S11. Nyquist plots of NUST-28-30% measured under 30 to 120 °C.

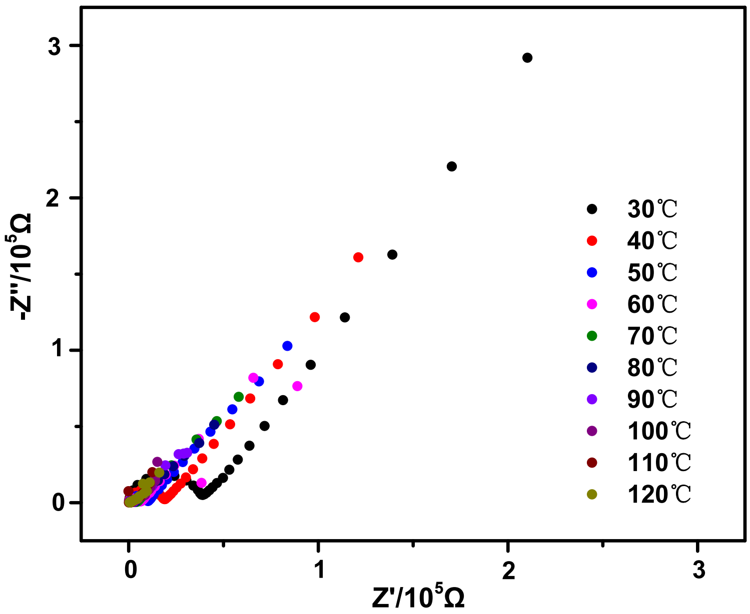

Figure S12. Nyquist plots of NUST-28-40% measured under 30 to 120 °C.

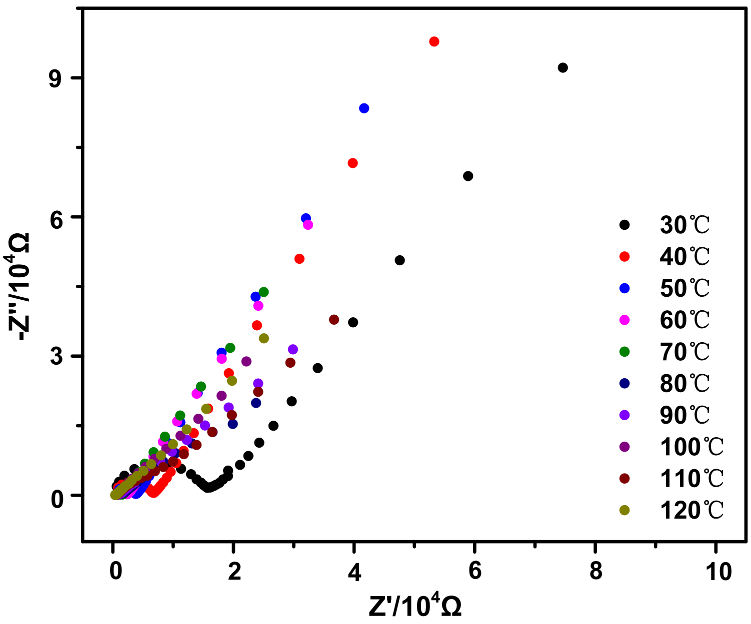

Figure S13. Nyquist plots of NUST-28-50% measured under 30 to 120 °C.

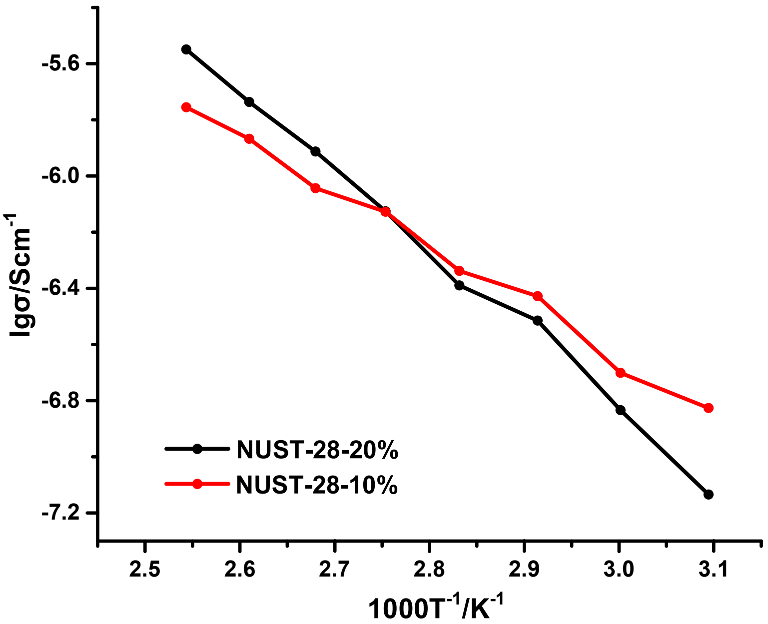

Figure S14. Proton conductivities of NUST-28-10% and NUST-28-20% measured under 30 to 120 °C.

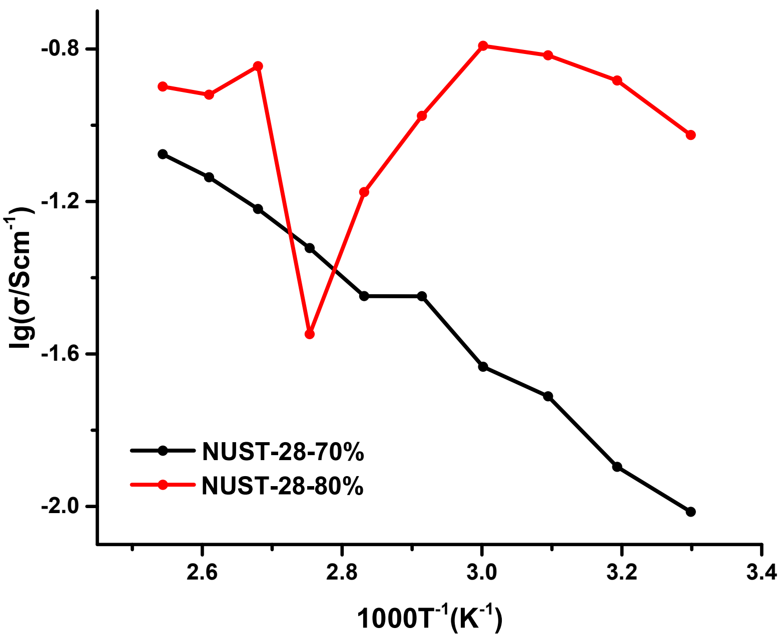

Figure S15. Proton conductivities of NUST-28-70% and NUST-28-80% measured under 30 to 120 °C.

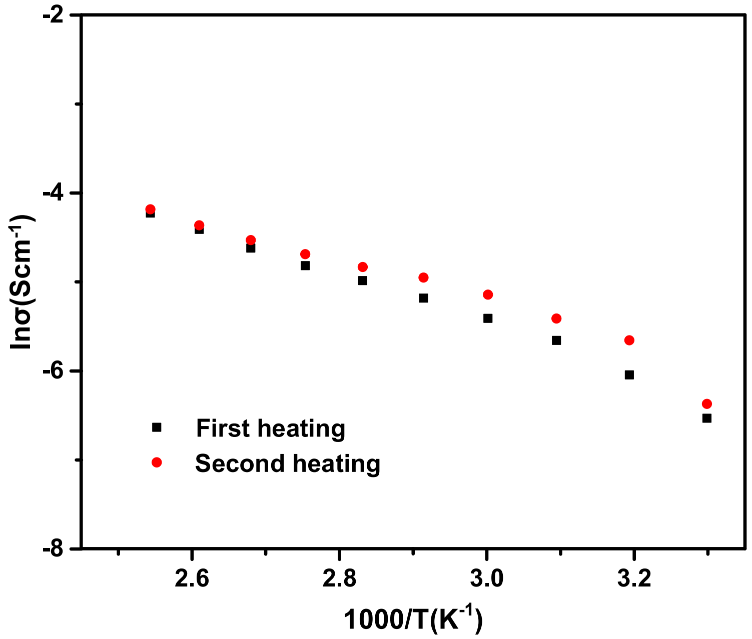

Figure S16. The proton conduction performance of NUST-28-60% during first and second heating.

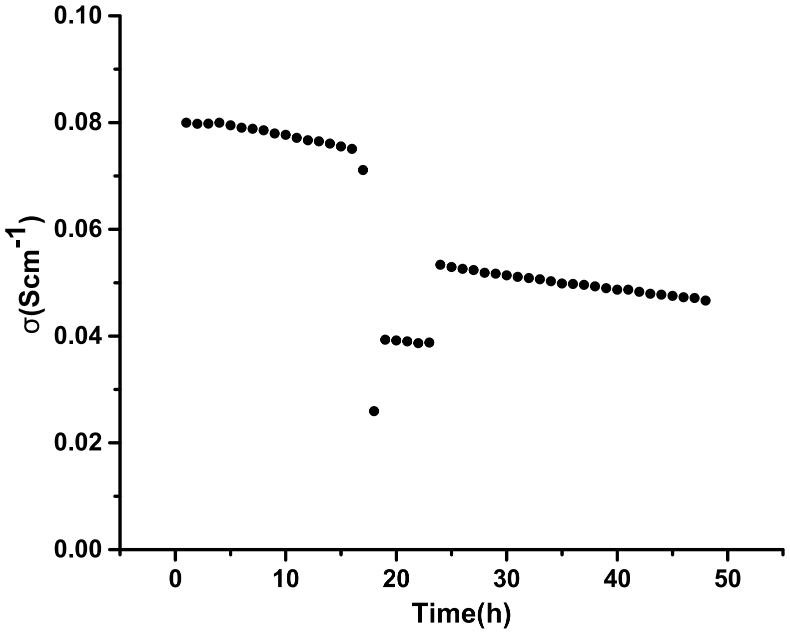

Figure S17. The long-term proton conductivity within 48h of NUST-28-70%.

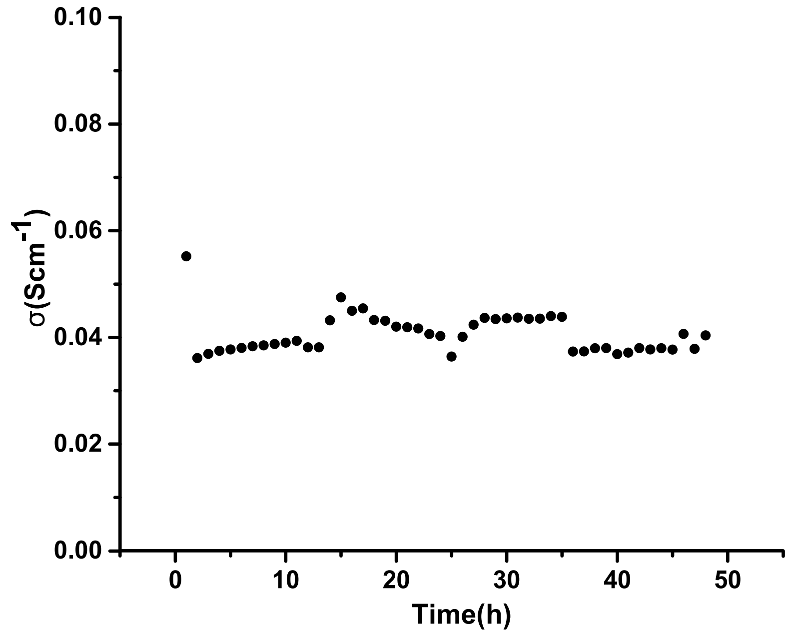

Figure S18. The long-term proton conductivity within 48h of NUST-28-80%.

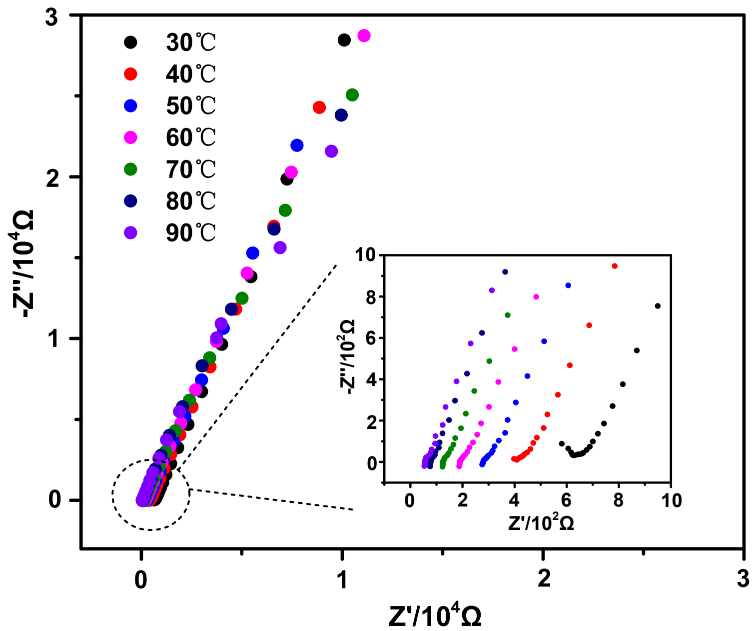

Figure S19. Nyquist plots of NUST-28-60% in an environment with 25% RH from 30 to 90 °C.

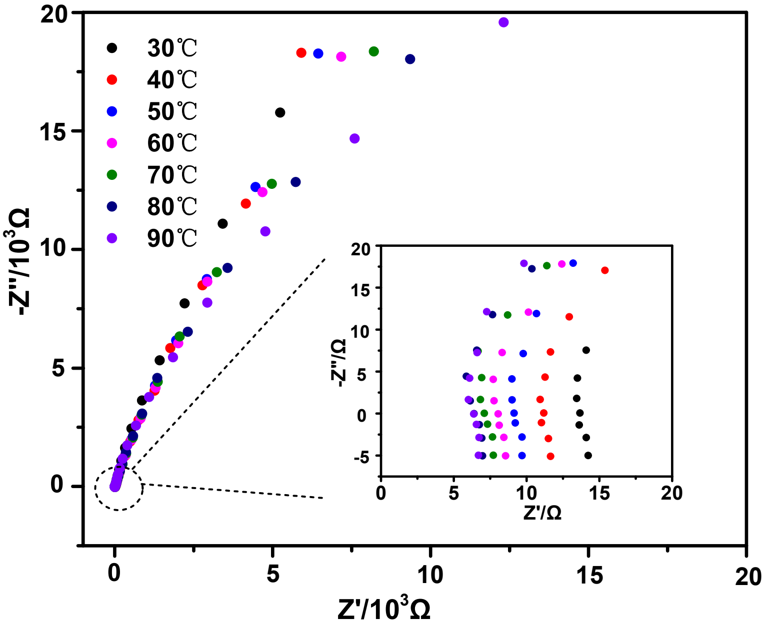

Figure S20. Nyquist plots of NUST-28-60% in an environment with 45% RH from 30 to 90 °C.

Table S2. Porous solid based proton conductors in anhydrous condition.[2]

Material	Proton conductivity ($S\ cm^{-1}$)	T (° C)	Ref.
H_3PO_4/gel	1.0×10^{-3}	70	Chem. Mater. 2003, 15, 2005
H_3PO_4 doped Porous PBI	5.00×10^{-2}	140	Chem. Mater. 2004, 16, 604
H_3PO_4 doped polyimide	1.00×10^{-4}	140	Eur. Polym. J. 2005, 41, 2505
$[Al(OH)(ndc)]_n$IIm	2.20×10^{-5}	120	Nat. Mater. 2009, 8, 831
$[Al(OH)(ndc)]_n \supset$His	1.70×10^{-3}	150	ACIE. 2011, 50, 11706
$[Zn_3(HPO_4)_6(H2O)_3]$ (Hbim)	1.30×10^{-3}	120	JACS. 2013, 135, 11345
H_3PO_4/m0.001eso-silica	6.00×10^{-2}	200	Chem. Commun. 2013, 49, 4655
H_3PO_4@Tp-Azo-COF	6.70×10^{-5}	67	JACS. 2014, 136, 657
Im@Td-PPI	3.49×10^{-4}	90	JACS. 2015, 137, 913
Im@Td-PNDI	9.04×10^{-5}	90	JACS. 2015, 137, 913
H_3PO_4@TpBpy-MC	2.50×10^{-3}	120	J. Mater. Chem. A. 2016, 4, 2682
Phyticacid@TpPa-(SO_3HPy)	5.00×10^{-4}	120	Chem. Mater. 2016, 28, 1489
Im@TPB-DMTP-COF	4.37×10^{-3}	130	Nat. Mater. 2016, 15, 722
Tri@TPB-DMTP-COF	1.10×10^{-3}	130	Nat. Mater. 2016, 15, 722
HL@0.202Him	6.57×10^{-5}	120	Chem. Commun. 2017, 53, 2475
H_3PO_4/PBI-ZIF(8/67)	9.20×10^{-2}	200	Nanomaterials. 2018, 8, 775
H_3PO_4@TPB-DMeTP-COF	1.91×10^{-1}	160	Nat. Commun. 2020, 11, 1981
COF-F6-H	4.2×10^{-2}	140	JACS.2020,142, 14357−14364
H_3PO_4@CMP-F6-60%	4.39×10^{-3}	120	Appl. Mater. Interfaces 2021, 13, 15536−15541
CMP-C2-P-45%	2.15×10^{-2}	130	Mater. Adv., 2023, 4, 504–514
NUST-28-60%	$\mathbf{1.46 \times 10^{-2}}$	**120**	**This work**

Reference:

[1] Wang L, Xia Q, Hou M, Yan C, Xu Y, Qu J, et al. A photostable cationic fluorophore for long-term bioimaging. Journal of materials chemistry B 2017;5:9183-8.

[2] Guo Z-C, Shi Z-Q, Wang X-Y, Li Z-F, Li G. Proton conductive covalent organic frameworks. Coordination Chemistry Reviews 2020;422:213465.