Supporting Information for

Hierarchical sub-stoichiometric isomeric covalent organic frameworks with absolutely diverse topologies via the same monomers for efficient atmospheric water harvesting

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Section S1 Synthetic procedures and characterizations

1.1 FT-IR and Solid-state ^{13}C ss NMR spectra

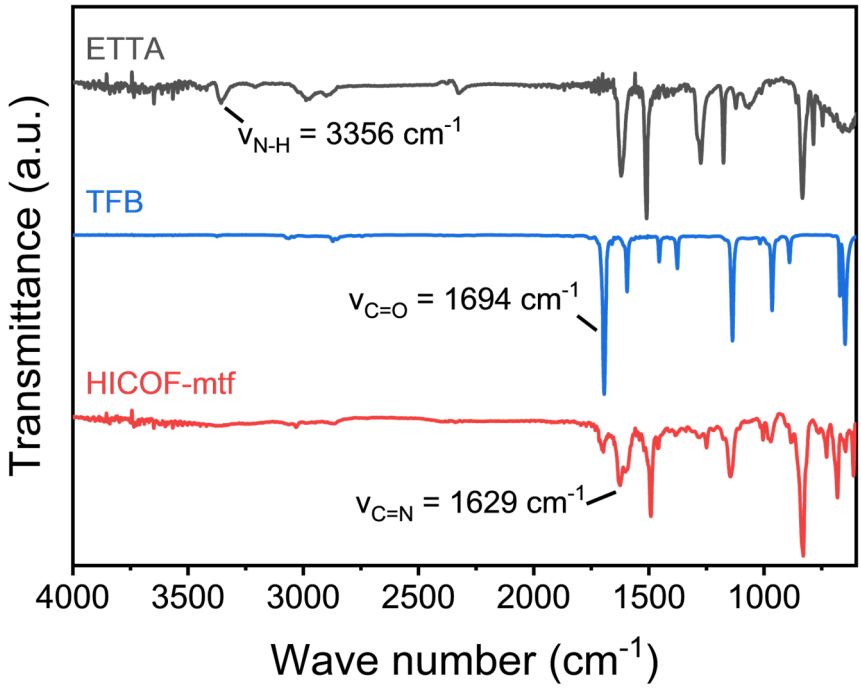

Figure S1 FT-IR spectra of HICOF-mtf.

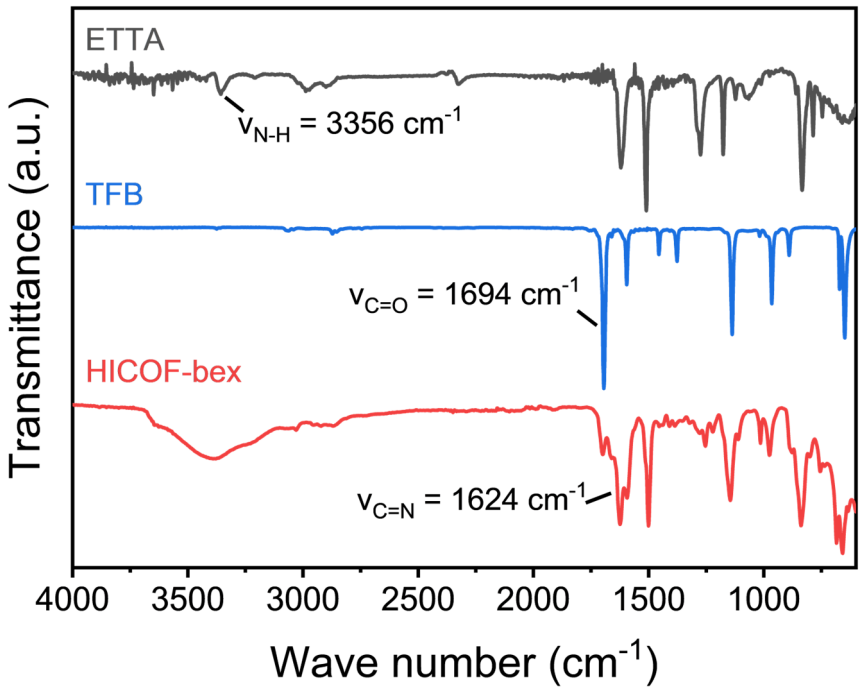

Figure S2 FT-IR spectra of HICOF-bex.

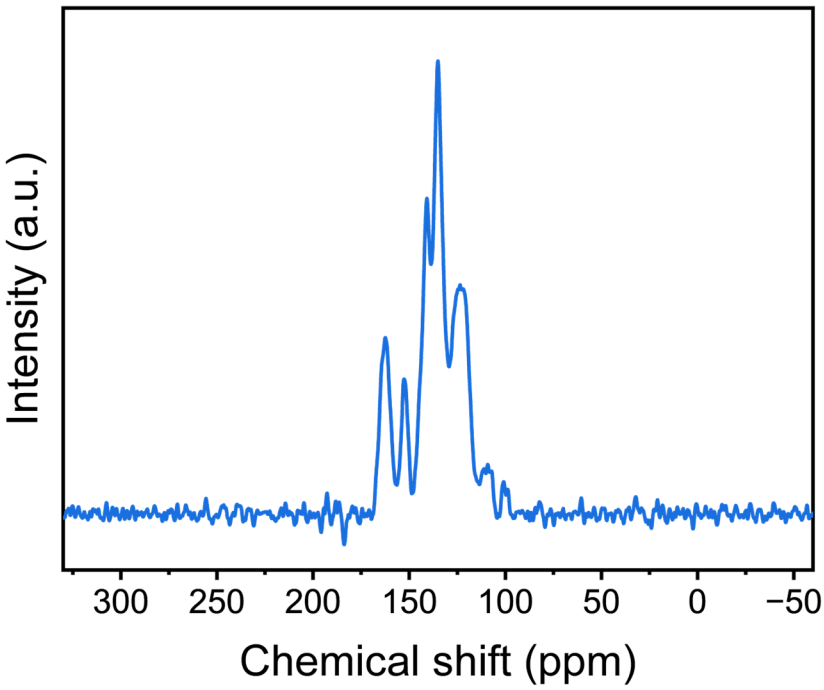

Figure S3 ^{13}C ss NMR spectra of HICOF-mtf.

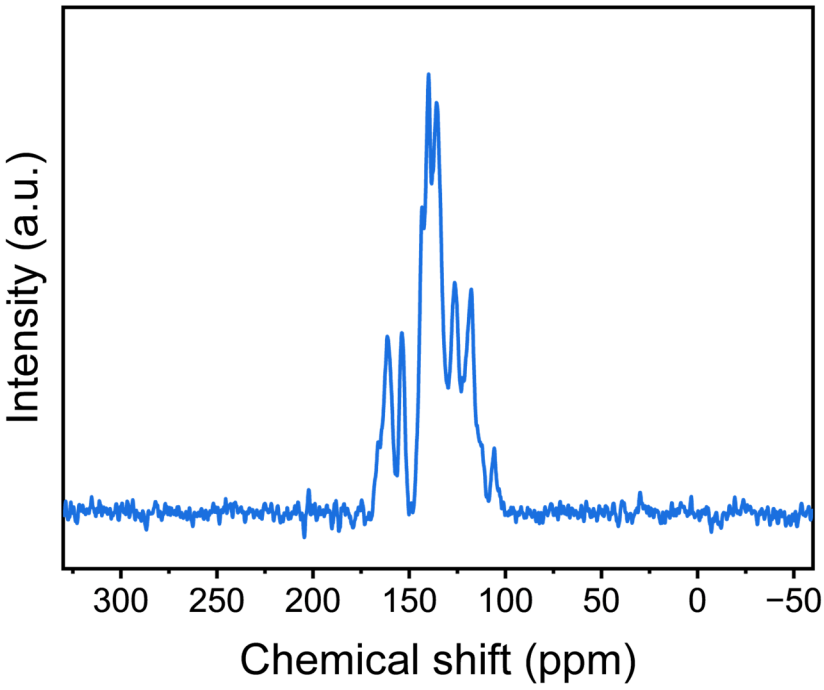

Figure S4 ^{13}C ss NMR spectra of HICOF-bex.

1.2 PXRD analysis and structure

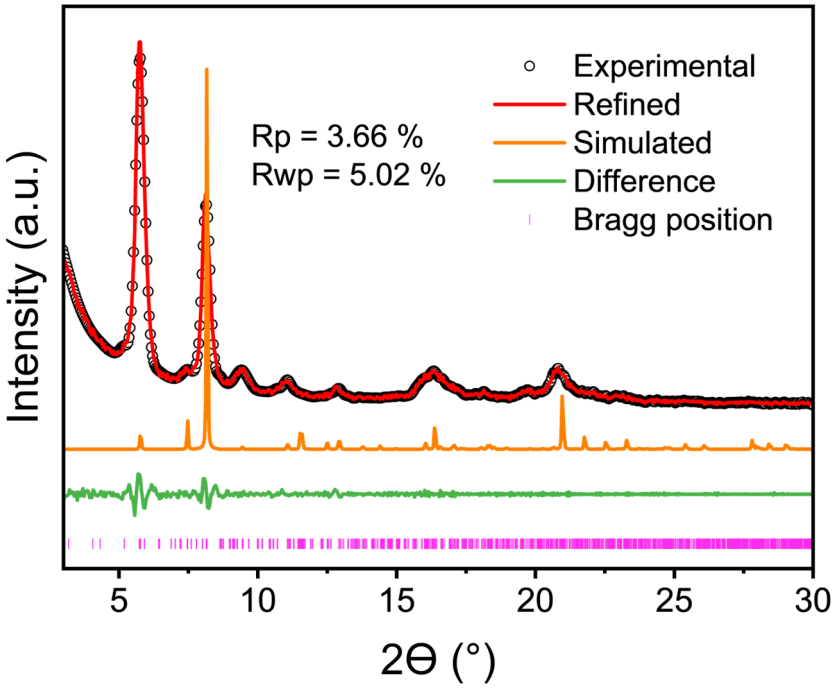

Figure S5 Experimental, calculated and pawley refined PXRD patterns of HICOF-mtf, Rwp = 5.66%, Rp = 3.22%

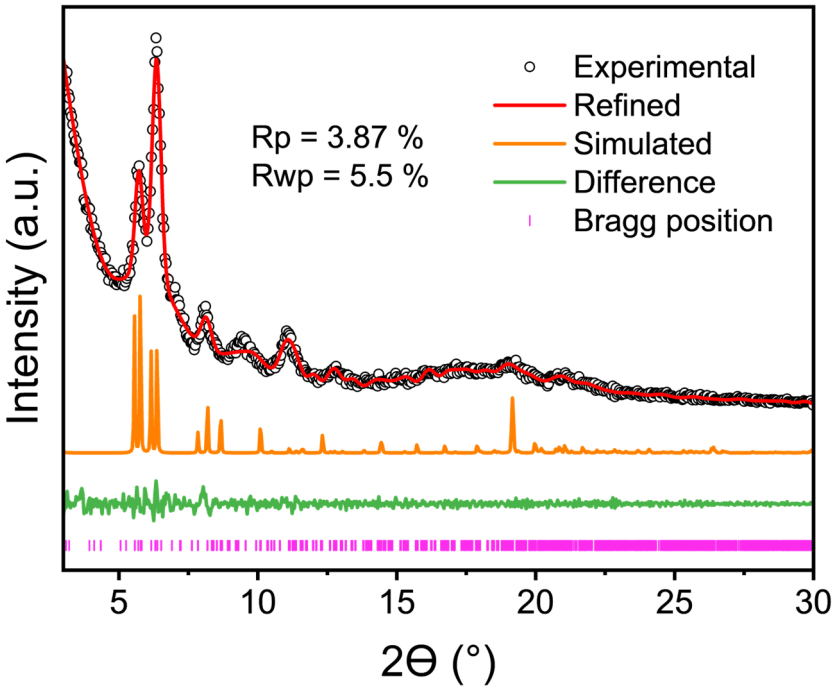

Figure S6 Experimental, calculated and pawley refined PXRD patterns of HICOF-bex, Rwp = 4.62%, Rp = 3.30%

Table S1 Atomic coordinates and refined unit cell parameters of HICOF-mtf.

Name	HICOF-mtf		
Space group	P21/C (No.14)		
a (Å)	30.8795	α (°)	90.0000
b (Å)	12.8964	β (°)	90.0000
c (Å)	30.6802	γ (°)	90.0000
Atom name	x	y	z
H1	0.12806	0.34687	0.31969
H2	0.96004	0.37732	0.21849
H3	0.399	0.09272	0.75985
H4	0.46245	0.12056	0.65544
H5	0.82618	0.25589	0.16703
H6	0.76666	0.28338	0.11571
H7	0.83573	0.11788	0.01872
H8	0.89842	0.11026	0.06712
H9	0.89988	0.22976	0.43296
H10	0.83624	0.21562	0.48029
H11	0.76467	0.39324	0.38846
H12	0.82577	0.39668	0.33996
H13	0.46529	0.41637	0.85498
H14	0.39637	0.36914	0.75672
H15	0.82513	0.51674	0.47747
H16	0.88103	0.52352	0.42313
H17	0.79473	0.68797	0.3393
H18	0.74371	0.706	0.39774
C19	0.09605	0.35222	0.33346
C20	0.05894	0.35944	0.30338
C21	0.98719	0.37589	0.24324
C22	0.43306	0.10384	0.76589
C23	0.46112	0.11048	0.73018
C24	0.44023	0.10244	0.68123
C25	0.82958	0.22408	0.13495
C26	0.79376	0.23904	0.10402
C27	0.79143	0.19809	0.06012
C28	0.83199	0.15052	0.05024
C29	0.86893	0.1425	0.07978
C30	0.86918	0.17276	0.12441
C31	0.87144	0.31613	0.38026
C32	0.87049	0.26655	0.42213
C33	0.8326	0.26021	0.45109
C34	0.79137	0.30892	0.44352
C35	0.79288	0.3556	0.40054
C36	0.82988	0.3578	0.37057
C37	0.44283	0.40542	0.82626
C38	0.46425	0.39218	0.77415
C39	0.43114	0.37356	0.74498
C40	0.27541	0.44892	0.00379

C41	0.78043	0.61762	0.44494
C42	0.81928	0.56233	0.44939
C43	0.85126	0.56467	0.41735
C44	0.84289	0.61127	0.37717
C45	0.80276	0.65618	0.37057
C46	0.77336	0.66515	0.40442
N47	0.09158	0.36072	0.37492
N48	0.9096	0.15594	0.1534
N49	0.91336	0.32539	0.3525
C50	0.77118	0.6127	0.49633
H51	0.62527	0.84687	0.81969
H52	0.46283	0.87732	0.71849
H53	0.8962	0.59272	0.25985
H54	0.95966	0.62056	0.15544
H55	0.32897	0.75589	0.66703
H56	0.26945	0.78338	0.61571
H57	0.33853	0.61788	0.51872
H58	0.40121	0.61026	0.56712
H59	0.40268	0.72976	0.93296
H60	0.33903	0.71562	0.98029
H61	0.26747	0.89324	0.88846
H62	0.32856	0.89668	0.83996
H63	0.9625	0.91637	0.35498
H64	0.89358	0.86914	0.25672
H65	0.32793	0.01674	0.97747
H66	0.38382	0.02352	0.92313
H67	0.29753	0.18797	0.8393
H68	0.2465	0.206	0.89774
C69	0.59326	0.85222	0.83346
C70	0.55614	0.85944	0.80338
C71	0.48999	0.87589	0.74324
C72	0.93026	0.60384	0.26589
C73	0.95833	0.61048	0.23018
C74	0.93743	0.60244	0.18123
C75	0.33237	0.72408	0.63495
C76	0.29655	0.73904	0.60402
C77	0.29423	0.69809	0.56012
C78	0.33478	0.65052	0.55024
C79	0.37172	0.6425	0.57978
C80	0.37197	0.67276	0.62441
C81	0.37424	0.81613	0.88026
C82	0.37328	0.76655	0.92213
C83	0.33539	0.76021	0.95109
C84	0.29417	0.80892	0.94352
C85	0.29568	0.8556	0.90054
C86	0.33267	0.8578	0.87057
C87	0.94004	0.90542	0.32626
C88	0.96146	0.89218	0.27415

C89	0.92834	0.87356	0.24498
C90	0.77262	0.94892	0.50379
C91	0.28323	0.11762	0.94494
C92	0.32207	0.06233	0.94939
C93	0.35405	0.06467	0.91735
C94	0.34569	0.11127	0.87717
C95	0.30555	0.15618	0.87057
C96	0.27616	0.16515	0.90442
N97	0.58879	0.86072	0.87492
N98	0.41239	0.65594	0.6534
N99	0.41615	0.82539	0.8525
C100	0.27397	0.1127	0.99633
H201	0.56968	0.59821	0.62472
H202	0.4685	0.62867	0.78718
H203	0.01264	0.34138	0.35102
H204	0.90266	0.36921	0.28755
H205	0.41705	0.50454	0.92105
H206	0.36573	0.53203	0.98058
H207	0.26876	0.36653	0.9115
H208	0.31715	0.35891	0.8488
H209	0.68293	0.48111	0.84734
H210	0.73026	0.46696	0.91099
H211	0.63844	0.64459	0.98257
H212	0.58994	0.64802	0.92146
H213	0.10775	0.66772	0.28471
H214	0.00951	0.62049	0.35364
H216	0.67311	0.77217	0.86619
H217	0.58929	0.93662	0.9525
C219	0.58345	0.60356	0.65673
C220	0.55337	0.61078	0.69385
C221	0.49324	0.62723	0.76002
C222	0.01868	0.35249	0.31695
C223	0.97739	0.35913	0.28889
C224	0.92844	0.35109	0.30978
C225	0.38497	0.47273	0.91765
C226	0.35404	0.48769	0.95348
C227	0.31015	0.44674	0.9558
C228	0.30027	0.39917	0.91525
C229	0.32981	0.39116	0.8783
C230	0.37443	0.42141	0.87805
C231	0.63024	0.56748	0.87578
C232	0.6721	0.5179	0.87674
C233	0.70106	0.51156	0.91463
C234	0.69349	0.56027	0.95586
C235	0.65051	0.60694	0.95435
C236	0.62055	0.60914	0.91735
C237	0.07904	0.65676	0.30718
C238	0.02694	0.64353	0.28575

C239	0.99219	0.62491	0.31887
C240	0.25382	0.70027	0.47462
C241	0.69492	0.86627	0.9668
C242	0.69936	0.81098	0.92796
C243	0.66733	0.81333	0.89597
C244	0.62716	0.85992	0.90434
C245	0.62055	0.90483	0.94448
C246	0.65439	0.9138	0.97388
N247	0.6249	0.61207	0.6612
N248	0.40341	0.40459	0.83762
N249	0.60248	0.57674	0.83386
H250	0.07247	0.09821	0.12472
H251	0.9657	0.12867	0.28718
H252	0.50984	0.84138	0.85102
H253	0.40545	0.86921	0.78755
H254	0.91425	1.00454	0.42105
H255	0.86294	1.03203	0.48058
H256	0.76597	0.86653	0.4115
H257	0.81435	0.85891	0.3488
H258	0.18573	-0.01889	0.34734
H259	0.23305	-0.03304	0.41099
H260	0.14124	0.14459	0.48257
H261	0.09274	0.14802	0.42146
H262	0.60496	0.16772	0.78471
H263	0.50672	0.12049	0.85364
H265	0.1759	0.27217	0.36619
H266	0.09208	0.43662	0.4525
C268	0.08624	0.10356	0.15673
C269	0.05616	0.11078	0.19385
C270	0.99045	0.12723	0.26002
C271	0.51589	0.85249	0.81695
C272	0.48018	0.85913	0.78889
C273	0.43124	0.85109	0.80978
C274	0.88217	0.97273	0.41765
C275	0.85125	0.98769	0.45348
C276	0.80735	0.94674	0.4558
C277	0.79748	0.89917	0.41525
C278	0.82701	0.89116	0.3783
C279	0.87163	0.92141	0.37805
C280	0.13303	0.06748	0.37578
C281	0.1749	0.0179	0.37674
C282	0.20385	0.01156	0.41463
C283	0.19629	0.06027	0.45586
C284	0.15331	0.10694	0.45435
C285	0.12335	0.10914	0.41735
C286	0.57625	0.15676	0.80718
C287	0.52414	0.14353	0.78575
C288	0.49498	0.12491	0.81887

C289	0.75103	0.20027	0.97462
C290	0.19771	0.36627	0.4668
C291	0.20215	0.31098	0.42796
C292	0.17012	0.31333	0.39597
C293	0.12995	0.35992	0.40434
C294	0.12335	0.40483	0.44448
C295	0.15719	0.4138	0.47388
N296	0.12769	0.11207	0.1612
N297	0.90062	0.90459	0.33762
N298	0.10528	0.07674	0.33386
H411	0.17487	0.48326	0.52253
H414	0.25629	0.294	0.60226
H461	0.67207	0.98326	0.02253
H464	0.7535	0.794	0.10226

Table S2 Atomic coordinates and refined unit cell parameters of HICOF-bex.

Name	HICOF-bex		
Space group	P2 (No.3)		
a (Å)	30.6469	α (°)	90.0000
b (Å)	4.6311	β (°)	92.4481
c (Å)	15.9089	γ (°)	90.0000
Atom name	x	y	z
C1	0.52235	0.50822	0.00919
C2	0.55359	0.4947	0.93642
C3	0.54357	0.5214	0.09494
C4	0.53001	0.69403	0.15728
C5	0.54992	0.69773	0.23729
C6	0.58523	0.53158	0.25799
C7	0.59943	0.35974	0.19597
C8	0.57904	0.35673	0.11619
C9	0.4093	0.65687	0.06182
C10	0.37985	0.6525	0.12586
C11	0.38669	0.48669	0.19541
C12	0.42246	0.31479	0.19583
C13	0.45152	0.31986	0.13113
C14	0.70284	0.48805	0.60304
C15	0.72936	0.49835	0.53377
C16	0.70978	0.50418	0.45196
C17	0.66436	0.50227	0.43973
C18	0.63811	0.49225	0.5102
C19	0.65701	0.48583	0.59169
C20	0.62841	0.4822	0.66306
C21	0.64473	0.51327	0.35423
C22	0.7769	0.50604	0.54741
C23	0.01104	0.50362	0.46957
C24	0.99938	0.48752	0.37398
C25	0.05941	0.5179	0.48017
C26	0.08088	0.69282	0.53589

C27	0.12607	0.69848	0.54604
C28	0.15204	0.53183	0.49901
C29	0.13098	0.35744	0.44242
C30	0.08568	0.35279	0.4331
C31	0.98776	0.64892	0.68092
C32	-0.00195	0.6437	0.77102
C33	0.03148	0.47177	0.79761
C34	0.0487	0.30489	0.73741
C35	0.03359	0.31419	0.65385
N1	0.64287	0.49643	0.74002
N2	0.60332	0.53736	0.34002
N3	0.19731	0.54022	0.51333
N4	0.04561	0.45787	0.88208
H1	0.50295	0.82518	0.14238
H2	0.53905	0.83206	0.28506
H3	0.62553	0.22194	0.21176
H4	0.59017	0.21997	0.06939
H5	0.40389	0.79089	0.00938
H6	0.35174	0.7823	0.12446
H7	0.42666	0.17275	0.24637
H8	0.47899	0.18583	0.13261
H9	0.71721	0.48368	0.66702
H10	0.7309	0.51206	0.39847
H11	0.60268	0.49105	0.49983
H12	0.59299	0.47394	0.64662
H13	0.66772	0.5049	0.30251
H14	0.78929	0.48622	0.61347
H15	0.06136	0.82384	0.57255
H16	0.14228	0.83488	0.58946
H17	0.15036	0.21847	0.40818
H18	0.06997	0.2139	0.38986
H19	0.96199	0.7856	0.66214
H20	0.98905	0.77646	0.80983
H21	0.07396	0.16505	0.75667
H22	0.04777	0.18421	0.60855
H23	0.07622	0.38703	0.89314
H24	0.03989	0.61818	0.91695

1.3 N_2 sorption isotherms and pore size distribution

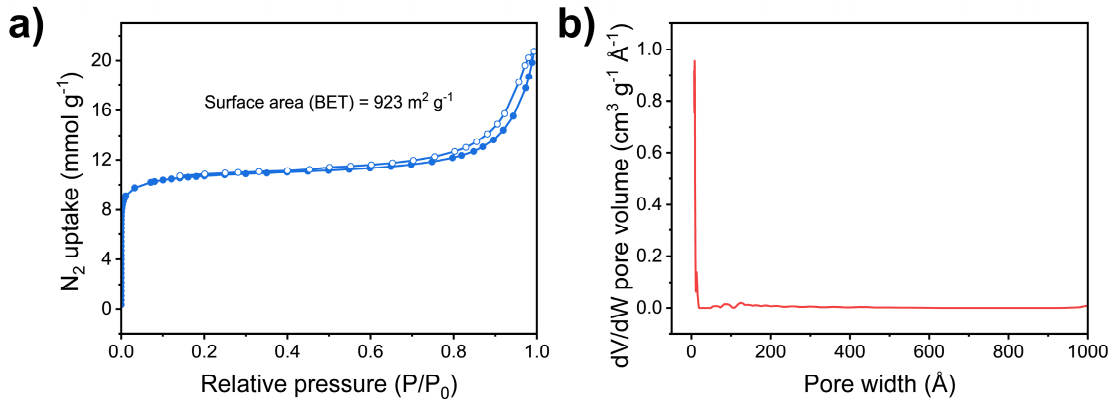

Figure S7 a) N_2 sorption isotherm of HICOF-mtf at 77 K, b) Pore size distribution of HICOF-mtf.

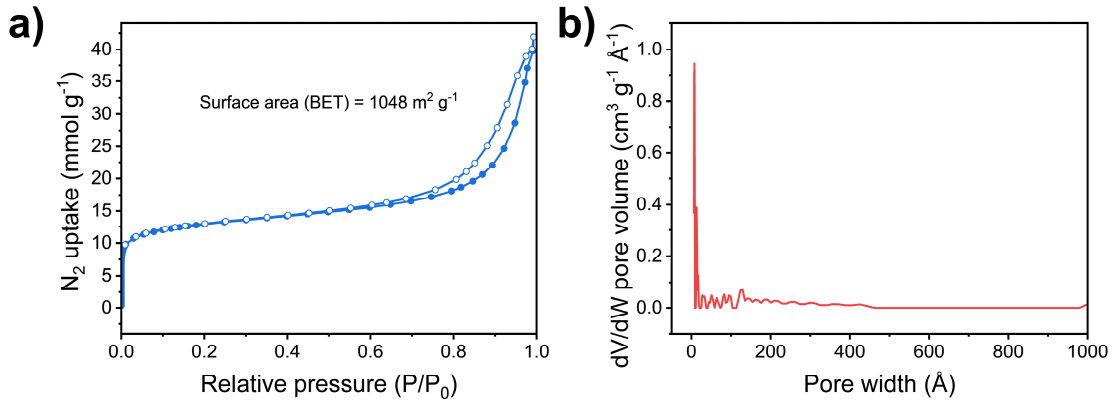

Figure S8 N_2 sorption isotherm of HICOF-bex at 77 K, b) Pore size distribution of HICOF-bex.

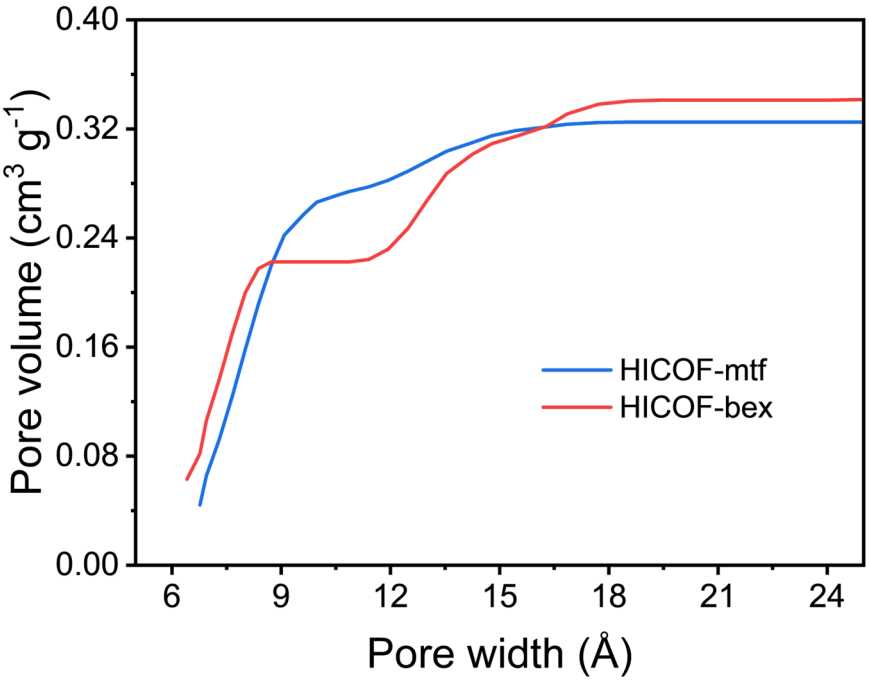

Figure S9 The pore volume distribution of HICOF-mtf and HICOF-bex.

1.4 Chemical stability

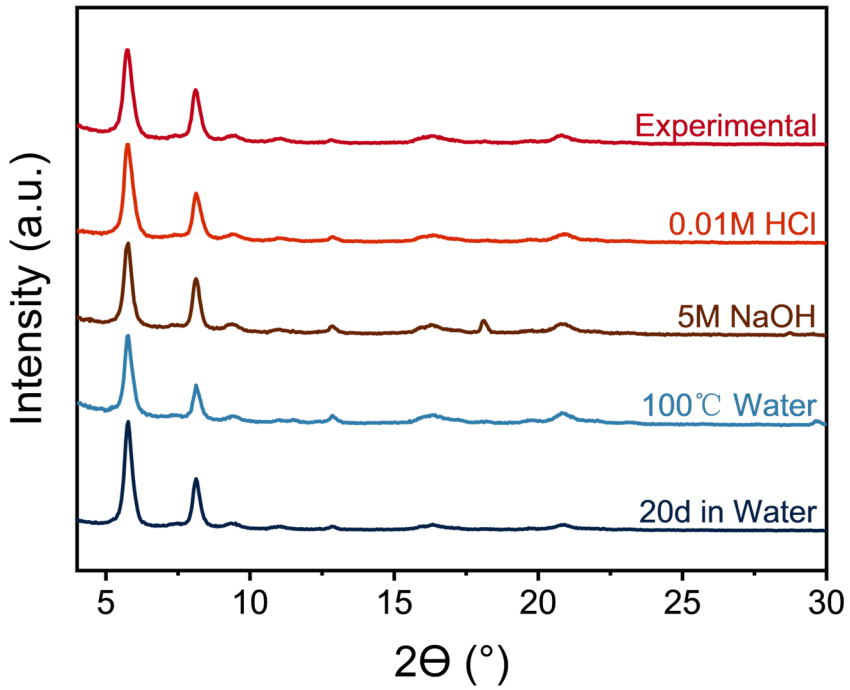

Figure S10 The PXRD pattern of HICOF-mtf after treatment under different conditions

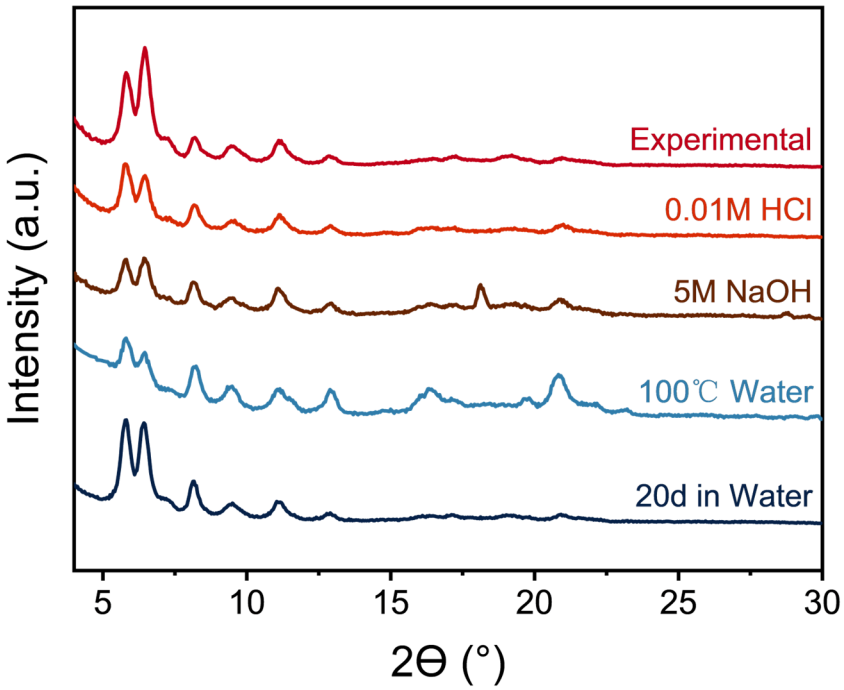

Figure S11 PXRD pattern of HICOF-bex after treatment under different conditions.

1.5 SEM and TEM image of HICOF-mtf

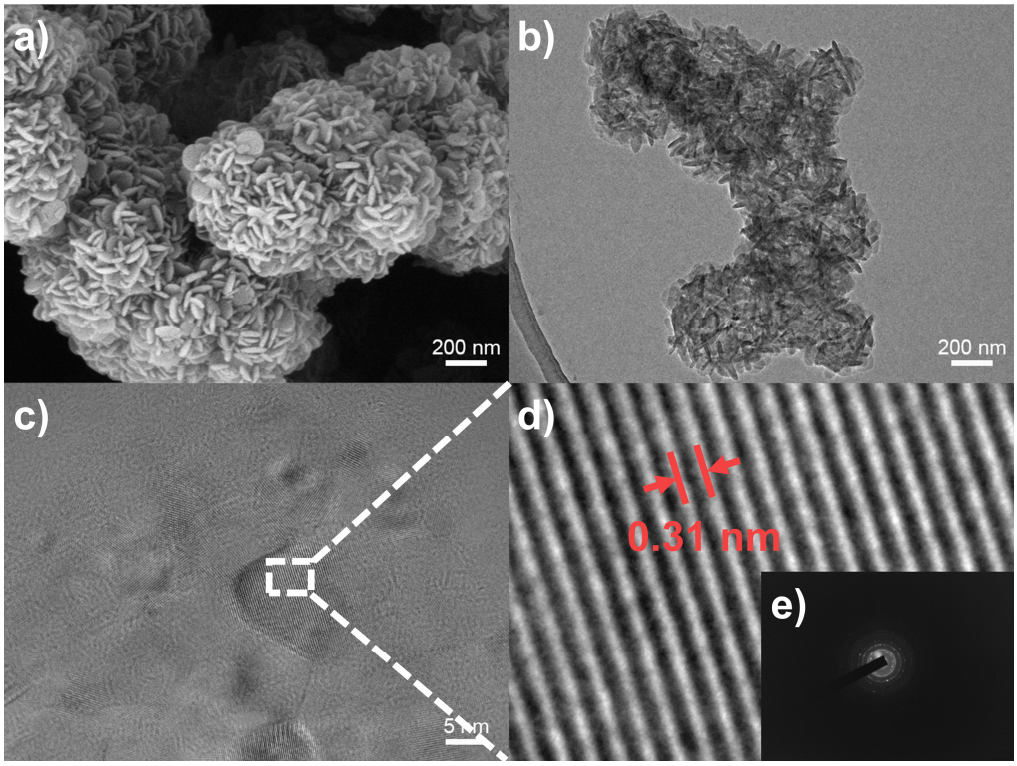

Figure S12 a) SEM image, b-d) TEM image and e) selective electron diffraction pattern of HICOF-mtf.

1.6 SEM and TEM image of HICOF-bex

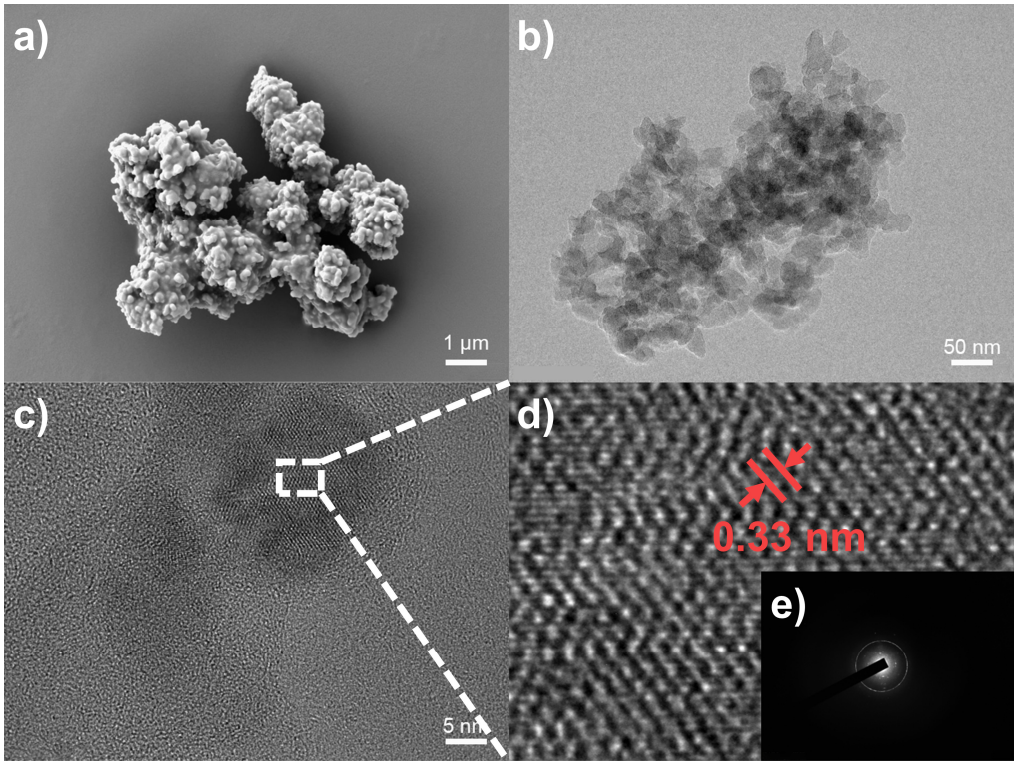

Figure S13 a) SEM image, b-d) TEM image and e) selective electron diffraction pattern of HICOF-bex.

1.7 Contact angle measurements

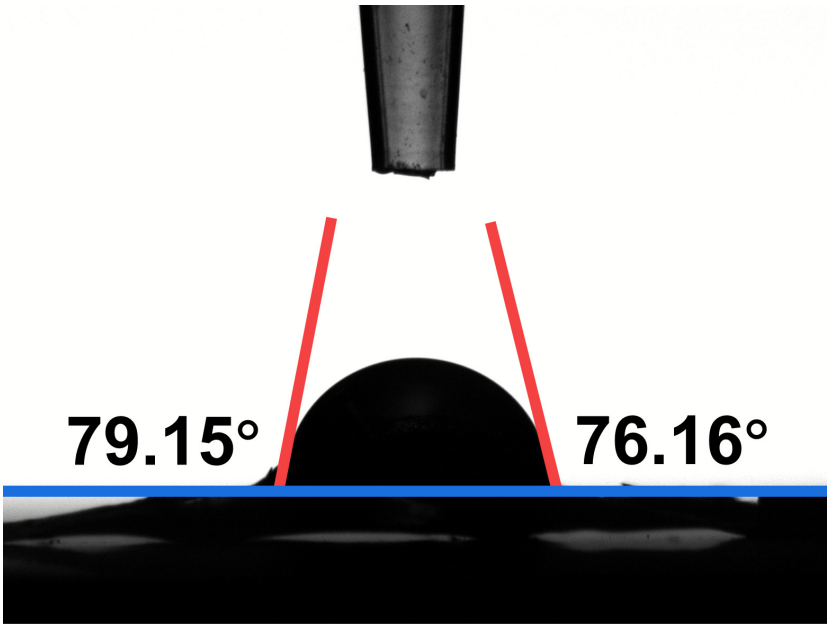

Figure S14 Water contact angle image of HICOF-mtf.

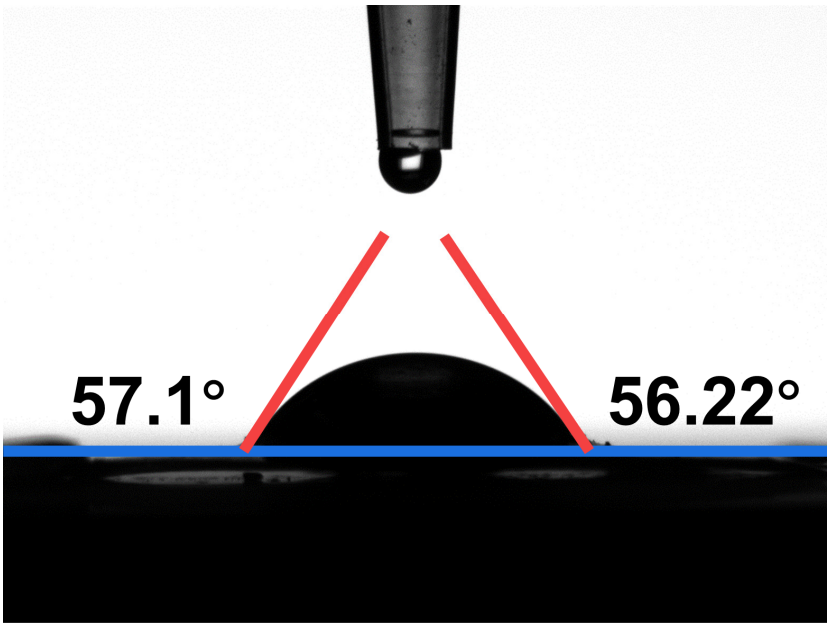

Figure S15 Water contact angle image of HICOF-bex.

Section S2 Water vapor sorption analysis

2.1 Water vapor sorption isotherm

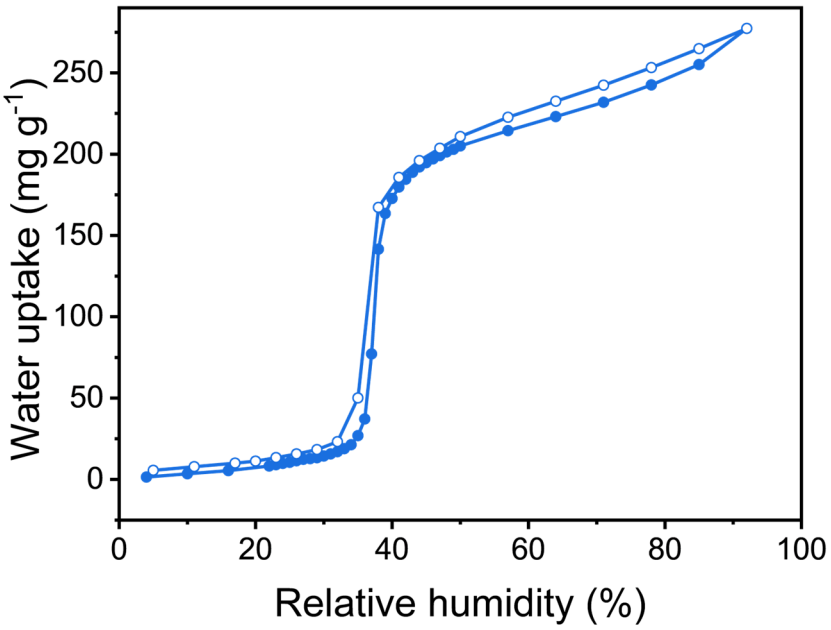

Figure S16 Water sorption analysis of HICOF-mtf at 298 K.

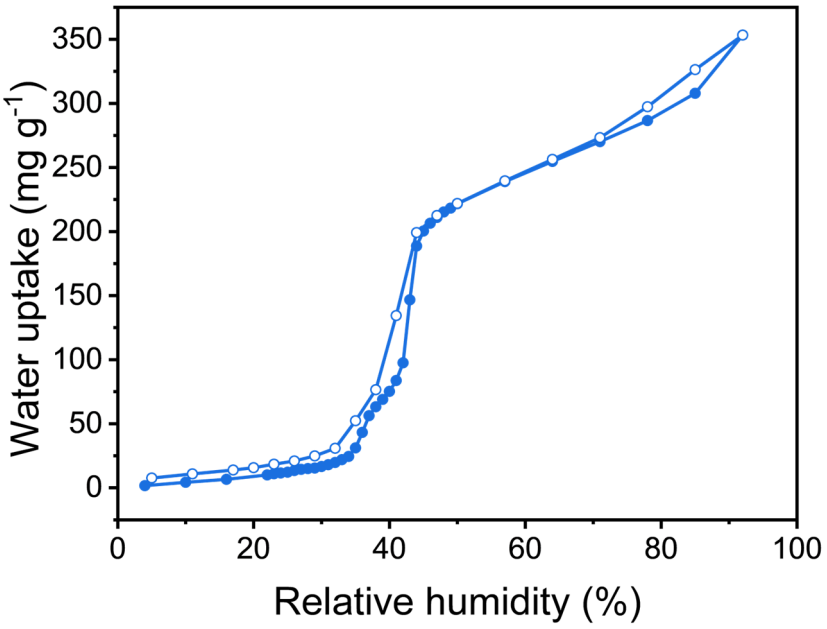

Figure S17 Water sorption analysis of HICOF-mtf at 298 K.

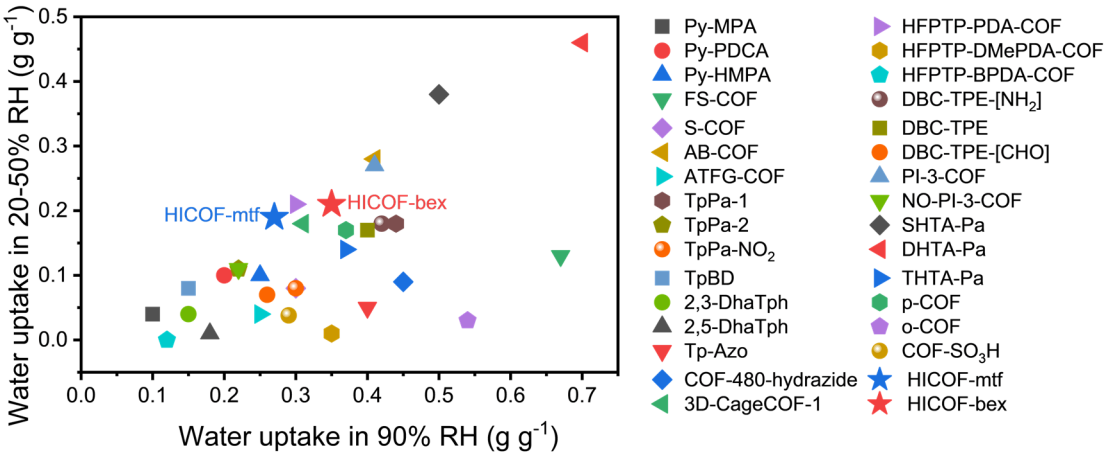

Figure S18 Water collection performance of HICOF-bex compared with most COFs used in atmospheric water collection at 298 K. Py-MPA[1], Py-PDCA[1], Py-HMPA[1], FS-COF[2], S-COF[2], AB-COF[3], ATFG-COF[3], TpPa-1[4], TpPa-2[4], TpPa-NO_2[4], TpBD[4], 2,3-DhaTph[4], 2,5-DhaTph[4], Tp-Azo[4], COF-480-hydrazide[5], 3D-CageCOF-1[6], HFPTP-PDA-COF[7], HFPTP-DMePDA-COF[7], HFPTP-BPDA-COF[7], DBC-TPE-[NH_2][8], DBC-TPE[8], DBC-TPE-[CHO][8], PI-3-COF[9], NO-PI-3-COF[9], SHTA-PA[10], DHTA-PA[10], THTA-PA[10], p-COF[11], o-COF[11],COF-SO_3H[12].

2.2 Water vapor sorption cycling stability

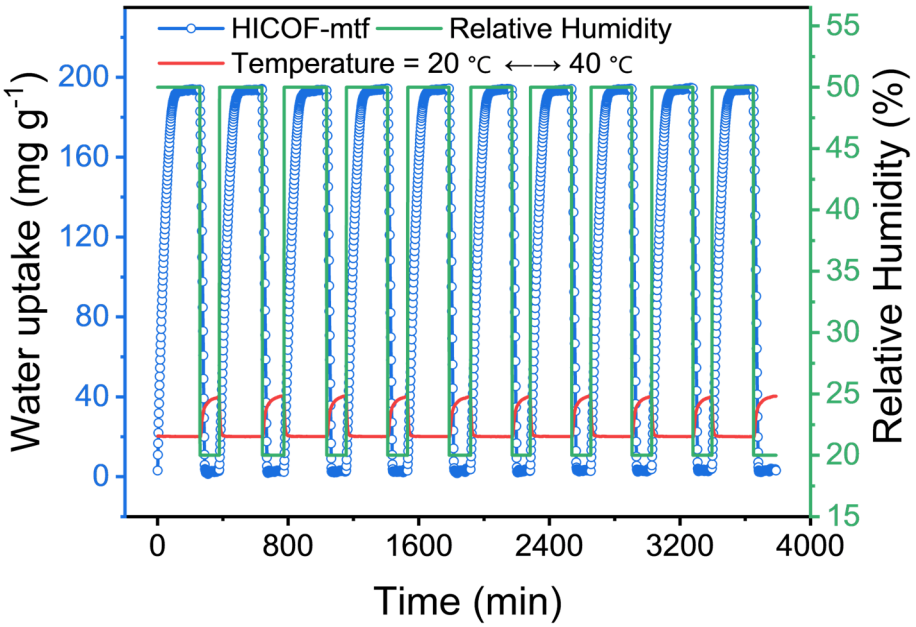

Figure S19 Water vapor adsorption and desorption cycle curve of HICOF-mtf.

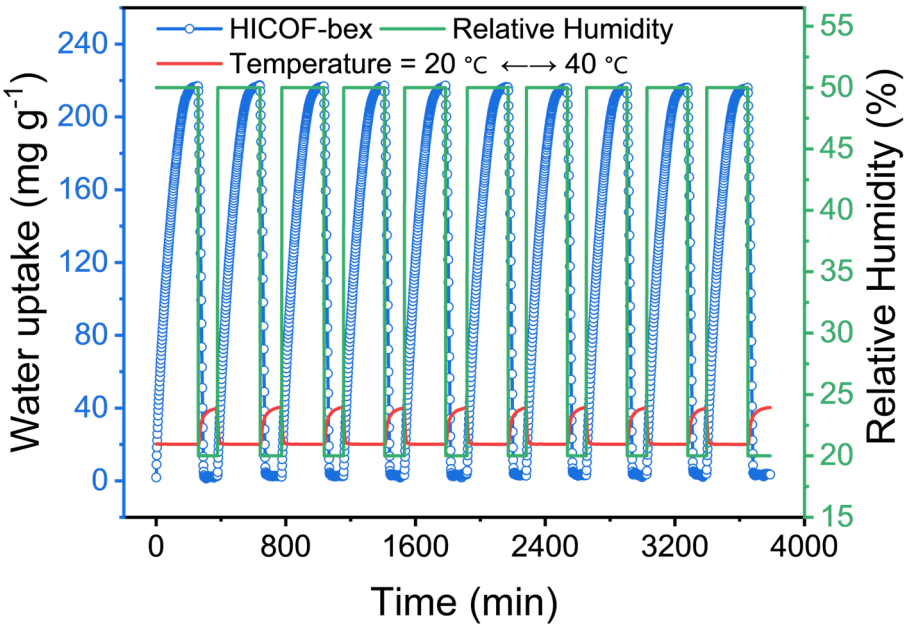

Figure S20 Water vapor adsorption and desorption cycle curve of HICOF-bex.

2.3 Material water collection stability

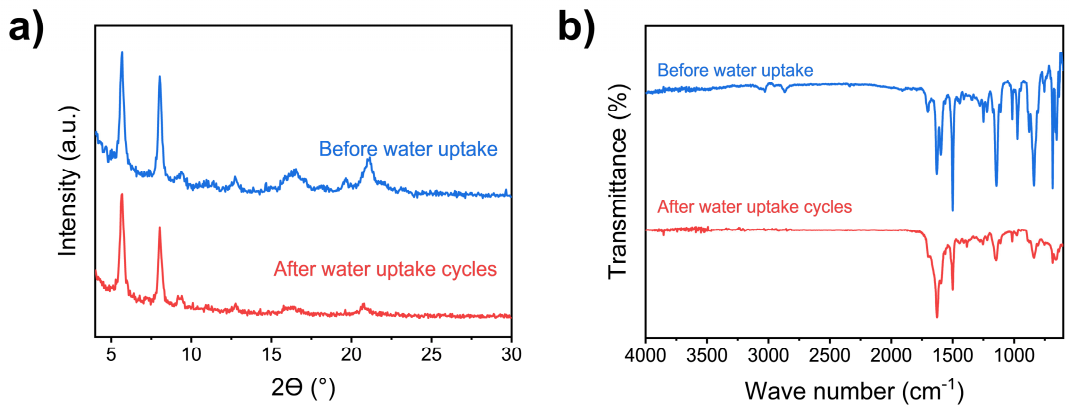

Figure S21 Comparison of PXRD a) and FT-IR b) curves before and after 10 water vapor adsorption and desorption cycles of HICOF-mtf.

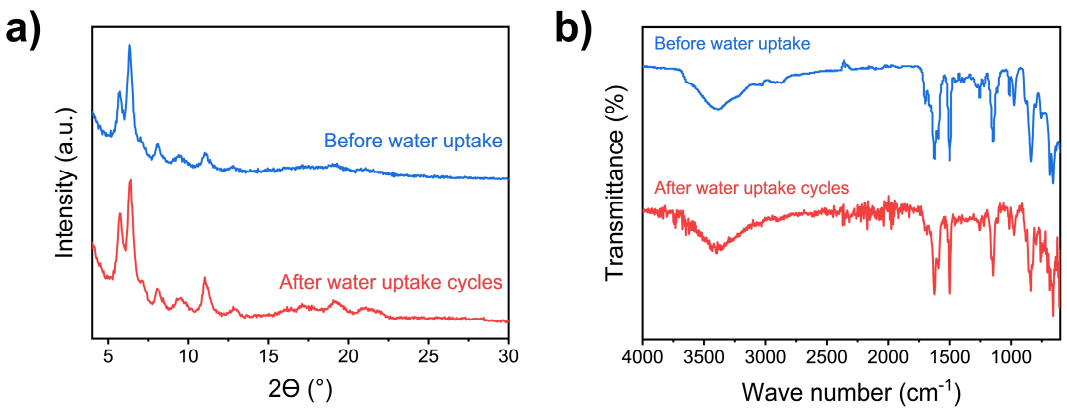

Figure S22 Comparison of PXRD a) and FT-IR b) curves before and after 10 water vapor adsorption and desorption cycles of HICOF-mtf.

Section S3 Reference

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