Host-guest Assembly of H-Bonding Networks in Covalent Organic Frameworks for Ultrafast and Anhydrous Proton Transfer

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This work dedicates to Professor Susumu Kitagawa on the occasion of his 70th birthday.

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1.Materials and general methods

All chemicals and solvents are commercially available, and used without further purification. All solvents were dried and distilled according to conventional methods.

Powder X-ray diffraction (PXRD): PXRD patterns were collected on a Rigaku MiniFlex with CuKα radiation.

Fourier transform infrared (FT-IR): IR spectrum was measured on a Bruker Optics ALPHA FT-IR spectrometer with Universal ATR accessory between the ranges of 4000 to 500 cm⁻¹.

Solution nuclear magnetic resonance (NMR): Liquid state ¹H/¹³C/¹⁹F/ nuclear magnetic resonance spectroscopy were collected on a Bruker Avance III instrument with AS500 magnet equipped with a cryoprobe (500 MHz).

Electrospray ionization mass spectrometry (ESI-MS): ESI mass spectra were collected on a Bruker model micrOTOF II using MeCN as a solvent with an ionization temperature of 150 °C.

Water contact angle (WCA): The water contact angles were measured ongoniometer (JC2000C, Japan) equipped with video capture.

Solid-state nuclear magnetic resonance (ssNMR): All experiments were measured using a JEOL JNM-ECZ600R spectrometer at 14.01 T with ¹H resonance frequency of 599.7 MHz, equipped with a 2 mm double resonance MAS probe (JEOL RESONANCE Inc, Japan). 1D ¹H spectra and ¹H T_2 relaxation time were measured using single pulse and spin-echo pulse sequence, respectively, at 20 kHz spinning rate in the temperature range of 0-100°C. 1D ¹³C and 2D ¹H-¹³C spectra were measured using cross polarization magic angle spinning (CPMAS) and heteronuclear correlation (HETCOR) sequence. ¹³C spectra were recorded at MAS of 20 kHz and recycle delay was 4.2 sec for COF-F6 and 2.0 sec for COF-F6-IL. RF field strength of ¹H and ¹³C nuclei was 166.7 kHz at the $\pi/2$ pulse width of 1.5 µs and 164.3 kHz at the $\pi/2$ pulse width of 1.52 µs, respectively. 1D and 2D ¹H double-quantum–single-quantum (DQ-SQ) spectra were measured using R122⁵ pulse sequence. The spectra were processed with the Delta software (JEOL RESONANCE Inc).

Scanning electron microscope (SEM): The SEM images were collected using a Hitachi S-3000N system.

Gas adsorption: Gas adsorption measurement N₂ adsorption measurements were performed on a BELSORP II mini. H₂O adsorption measurements were performed on a BELaqua3 (BEL-Japan, Inc.). Samples were activated at 120 °C for 16 h before the

measurement.

Thermogravimetric analysis (TGA): TGA was performed using a RigakuTG8120 under flowing N₂ with 10 K min⁻¹ ramp rate. Samples were heated in a Platinum pan (900 °C, 10 °C min⁻¹) under a N₂ flux (60 mL min⁻¹).

AC impedance measurements: Impedance results of COFs powders were collected and analyzed by Solartron 1260A frequency response analyzer. The powders were degassed at 100 °C under vacuum for 12 h in advance. Then powders (ca. 20 mg) were pressed into pellets at 500 kg for 5 minutes by a 5 mm die and sandwiched between two stainless steel electrodes under Ar atmosphere (in a glove box). The measurements were performed over a frequency range from 1 MHz to 1 Hz with a voltage amplitude of 30 mV from 40 to 140 °C inside an Ar filled glove box. Impedance data were fitted by equivalent circuit simulation to obtain resistance values using ZView software. The proton conductivity was calculated by **Equation S1**.

Equation S1. $\sigma = L/(Z \times A)$. (where L is thickness of the pellet (cm), A is the electrode area (cm²), and Z is the impedance (Ω))

2. Synthetic procedures

Ionic liquid (dema)(H₂PO₄) and (dema)(HSO₄) were synthesized according to reported procedure.^[1] COF-C2 (COF-42 in Ref 2) were synthesized following the reported method.^[2]





2,5-Bis(hexyloxy)terephthalohydrazide (Mono-C6): S1c was synthesized according to the reported method (*Org. Lett.* 2004, 6, 229). 1.09 g (2.0 mmol) of S1c was dissolvd in 15 ml of ethanol and 2 ml of hydrazine hydrate. The mixture was stirred and heated to reflux for 12 h. After cooling, white crystals precipitated, which were isolated by filtration, and recrystallization with ethanol. The white crystal was then dried to obtain

the final product **Mono-C6** as white solid (0.93 g, 90% yield). ¹H NMR (500 MHz, CDCl₃): δ 9.20 (s, 2H), 7.85 (s, 2H), 4.18 (dd, J = 8.3, 4.7 Hz, 8H), 1.99 – 1.80 (m, 4H), 1.47 (dd, J = 14.3, 6.7 Hz, 4H), 1.42 – 1.30 (m, 8H), 0.92 (t, J = 6.6 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ = 165.5, 151.0, 123.1, 115.7, 72.6, 38.0, 31.9, 31.8, 31.7, 29.6, 29.3, 26.8, 22.7, 22.6, 14.1.

Scheme S2. Synthesis of 2,5-bis(3,3,4,4,4-entafluorobutoxy)terephthalohydrazide (Mono-F4)



Diethyl 2,5-bis(3,3,4,4,4-pentafluorobutoxy)terephthalate (S2c): S2c was synthesized according to the reported literature with a modified procedure (*J. Am. Chem. Soc.* 2020, 142, 14357). Diisopropyl azodicarboxylate (1.56 mL, 8.0 mmol) was added to a mixture of diethyl 2,5-dihydroxyterephthalate S1a (1.02 g, 4.0 mmol) and triphenylphosphine (2.08 g, 8.0 mmol) in tetrahydrofuran (20 mL), and the mixture was stirred at room temperature for 30 min under argon atmosphere. Then S2b (1.313 mg, 8.0 mmol) was added to the solution and the solution was stirred and heated to reflux under argon atmosphere for 3 days. The reaction mixture was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (dichloromethane/methanol 40/1 to 20/1) to give the title compound S2c as white solid (1.64 g, 75% yield).

2,5-bis(3,3,4,4,4-pentafluorobutoxy)terephthalohydrazide (Mono-F4). 1.09 g (2.0 mmol) of S2c was dissolved in 15 mL of ethanol and 2 mL of hydrazine hydrate. The mixture was stirred and heated to reflux for 12 h. After cooling to room temperature,

the suspension was filtered, and the residue was recrystallized from ethanol to afford **Mono-F4** as colorless crystals (0.88 g, 85% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.57 (s, 2H), δ 7.41 (s, 2H), 4.42 (q, 4H), 2.81 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ = 170.18, 168.02, 155.97, 152.57, 122.92, 122.20, 114.57, 64.48, 33.02. ¹⁹F NMR (470 MHz, CDCl₃) δ -85.8, -117.4.





Diethyl 2,5-bis((3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy)terephthalate (S3c): S3c was synthesized according to the reported literature (J. Am. Chem. Soc. 2020, 142, 14357) Diisopropyl azodicarboxylate (1.56 mL, 8.0 mmol) was added to a mixture of diethyl 2,5-dihydroxyterephthalate S1a (1.02 g, 4.0 mmol) and triphenylphosphine (2.08 g, 8.0 mmol) in tetrahydrofuran (20 mL), and the mixture was stirred at room temperature for 30 min under argon atmosphere. Then S3b (1.29 mL, 8.0 mmol) was added to the solution and the solution was stirred and heated to reflux under argon atmosphere for 3 days. The reaction mixture was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (dichloromethane/methanol 40/1 to 20/1) to give the title compound as white solid (1.85 g, 2.48 mmol, 62% yield).

2,5-Bis((3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy)terephthalohydrazide (**Mono-F6**). 1.49 g (2.0 mmol) of **S3c** was dissolved in 15 mL of ethanol and 2 mL of hydrazine hydrate. The mixture was stirred and heated to reflux for 12 h. After cooling to room temperature, the suspension was filtered, and the residue was recrystallized from ethanol to afford **Mono-F6** as colorless crystals (1.19 g, 1.60 mmol, 80% yield).

Scheme S4. Synthesis of COF-C6



1,3,5-Trisformylbenzene 1 (16.2)0.10 mmol) 2,5mg, and bis(hexyloxy)terephthalohydrazide Mono-C6 (59.1 mg, 0.15 mmol) were weighed into a glass ampoule (volume of ca. 20 mL, body length of 18 cm, neck length of 9 cm). To the mixture was added 1,4-dioxane (1.0 mL), mesitylene (3.0 mL), and the ampoule was immersed in an ultrasonic bath for 5 min; following 0.4 mL of 6.0 mol L⁻¹ aqueous acetic acid was added and the ampoule was immersed in an ultrasonic bath for 10 min. Then the ampoule was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 0 mbar and flame sealed, reducing the total length by ca. 10 cm. Upon warming to room temperature, the ampoule was placed in an oven at 120 °C and left undisturbed for 3 days, yielding a white solid. The ampoule was broken at the neck, and the white solid was isolated by centrifugation and washed with acetone $(3 \times 10 \text{ mL})$, and soaking in dry acetone for 12 h, and dried at 80 °C under vacuum for 12 h to yield COF-C6 as a white powder (65.7 mg, 93% yield).

Scheme S5. Synthesis of COF-F4



1,3,5-Trisformylbenzene 1 (16.2 mg, 0.10 mmol) and **Mono-F4** (77.7 mg, 0.15 mmol) were weighed into a glass ampoule (volume of ca. 20 mL, body length of 18 cm, neck length of 9 cm). To the mixture was added 1,4-dioxane (1.0 mL), mesitylene (3.0 mL), and the ampoule was immersed in an ultrasonic bath for 5 min; following 0.4 mL of 6.0 mol L^{-1} aqueous acetic acid was added and the ampoule was immersed in an ultrasonic bath for 10 min. Then the ampoule was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 0 mbar and flame sealed, reducing the total length by ca. 10 cm. Upon warming to room temperature, the ampoule was placed in an oven at 120 °C and left undisturbed for 3 days, yielding a white solid. The ampoule was broken at the neck, and the white solid was isolated by centrifugation and washed with acetone (3 × 10 mL), and soaking in dry acetone for 12 h, and dried at 80 °C under vacuum for 12 h to yield COF-**F4** as white powder (67.0 mg, 76% yield).

Scheme S6. Synthesis of COF-F6



1,3,5-Trisformylbenzene **1** (16.2 mg, 0.10 mmol) and 2,5-bis((3,3,4,4,5,5,6,6,6nonafluorohexyl)oxy)terephthalohydrazide **Mono-F6** (107.7 mg, 0.15 mmol) were weighed into a glass ampoule (volume of ca. 20 mL, body length of 18 cm, neck length of 9 cm). To the mixture was added 1,4-dioxane (1.0 mL), mesitylene (3.0 mL), and the ampoule was immersed in an ultrasonic bath for 5 min; following 0.4 mL of 6.0 mol L^{-1} aqueous acetic acid was added and the ampoule was immersed in an ultrasonic bath for 10 min. Then the ampoule was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 0 mbar and flame sealed, reducing the total length by ca. 10 cm. Upon warming to room temperature, the ampoule was placed in an oven at 120 °C and left undisturbed for 3 days, yielding a white solid. The ampoule was broken at the neck, and the white solid was isolated by centrifugation and washed with acetone (3 × 10 mL), and soaking in dry acetone for 12 h, and dried at 80 °C under vacuum for 12 h to yield COF-**F6** as white powder (100.0 mg, 81% yield).



Figure S1. TGA profiles for C6-[dema]-HSO4-1.0



Figure S2. FT-IR spectra for F4-[dema]-HSO4-1.0



Figure S3. FT-IR spectra for F6-[dema]-HSO4-1.0



Figure S4. FT-IR spectra for C6-[dema]-IL-1.0



Figure S5. PXRD pattern for C6-[dema]-HSO4-1.0



Figure S6. PXRD pattern for F4-[dema]-HSO4-1.0



Figure S7. N₂ sorption profile for C6-[dema]H₂PO₄-1.0



Figure S8. Water sorption curves for COF-Cx/Fx



Figure S9. Pore size distribution for COF-Cx/Fx



Figure S11 ¹³C CP-MAS spectra of COF-C6.



Figure S12 PXRD patterns of COF-F6 after base treatment.



Figure S13 N_2 sorption of COF-F6 after base treatment.



Figure S14. SEM images for COF-C6



Figure S15. SEM images for COF-F4



Figure S16. SEM images for COF-F6





Figure S17. (a) 1 H NMR and (b) 13 C NMR spectra of Mono-C6.





3. Structural Modeling of COFs

Crystal structural modeling of COFs were generated by Material Studio, 2019 and optimized by the Density Functional Tight-Binding method (SCC-DFTB). Powder indexing and Pawley fitting were performed using *Reflex* module, Material Studio. Pore size distribution (PSD) were calculated from N₂ sorption curves (experimental data).

Space	Space group: P3			
3D hexagonal; $a = b = 29.63$ Å, $c = 4.54$ Å; $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$				
Atom	Х	у	Z	
C1	0.2719	-0.85472	0.75027	
C2	0.29209	-0.88804	0.81032	
C3	0.34382	-0.87223	0.73669	
C4	0.3752	-0.8251	0.59012	
C5	0.35406	-0.79386	0.50348	
C6	0.30258	-0.80884	0.58819	
07	0.38535	-0.74938	0.33007	
C8	0.36683	-0.71444	0.26128	
C9	0.41058	-0.66629	0.1104	
C10	0.39545	-0.62445	0.04738	
C11	0.44149	-0.57493	-0.08195	
C12	0.4246	-0.54147	-0.1765	
014	0.2613	-0.9361	0.95057	
C15	0.25648	-0.98109	0.80441	
C16	0.19856	-1.01996	0.75744	
C17	0.18901	-1.07197	0.62716	
C18	0.13097	-1.10901	0.56447	
C21	0.43053	-0.80877	0.53447	
N22	0.46885	-0.75826	0.57861	
023	0.44207	-0.84123	0.45848	
N24	0.5215	-0.74373	0.54609	
C25	0.5583	-0.69558	0.56944	
C26	0.61359	-0.68124	0.55278	
C27	0.62844	-0.71945	0.55203	
C28	0.21774	-0.86841	0.83156	
029	0.19514	-0.8517	0.6814	
N30	0.19255	-0.89928	1.06865	

Table S1. Fractional atomic coordinates for simulated COF-F4

C31	0.11048	-0.95923	1.26433
C32	0.05414	-0.97972	1.28728
C33	0.03371	-0.94603	1.28931
N34	0.13923	-0.91773	1.11077
F35	0.37972	-0.61118	0.30346
F36	0.35406	-0.64418	-0.14735
F37	0.46297	-0.58708	-0.31719
F38	0.47972	-0.54967	0.12869
F44	0.20635	-1.09607	0.82077
F45	0.21671	-1.0625	0.36824
F46	0.10291	-1.1233	0.8241
F47	0.11141	-1.08532	0.38348
H53	0.35987	-0.89663	0.79964
H54	0.28581	-0.78503	0.52892
H55	0.35589	-0.70215	0.46691
H56	0.33259	-0.73386	0.112
H57	0.42047	-0.67865	-0.09938
H58	0.4457	-0.64972	0.25334
H59	0.27418	-0.99863	0.94614
H60	0.27665	-0.97154	0.58719
H61	0.1829	-1.00172	0.60611
H62	0.17774	-1.0271	0.97063
H63	0.45923	-0.73085	0.65527
H64	0.5485	-0.66532	0.60667
H65	0.599	-0.76039	0.55697
H66	0.21218	-0.90996	1.21874
H67	0.12685	-0.98199	1.35057
H68	0.05978	-0.90423	1.28353
F69	1.15346	0.27811	0.42688

Table S2. Fractional atomic coordinates for simulated COF-F6

Space group: P3				
3D hexagonal; $a = b = 29.79$ Å, $c = 4.72$ Å; $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$				
Atom	Х	у	Z	
C1	0.27161	-0.86703	0.71146	
C2	0.29328	-0.89779	0.78978	
C3	0.34553	-0.88056	0.73345	
C4	0.37658	-0.83385	0.59052	

C5	0.35427	-0.80496	0.48922
C6	0.30194	-0.82179	0.55388
07	0.38507	-0.76109	0.3204
C8	0.36534	-0.72781	0.24576
C9	0.4083	-0.67929	0.10329
C10	0.39208	-0.63843	0.04726
C11	0.43822	-0.58738	-0.06501
C12	0.42417	-0.54424	-0.10835
C13	0.47021	-0.49316	-0.21445
014	0.26331	-0.94511	0.92817
C15	0.25383	-0.99021	0.7737
C16	0.19524	-1.02553	0.73939
C17	0.18091	-1.07902	0.61836
C18	0.12154	-1.11335	0.57912
C19	0.10543	-1.16871	0.47383
C20	0.04643	-1.20342	0.44191
C21	0.43247	-0.81589	0.55118
N22	0.46921	-0.76488	0.5864
023	0.44581	-0.84748	0.49577
N24	0.52219	-0.74862	0.56368
C25	0.55751	-0.70015	0.58335
C26	0.61327	-0.6835	0.57161
C27	0.6304	-0.71969	0.57112
C28	0.21667	-0.88252	0.77201
029	0.19386	-0.8692	0.6093
N30	0.19107	-0.91094	1.00448
C31	0.10862	-0.96618	1.19979
C32	0.05321	-0.98319	1.22104
C33	0.03623	-0.94697	1.22287
N34	0.13847	-0.92705	1.04193
F35	0.37396	-0.62868	0.29427
F36	0.35211	-0.65815	-0.14703
F37	0.45427	-0.59768	-0.31797
F38	0.47902	-0.56997	0.12315
F39	0.38412	-0.56064	-0.30032
F40	0.40758	-0.53404	0.14304
F41	0.4901	-0.50089	-0.46022
F42	0.50914	-0.47229	-0.01483
F43	0.45388	-0.45794	-0.26684

F44	0.19875	-1.103	0.79972
F45	0.20534	-1.0722	0.36126
F46	0.09712	-1.11691	0.83253
F47	0.10535	-1.08946	0.38694
F48	0.12828	-1.16558	0.21607
F49	0.12243	-1.19265	0.66068
F50	0.03547	-1.2503	0.32459
F51	0.02631	-1.18052	0.26876
F52	0.02258	-1.21296	0.70207
H53	0.3621	-0.90357	0.8064
H54	0.28413	-0.79995	0.48214
H55	0.35291	-0.71611	0.43944
H56	0.33208	-0.74812	0.09869
H57	0.41879	-0.69057	-0.09863
H58	0.44288	-0.66271	0.24258
H59	0.27022	-1.01044	0.8955
H60	0.27237	-0.98073	0.56169
H61	0.18065	-1.00593	0.59817
H62	0.17651	-1.03049	0.9483
H63	0.45802	-0.73814	0.64593
H64	0.54616	-0.67111	0.61173
H65	0.60246	-0.76077	0.57463
H66	0.21009	-0.92036	1.15754
H67	0.12324	-0.98937	1.29471
H68	0.06425	-0.9059	1.21748

Table S3. Fractional atomic coordinates for simulated COF-C6

Space group: P3					
3D hex	3D hexagonal; $a = b = 29.40$ Å, $c = 3.99$ Å; $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$				
Atom	Х	у	Z		
C1	0.26937	-0.84963	0.77568		
C2	0.2863	-0.88696	0.76396		
C3	0.3386	-0.8703	0.67775		
C4	0.373	-0.81831	0.58048		
C5	0.35437	-0.78269	0.5498		
C6	0.30268	-0.79872	0.65359		
07	0.38854	-0.73244	0.41534		
C8	0.36922	-0.6972	0.35679		

C9	0.41402	-0.64535	0.22445
C10	0.39578	-0.60552	0.16141
C11	0.44147	-0.55277	0.04309
C12	0.4232	-0.51312	-0.02569
C13	0.46867	-0.46053	-0.1426
014	0.25136	-0.93945	0.85433
C15	0.25379	-0.98076	0.67947
C16	0.19789	-1.02268	0.58338
C17	0.19359	-1.07497	0.48204
C18	0.13622	-1.11607	0.40497
C19	0.13072	-1.16863	0.29711
C20	0.0735	-1.20936	0.22397
C21	0.42881	-0.80172	0.51938
N22	0.46786	-0.75416	0.63174
023	0.43999	-0.83165	0.37807
N24	0.52072	-0.74026	0.59715
C25	0.55833	-0.69323	0.66423
C26	0.6136	-0.68004	0.64635
C27	0.62723	-0.71949	0.64598
C28	0.21598	-0.86331	0.89366
029	0.19475	-0.84035	0.77511
N30	0.19036	-0.90075	1.13352
C31	0.11086	-0.95789	1.4042
C32	0.0545	-0.97894	1.44636
C33	0.03337	-0.94554	1.44968
N34	0.13758	-0.9182	1.20782
F35	0.37921	-0.5994	0.39556
F36	0.36408	-0.62131	-0.02974
F37	0.4585	-0.55897	-0.18873
F38	0.47277	-0.53672	0.23689
F39	0.40612	-0.5066	0.2049
F40	0.39215	-0.52882	-0.22092
F41	0.48797	-0.46607	-0.36503
F42	0.49832	-0.44199	0.05937
F43	0.45373	-0.43374	-0.21037
F44	0.20832	-1.08955	0.6878
F45	0.21841	-1.06876	0.25828
F46	0.12119	-1.10108	0.20305
F47	0.1117	-1.12236	0.63072

F48	0.14563	-1.18402	0.49714
F49	0.15457	-1.16277	0.06899
F50	0.07114	-1.24577	0.12467
F51	0.05671	-1.19412	0.03557
F52	0.04964	-1.21927	0.45621
H53	0.35312	-0.89756	0.69729
H54	0.28789	-0.7717	0.64475
H55	0.35477	-0.68929	0.59381
H56	0.33673	-0.71446	0.17106
H57	0.42929	-0.65282	-0.01111
H58	0.44656	-0.6291	0.4099
H59	0.27113	-0.99788	0.84995
H60	0.27807	-0.96682	0.44822
H61	0.18495	-1.00771	0.37058
H62	0.17117	-1.02944	0.79787
H63	0.45848	-0.72926	0.76419
H64	0.54923	-0.66307	0.7354
H65	0.59681	-0.76047	0.65194
H66	0.20965	-0.91698	1.26239
H67	0.12856	-0.97917	1.51003
H68	0.05921	-0.90334	1.43885



Figure S19. 1D ¹H single pulse and DQ-SQ of (a) COF-F6, (b) F6-[dema]HSO4-1.0, (IL is short for [dema]HSO4 in this ESI) measured at -20, 40, and 100 °C. The number denotes the ¹H DQ filtering efficiency comparing to the ¹H signal intensity of the single

pulse.

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Figure S20. (a-c) ¹H single pulse spectra of F6-[dema]HSO4-1.0, F6, and IL ([dema]HSO4) measured at -20 (a), 40 (b), and 100 °C (c) with the ¹H assignment of the structural formula of F6-[dema]HSO4.

*Note: The comparison of IL and F6-IL spectra measured at low and high temperature of -20 and 100 °C shows identical ¹H chemical shifts of **dema** (**a**,**b**,**c** peak), which means that the chemical environment of IL in COF-F6 system would be the same as that of pristine IL. The small differences of peak **d** and **e** would come from hydrogen bonding to COF-F6.



Figure S21 2D ¹H DQ/SQ spectra of COF-F6 and F6-IL at -20 and 40 °C.

*Note: The almost identical 2D ¹H DQ-SQ spectra of COF-F6 and F6-IL also confirm the COF-F6 structure. In the case of COF-F6, the correlations indicated by the red boxes are due to inter-frame interaction (NH), which indicates the distance between the frames below ~3.5Å.



Figure S22 1D {¹H}¹³C CPMAS spectra of **F6-[dema]HSO4-1.0** and **IL (a)**, measured at -20 °C and contact time during cross polarization of 2 ms, with the ¹³C assignment of the structural formula of **F6-[dema]HSO4 (b)**. 1D {¹H}¹³C CPMAS spectra of COF-**F6 (c)** and **F6-[dema]HSO4-1.0 (d)** measured at different temperatures. The contact time of 1D {¹H}¹³C CPMAS spectra of **F6-[dema]HSO4-1.0** measured at 100 °C set up 0.5 us and the contact time of the other spectra was 2 ms during cross polarization.

*Note: The ¹³C signal intensity of COF-F6 is almost similar as a function of temperature while the ¹³C signal intensity of F6-IL decreased due to the increased mobility at high temperature. Especially, the IL signals at ¹³C = 50.2, 38.4, and 9.3 ppm disappeared at 40 and 100 °C due to the increased molecular motion as the temperature increases. The disappearance of quaternary carbon signals of COF-F6 frameworks at ¹³C = 158.7 and 134.0 ppm also indicate wobbling of COF framework at 100 °C.



Figure S23 Comparison of ¹H-¹³C HETCOR spectra of COF-F6 (a) and F6-IL (b) measured at low temperature (-20 °C) and contact time of 2 ms. Comparison of ¹H-¹³C HETCOR spectra of COF-F6 (c) and F6-IL (d) measured at high temperature (80 and 100 °C) and contact time of 2 ms. In (b), the red spectra are ¹H single pulse and $\{^{1}H\}^{13}C$ CPMAS of IL.

*Note: The comparison of ¹H-¹³C spectra of COF-F6 and F6-IL shows almost identical spectra at low and high temperature, which means the frameworks are stable at low and high temperature. The signals enclosed the red boxes in the 2D ¹H-¹³C HETCOR spectrum of F6-IL at -20 °C would be intra-interaction of IL.



Figure S24. ¹H-¹⁵N HETCOR spectra of COF-F6 and F6-IL were measured at -15 and 40 °C and contact time of 2 ms.

*Note: IL insertion introduces small ¹H downfield shift (black spectra, ~ 0.3 ppm shift comparing the ¹H signal of NH for COF-**F6**, which may be due to weak hydrogen bonding between IL and framework.



Figure S25. (a) H-bondings in COF-F6, which exists between (b) hydrazone and HSO_4^{-1} (N-H...O), (c) (O-H...F) and (d) [dema] and CF chains (N-H...F)

*Note: The geometrical structure of [dema]HSO4 molecule was optimized by Gaussian

09 (E.01) program with b3lyp/6-31g(d) level. Simulation of hydrogen bonds between the COF-F6 framework and the [dema]HSO₄ molecules were done by molecular dynamics method, initially several [dema]HSO₄ molecules were put into the pores of COF-F6, subsequently followed by geometry optimization performed in Material Studio utilizing *Forcite* module in which COMPASSII were adopted as the forcefield and Rappe and Goddard's QEq scheme were taken into account. The results clearly demonstrated that H-bonding exists between hydrazone and HSO₄⁻¹ (N-H^{...}O, Fig S25b), CF chains and HSO₄⁻¹ (O-H^{...}F, Fig S25c) and [dema] and CF chains (N-H^{...}F, Fig S25d).



Figure S26. Water contact angles for COF-C4/F4.



Figure S27. Size of [dema]HSO₄ based on the calculated structure optimized by Gaussian 09 (E.01) program with b3lyp/6-31g(d) level.



Figure S28. N2 adsorption-desorption measurements for IL-doped COF.



Figure S29. Nyquist plots of C6-[dema]H₂PO₄-1.0 measured at different temperatures under anhydrous conditions.



Figure S30. Nyquist plots of C6-[dema]HSO4-1.0 measured at different temperatures under anhydrous conditions.



Figure S31 Nyquist plots of F6-[dema]HSO4-0.5 measured at different temperatures under anhydrous conditions.



Figure S32. Nyquist plots of **F6-[dema]HSO4-1.0** measured at different temperatures under anhydrous conditions.



Figure S33. Nyquist plots of F6-[dema]HSO4-1.5 measured at different temperatures under anhydrous conditions.



Figure S34. Temperature profiles of proton conductivities of C2/C6/F6-[dema]HSO₄-1.0

Material	Proton conductivity	Т	References.
	$(S \text{ cm}^{-1})$	(°C)	
H ₃ PO ₄ @TPB-DABI-COF (66	1.52×10^{-1}	160	Angew. Chem. Int. Ed. 2021 , 60,
wt%)			12918
CMP-F6	4.39 × 10 ⁻³	120	ACS Appl. Mater. Interfaces. 2021,
			13, 15536
H ₃ PO ₄ @TPB-DMeTPCOF	$1.91 imes 10^{-1}$	160	Nat. Commun. 2020, 11, 1981
H ₃ PO ₄ @Tp-Azo-COF	$6.70 imes10^{-5}$	67	<i>JACS</i> . 2014 , 136, 6570
H ₃ PO ₄ @COF-F6	$4.2 imes 10^{-2}$	140	J. Am. Chem. Soc. 2020, 142, 14357
H ₃ PO ₄ @EB-COF	$2.77 imes 10^{-2}$	140	J. Mater. Chem. A. 2020, 8, 13702
H ₃ PO ₄ @TpBpy-MC	$2.50 imes 10^{-3}$	120	J. Mater. Chem. A. 2016, 4, 2682
Phytic acid@TpPa-(SO ₃ H-	$5.00 imes 10^{-4}$	120	Chem. Mater. 2016, 28, 1489
Py)			
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
F6-[dema]HSO ₄ -1.5	1.33×10^{-2}	140	This work

Table S4. Comparison of proton conductivities in anhydrous conditions.

Reference:

[1] Nakamoto, H.; Watanabe, M. Bronsted Acid-Base Ionic Liquids for Fuel Cell Electrolytes. *Chem Commun (Camb)*. **2007**, *24*, 2539-2541.

[2] Uribe-Romo, F. J.; Doonan, C. J.; Furukawa, H.; Oisaki, K.; Yaghi, O. M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133*, 11478-11481.