Supplementary Information

0.1 Membrane Fabrication Methods

The synthesized COF material was sufficiently exfoliated in dimethylformamide (DMF) at a concentration of 0.5 mg/mL at room temperature for 90 minutes. The suspensions were allowed to sit at room temperature overnight before transferring 10 mL of the supernatant into a Sterlitech dead-end permeation cell loaded with an anodic aluminum oxide (AAO) membrane support (20 nm pore size, Whatman). The membranes were fabricated by applying 1.2 bar of pressure to the suspension followed by permeance testing.

0.2 Permeance Testing

All filtration tests were performed at room temperature with trans-membrane pressures ranging 0.5–1.6 bar using a Sterlitech dead-end permeation cell. The effective membrane area for all tests is 2.24 cm^2. Membrane permeance (L m^{-2} h^{-1} bar^{-1}) was calculated following **Equation S1**.

$$Permeance = \frac{\Delta V}{\Delta t A_{\text{eff}} \Delta P} \tag{S1}$$

ΔV is the amount of solvent volume (L) that has permeated through the membrane, and Δt is the amount of time (h) that the solvent was allowed to permeate. A_{eff} (m^2) is the effective area of the membrane and P is the pressure utilized (bar) for solvent permeation. The fabricated membrane had the desired solvents permeated through the membrane three times prior to testing. These solvents included ethanol, DMF, methanol, tetrahydrofuran, and acetone. The inverse viscosities of each of these solvents are given in **Table S5**.

0.3 Supplemental Tables

Table S1: Cohesive energy and enthalpy of formation values calculated from DFTB+ for all COFs, oxalyl chloride, and hexofluoro glutaryl chloride. E_{COH} and ΔH_f calculated in this table are from **Equations 1, 2** and **3** in the paper.

Material/Molecule	E_{COH} (eV)	ΔH_f (eV)	Interlayer Spacing (Å)
COF-Quin	7.23	-1.29	3.45
OC 1-3	7.30	-1.32	3.29
OC 1-3 Layers	7.26	-1.31	3.20
OC 1-3 Pore	7.24	-1.30	3.33
OC 1-4	7.29	-1.32	3.17
OC 1-4 Layers	7.26	-1.30	3.07
OC 1-4 Pore	7.24	-1.29	3.17
HFG 1-2	7.02	-1.35	3.95
HFG 1-2 Layers	7.12	-1.32	3.91
HFG 1-2 Pore	7.16	-1.30	3.87
HFG 1-3	7.02	-1.34	3.85
HFG 1-3 Layers	7.12	-1.32	3.47
HFG 1-3 Pore	7.17	-1.31	3.45
HFG 1-4	7.00	-1.32	8.53
HFG 1-5	7.00	-1.32	8.76
HFG 1-6	6.99	-1.31	8.62
OC	6.85	-1.95	N/A
HFG	5.40	-1.51	N/A

Table S2: Cohesive energy and enthalpy of formation values calculated from DFTB+ for all cross-linked COFs. E_{COH} and ΔH_f calculated in this table are from **Equations 4** and **5** in the paper.

Material/Molecule	E_{COH} (eV)	ΔH_f (eV)
OC 1-3	7.32	-1.28
OC 1-3 Layers	7.28	-1.29
OC 1-3 Pore	7.25	-1.29
OC 1-4	7.32	-1.28
OC 1-4 Layers	7.27	-1.28
OC 1-4 Pore	7.24	-1.28
HFG 1-2	7.36	-1.32
HFG 1-2 Layers	7.29	-1.30
HFG 1-2 Pore	7.25	-1.29
HFG 1-3	7.35	-1.31
HFG 1-3 Layers	7.29	-1.30
HFG 1-3 Pore	7.26	-1.30
HFG 1-4	7.32	-1.28
HFG 1-5	7.32	-1.28
HFG 1-6	7.32	-1.27

Table S3: Reference states and reference energies for all atoms present in this work. The reference energy is divided by the number of atoms in the reference state. The atomic energy is the internal energy calculated from an atom in isolation

Element	Reference State	Reference Energy (eV)	Atomic Energy (eV)
Carbon	C_4	-176.48	-38.06
Hydrogen	H_2	-18.22	-6.49
Nitrogen	N_2	-130.85	-57.20
Oxygen	O_2	-175.43	-83.98
Bromine	Br_2	-162.34	-79.53
Fluorine	F_2	-234.79	-115.25
Chlorine	Cl_2	-172.41	-84.11

Table S4: DFTB+ Optimized simulation cell lattices and angles for all COFs

Material	a, b, c (Å)	α, β, γ (°)
COF-Quin	20.9, 20.7, 4.4	95.7, 121.2, 119.6
OC 1-3	20.9, 20.5, 5.93	85.2, 141.2, 110.3
OC 1-3 Layers	20.8, 20.6, 10.9	88.1, 137.1, 119.4
OC 1-3 Pore	41.6, 41.3, 5.37	87.4, 136.4, 119.5
OC 1-4	21.1, 20.0, 10.7	90.3, 148.2, 118.5
OC 1-4 Layers	20.6, 20.5, 20.6	88.7, 148.3, 119.9
OC 1-4 Pore	42.0, 40.1, 10.7	90.6, 147.9, 118.5
HFG 1-2	20.5, 21.1, 10.1	158.0, 47.6, 121.0
HFG 1-2 Layers	20.8, 21.0, 20.3	157.7, 46.3, 121.7
HFG 1-2 Pore	41.5, 42.0, 10.0	156.7, 45.5, 121.3
HFG 1-3	21.1, 20.7, 5.2	48.3, 120.1, 121.7
HFG 1-3 Layers	21.0, 20.8, 9.9	44.8, 121.8, 120.5
HFG 1-3 Pore	41.8, 41.5, 4.9	49.7, 127.8, 121.2
HFG 1-4	20.7, 20.9, 11.2	89.5, 123.8, 120.0
HFG 1-5	20.7, 20.8, 13.6	124.6, 98.7, 120.5
HFG 1-6	20.9, 20.8, 13.3	130.6, 92.8, 119.9

Table S5: Inverse viscosities for solvents used in membrane permeance tests

Solvent	Viscosity^{-1} (mPa^{-1} s^{-1})
Ethanol	0.962
DMF	1.087
Methanol	1.334
Tetrahydrofuran (THF)	2.084
Acetone	2.778

Table S6: Average bond lengths from molecular dynamics of COF-Quin, HFG (1-2, 1-3, and 1-4) and OC (1-3 and 1-4) at 300 K and 600 K.

Bonds	300 K Average Bond Length (Å)	600 K Average Bond Length (Å)
	COF-Quin	
C-C	1.44 ± 0.09	1.44 ± 0.13
C-N	1.37 ± 0.09	1.38 ± 0.13
C-Br	1.89 ± 0.24	1.9 ± 0.25
N-H	1.02 ± 0.31	1.03 ± 0.33
	HFG 1-2	
C-C	1.46 ± 0.17	1.46 ± 0.22
C-N	1.38 ± 0.18	1.39 ± 0.22
C-Br	1.89 ± 0.21	1.89 ± 0.24
C-O	1.21 ± 0.24	1.21 ± 0.27
C-F	1.38 ± 0.23	1.39 ± 0.26
N-H	1.03 ± 0.28	1.03 ± 0.31
	HFG 1-3	
C-C	1.46 ± 0.17	1.46 ± 0.20
C-N	1.38 ± 0.18	1.39 ± 0.21
C-Br	1.89 ± 0.21	1.89 ± 0.24
C-O	1.21 ± 0.25	1.21 ± 0.27
C-F	1.37 ± 0.24	1.38 ± 0.26
N-H	1.03 ± 0.29	1.03 ± 0.30
	HFG 1-4	
C-C	1.46 ± 0.21	1.47 ± 0.22
C-N	1.38 ± 0.21	1.39 ± 0.22
C-Br	1.89 ± 0.23	1.90 ± 0.24
C-O	1.22 ± 0.27	1.22 ± 0.27
C-F	1.38 ± 0.26	1.39 ± 0.26
N-H	1.03 ± 0.30	1.03 ± 0.31
	OC 1-3	
C-C	1.44 ± 0.15	1.45 ± 0.18
C-N	1.38 ± 0.19	1.39 ± 0.20
C-Br	1.89 ± 0.22	1.89 ± 0.24
C-O	1.22 ± 0.24	1.22 ± 0.27
N-H	1.03 ± 0.29	1.03 ± 0.31
	OC 1-4	
C-C	1.44 ± 0.16	1.45 ± 0.19
C-N	1.38 ± 0.19	1.39 ± 0.20
C-Br	1.89 ± 0.22	1.89 ± 0.23
C-O	1.22 ± 0.24	1.21 ± 0.26
N-H	1.03 ± 0.30	1.03 ± 0.31

0.4 Supplemental Figures

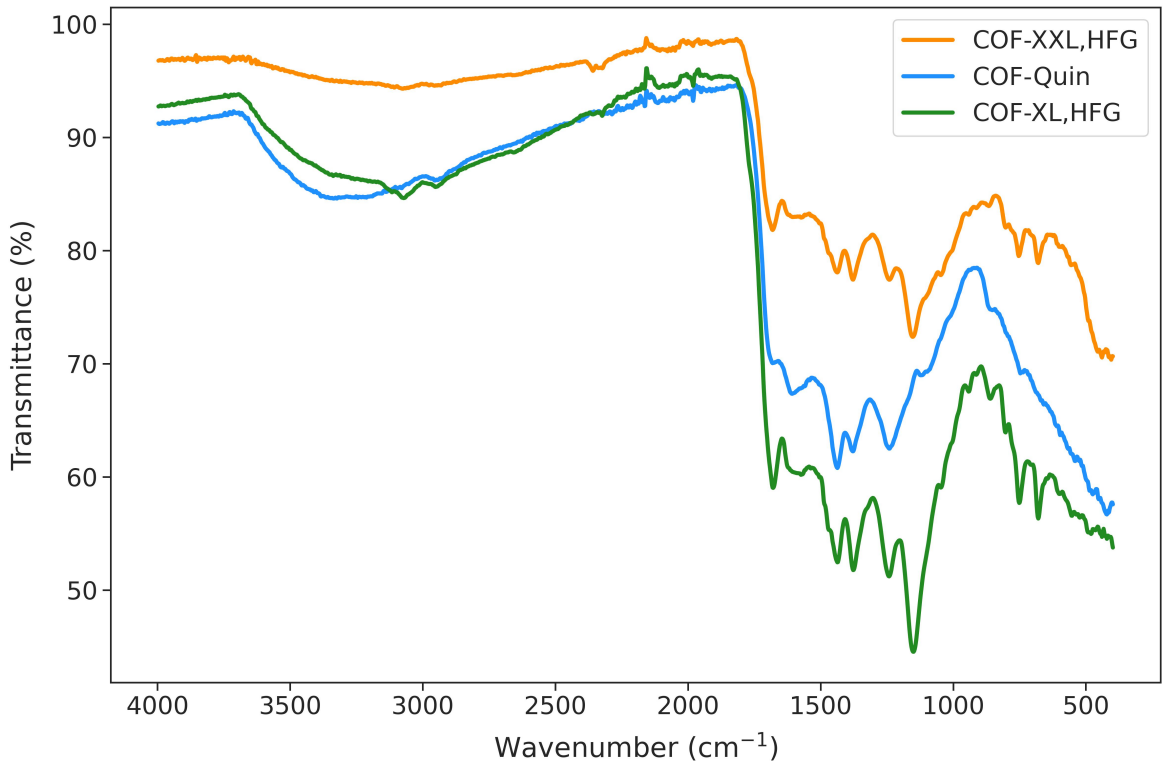

Figure S1: FTIR spectra for COF-XXL,HFG (orange), COF-Quin (blue), and COF-XL,HFG (green). In COF-XL,HFG and COF-XXL,HFG, there is a strong peak at 1151 cm^{-1}, indicative of C-F bonds. Additionally, the peak in COF-Quin at 3000 and 3500 cm^{-1} has decreased in strength in COF-XL,HFG and COF-XXL,HFG, which confirms that N-H bonds have decreased due to cross-linking.

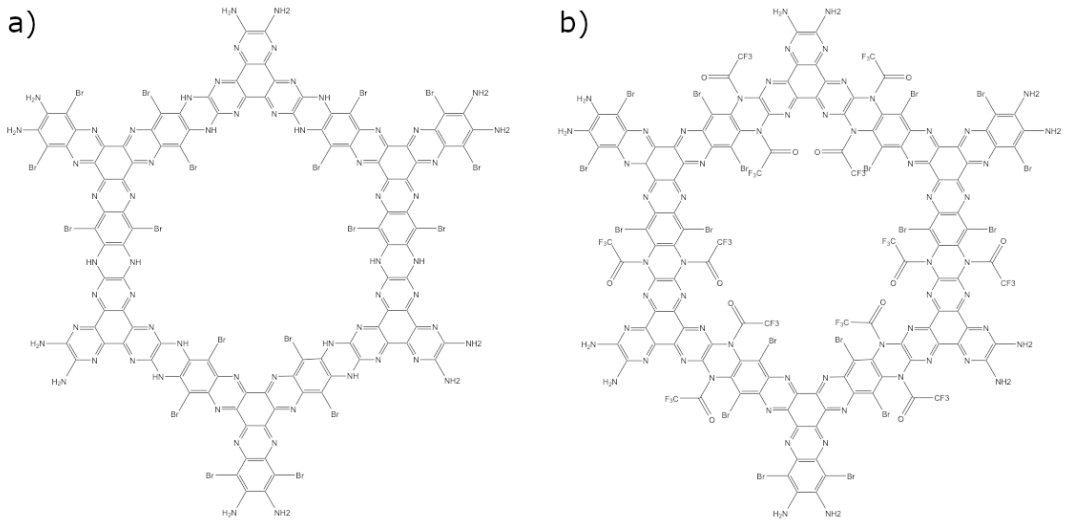

Figure S2: Visual representations for COF-Quin (a) and COF-Quin$_{CF3}$ (b). COF-Quin$_{CF3}$ was also fabricated into a membrane for permeance testing and water contact angle shown in **Figure S3**.

Figure S3: Water contact angle images for COF-Quin (a), COF-Quin$_{CF3}$ (b), and COF-XL,HFG. In (a), there is no hydrophobic behavior. In (b), there is a degree of hydrophobicity seen due to the fluorine atoms in the cross-linking moiety. Finally, in (c), the fluorinated functional group from **Figure S2** increase the hydrophobicity of the framework.

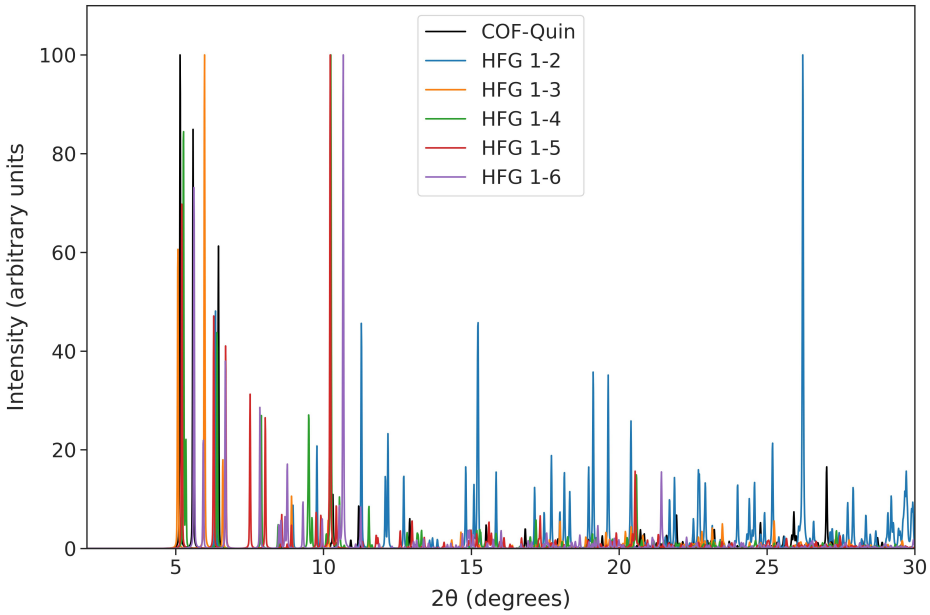

Figure S4: Simulated XRD patterns for the five "saturated" hexafluoroglutaryl cross-linked geometries compared to the non-cross-linked COF-Quin$_{3D}$. HFG 1-4, 1-5, and 1-6 correspond to heights 8.53-8.76 Å, HFG 1-3 is at peak 3.85 Å, and HFG 1-2 is at peak 3.95 Å. COF-Quin$_{3D}$ appears at 3.5 Å.

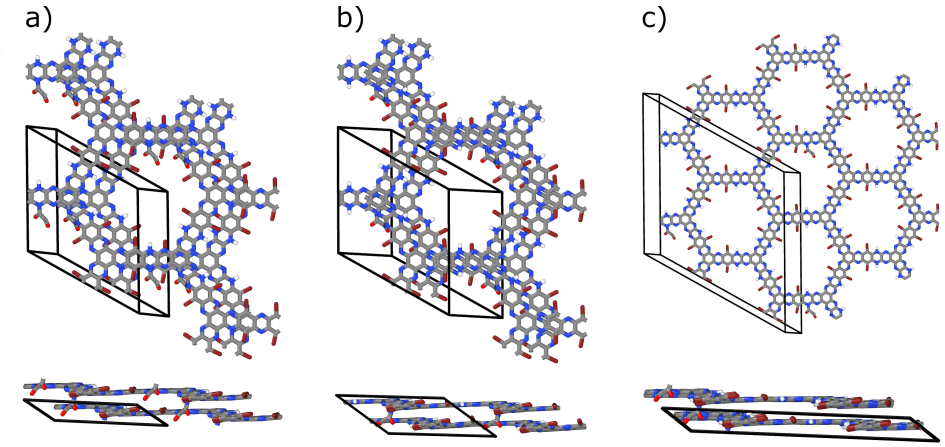

Figure S5: COF-XL,OC with a linker every pore and every layer (a), a linker every pore and every other layer (b), and a linker every other pore and every layer (c).