Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Hydrolytically Stable Ionic Fluorogels for High-Performance Remediation of Per- and Polyfluoroalkyl Substances (PFAS) from Natural Water

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1. MATERIALS AND INSTRUMENTATION

Materials:

All materials were purchased from commercial source and used as received without further purification unless otherwise mentioned. Perfluoropolyether Fluorolink® E10H (Mwt: 1.8-2.0 kg·mol^{-1}) was purchased from Solvay Solexis. Perfluorostyrene was purchased from Oakwood Chemical. 1H,1H,11H,11H-Perfluoro-3,6,9-trioxaundecane-1,11-diol was purchased from Exfluor. 2-(dimethylamino)ethanol, 2-(dimethylamino)ethyl methacrylate, azobisisobutyronitrile (AIBN), humic acid and perfluorooctanoic acid (PFOA) were purchased from Sigma-Aldrich. Trifluoroethanol was purchased from Synquest labs. Perfluorohexanoic acid (PFHxA) and GenX were purchased from TCI and Matrix respectively.

Surface water was collected from the Jones Ferry Road Drinking Water Treatment Plant in Carrboro, NC. For a representative water matrix, sampling took place after sedimentation and prior to filtration in the conventional water treatment system. Collected water samples were stored in 20-L low-density polyethylene cubitainers™ (Fisher Scientific, Pittsburg, PA) at 4ºC. Prior to testing, water samples were filtered through a 5-micron spun-bonded polypropylene (PP) filter cartridge (Culligan, Rosemont, IL) into a 75-L high-density polyethylene carboy (Foxx Life Sciences, Salem, NH) to achieve filtered settled conventional water with pH = 5.34, TOC ≤ 0.5 mg/L, conductivity 180 uS/cm.

Deionized water used in this study is a type 1, 18.2 megohm-cm water obtained from Labconco – waterpro PS series. This water was amended with sodium chloride and humic acid as described for specific experiments.

Instrumentation::

Spectroscopy: Proton, fluorine and carbon magnetic resonance spectra (^{1}H NMR, ^{19}F NMR, and ^{13}C NMR) were recorded on a Bruker model AVANCE III 600 MHz CryoProbe spectrometer or Bruker AVANCE NEO 400 MHz Prodigy probe spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm or CD_3OD at 2.05 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm or CD_3OD at 30.60 ppm). Infrared Spectroscopy (IR) spectra were obtained using a PerkinElmer Frontier FT-IR spectrometer. High Resolution Mass Spectrometry (HRMS) data were obtained using a Q Exactive HF-X mass spectrometer with electrospray induction and external calibration.

Size exclusion chromatography (SEC) spectra were obtained using an Agilent 1260 series separations module liquid chromatograph and refractive index detector at 50 ºC with two Poroshell 120 C18 columns in series. *N,N*-Dimethylformamide was the mobile phase and the flow rate was set to 1 mL/min. The instrument was calibrated using poly(ethylene glycol) standards from 194 g/mol to 122,200 g'mol. Standards were obtained from Sigma-Aldrich.

Thermal Analysis: Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA (Discovery Series) using 5-8 mg of the sample. The samples were heated to 25-600 °C at a temperature ramp rate of 10 °C/min. Infrared (IR) spectra were obtained using PerkinElmer Frontier FT-IR spectrometer. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery DSC. T_g values were determined from the second heating scan. All experiments were run at a ramp rate of 10 ºC/min.

Mechanical Analysis: Dynamic Oscillatory rheology was performed on a TA Instruments Discovery HR-3 Rheometer using an 8mm Aluminum Peltier Plate. Experiments were run at 25 ºC at 1.0 % strain from 0.1 to 500 rad/s to obtain G' and G''.

Centrifugation was performed using a benchtop centrifuge - Mini mouse II by Denville.

Targeted LCMS of PFOA, PFHxA, and GenX: Water samples were stored under refrigeration until analysis. A 180 µL aliquot of sample and 20 µL of stable isotope-labeled analogues (Wellington Labs, Guelph, CA, product numbers MPFAC-C-ES and M3HFPO-DA) were transferred to polypropylene autosampler vials and closed with caps fitted with silicone septa. No other processing was done as per a direct injection method by M. Sun et al.[1]

Analysis of target compounds was performed using an Accela HPLC system coupled to a TSQ-Quantum Ultra triple-quadrupole mass analyzer (Thermo Scientific, San Jose, CA) operated in negative ion mode. Analytes were separated on a 2.1 × 50 mm Sunfire C18 3.5 µm column (Waters Corporation, Milford, MA) with gradient elution at a flow rate of 350 µL per min. Binary mobile phase consisted of 95:5:water:methanol containing 2 mM ammonium acetate (A) and 5:95:water:methanol containing 2 mM ammonium acetate (B). Composition started at 25% B, was held for 0.5 min., increased linearly to 90% B over 2 min., was held at 90% B for 1.5 min., decreased linearly to 25% B over 0.1 min., and held at 25% B for 0.9 min for column equilibration. Mass spectrometer parameters were as follows: spray voltage of 3000 V, vaporizer temperature of 150 ˚C, sheath gas flow rate 40, auxiliary gas flow rate 20, capillary temperature of 225 ˚C, argon collision gas pressure of 1.0 mTorr, 0.05 sec per scan, quadrupole 1 resolution of 0.5 amu, quadrupole 3 resolution of 0.7 amu and collision energy 10 eV. Linear or quadratic calibration curves using the analyte to internal standard ratio were used to calculate analyte amounts. Calibration points were 2, 10, 50, 200, and 1000 pg analyte versus 200 pg internal standard for PFCAs and PFASs.

Targeted Analysis of 21 PFAS and Nontargeted Analysis: LCMS grade acetonitrile was purchased from Fisher Scientific (Fair Lawn, NJ) and methanol from Honeywell - Burdick & Jackson (Muskegon, MI). ACS reagent ammonium acetate was purchased from Sigma-Aldrich (St. Louis, MO). In-house deionized water was used. Native standard solution PFAC-MXA (2000 ng/mL) and mass-Labelled PFC extraction standard solution MPFAC-C-ES (2000 ng/mL) were purchased from Wellington Laboratories (Ontario, Canada). GenX native standard was purchased from SynQuest Laboratories (Alachua, FL). All other perfluoroalkyl ether acid (PFEA) native standards were donated by The Chemours Company (Wilmington, DE). Analyte-

specific information including mass transitions are listed in Table S1. Methods for nontargeted analysis and 21 PFAS targeted analysis are described in Section 6.2 and 7.

Table S1. List of Target PFAS Analytes

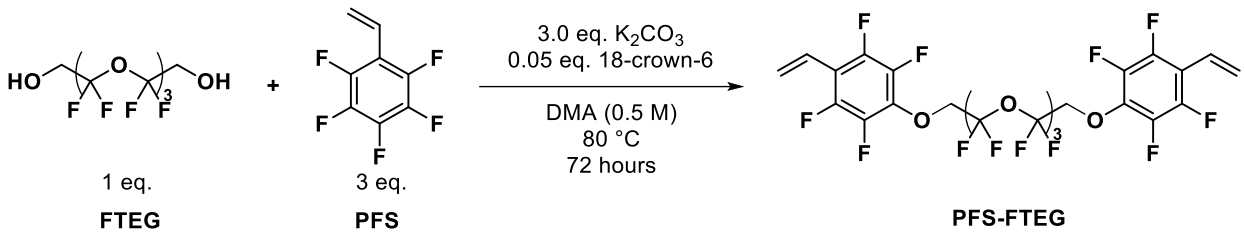
Analyte	Acronym	CAS #	Exact Mass (g/mol)	Acquisition Window (min)	MS/MS Transition (*m/z*)	Collision Energy (V)	Min Dwell Time (ms)	RF Lens (V)	Internal Standard	Detection Limit (pg on column)
Perfluoroalkylcarboxylic Acids (PFCA)										
Perfluorobutanoic acid	PFBA	375-22-4	213.9865	0 - 4.0	213 → 169	8.66	16.306	59	M4PFBA	2
Perfluoropentanoic acid	PFPeA	2706-90-3	263.9833	3.8 - 5.2	263 → 219	7.91	2.719	65	M5PFPeA	0.5
Perfluorohexanoic acid	PFHxA	307-24-4	313.9801	4.5 - 5.7	313 → 269	8.37	2.719	75	M5PFHxA	0.25
Perfluoroheptanoic acid	PFHpA	375-85-9	363.9769	4.7 - 5.7	363 → 169 363 → 319	16.54 8.71	2.719	84	M4PFHpA	0.1
Perfluorooctanoic acid	PFOA	335-67-1	413.9737	5.0 - 6.0	413 → 169 413 → 369	17.26 9.25	2.719	91	M8PFOA	0.5
Perfluorononanoic acid	PFNA	375-95-1	463.9705	5.1 - 6.1	463 → 219 463 → 419	15.95 9.68	2.719	103	M9PFNA	1
Perfluorodecanoic acid	PFDA	335-76-2	513.9673	5.3 - 6.3	513 → 269 513 → 469	16.88 10.14	3.155	109	M6PFDA	0.25
Perfluoroalkylsulfonates (PFSA)										
Potassium perfluorobutanesulfonate	PFBS	29420-49-3	337.9062	4.5 - 5.5	299 → 80 299 → 99	32.67 28.88	2.719	168	M3PFBS	0.5
Sodium perfluorohexanesulfonate	PFHxS	82382-12-5	421.9258	5.0 - 6.0	399 → 80 399 → 99	37.31 34.78	2.719	222	M3PFHxS	1
Sodium perfluorooctanesulfonate	PFOS	4021-47-0	521.9194	5.1 - 6.5	499 → 80 499 → 99	41.18 40.55	2.719	299	M8PFOS	2
Perfluoroalkyl Ether Acids (PFEA)										
Difluoro(perfluoromethoxy)acetic acid	PFMOAA	674-13-5	179.9846	0 - 4.0	179 → 85	10.39	16.306	65	MPFBA	0.25
Perfluoro-2-(perfluoromethoxy)propanoic acid	PMPA	13140-29-9	229.9814	0.8 - 4.5	185 → 85 185 → 119	14.56 9.76	14.96	68	MPFBA	2

Perfluoro-3,5-dioxahexanoic acid	PFO2HxA	39492-88-1	245.9763	3.7 - 5.1	201 → 85 201 → 135	13.3 9.04	3.817	70	M5PFPeA	1
1,1,2,2-Tetrafluoro-2-(1,2,2,2-tetrafluoroethoxy)ethane-1-sulfonic acid	NVHOS	801209-99-4	297.9546	4.0 - 5.3	297 → 80 297 → 135	34.82 26.27	2.719	170	M5PFPeA	1
2,3,3,3-Tetrafluoro-2-(pentafluoroethoxy)propanoic acid	PEPA	267239-61-2	279.9782	4.0 - 5.3	235 → 119 235 → 135	8.96 15.19	2.719	71	M5PFPeA	0.25
Perfluoro-3,5,7-trioxaoctanoic acid	PFO3OA	39492-89-2	311.9680	4.6 - 5.6	311 → 85 311 → 151	10.9 5.25	2.719	49	M5PFHxA	0.5
Perfluoro-2-methyl-3-oxahexanoic acid	HFPO-DA or GenX	13252-13-6	329.9750	4.6 - 5.6	285 → 169 285 → 185	5.34 16.92	2.719	48	M5PFHxA	1
Perfluoro-3,5,7,9-butaoxadecanoic acid	PFO4DA	39492-90-5	377.9597	4.9 - 5.9	377 → 85 377 → 151	11.36 5.25	2.719	58	M8PFOA	2
2,2,3,3-Tetrafluoro-3-{[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxy}propanoic acid	HydroEve	773804-62-9	427.9730	4.9 - 5.9	427 → 283	11.7	2.719	106	M8PFOA	0.5
1,1,2,2-Tetrafluoro-2-{[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxy}ethane-1-sulfonic acid	Nafion Byproduct 2	749836-20-2	463.9399	5.1 - 6.1	463 → 263	26.95	2.719	168	M9PFNA	0.1
Perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	PFO5DA	39492-91-6	443.9515	5.1 - 6.1	443 → 85 443 → 151	12.88 5.25	2.719	75	M9PFNA	1
Internal Standards										
Perfluoro-n-[$^{13}C_4$]butanoic acid	M4PFBA	n/a	218.0001	0 - 4.0	217 → 172	8.75	16.306	60	n/a	n/a
Perfluoro-n-[$^{13}C_5$]pentanoic acid	M5PFPeA	n/a	269.0003	3.8 - 5.2	268 → 223	8.12	2.719	69	n/a	n/a
Sodium perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	M3PFBS	n/a	324.9424	4.5 - 5.5	302 → 80 302 → 99	32.3 29.09	2.719	165	n/a	n/a
Perfluoro-n-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	M5PFHxA	n/a	318.9971	4.5 - 5.7	318 → 273	8.41	2.719	74	n/a	n/a

Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	M4PFHpA	n/a	367.9905	4.7 - 5.7	367 → 322	8.92	2.719	86	n/a	n/a
Perfluoro-n-[$^{13}C_8$]octanoic acid	M8PFOA	n/a	422.0009	5.0 - 6.0	421 → 376	9.42	2.719	95	n/a	n/a
Sodium perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonate	M3PFHxS	n/a	424.9360	5.0 - 6.0	402 → 80 402 → 99	36.84 35.2	2.719	225	n/a	n/a
Perfluoro-n-[$^{13}C_9$]nonanoic acid	M9PFNA	n/a	473.0011	5.1 - 6.1	472 → 427	9.59	2.719	105	n/a	n/a
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	M6PFDA	n/a	519.9877	5.3 - 6.3	519 → 474	10.05	3.155	114	n/a	n/a
Sodium perfluoro-1-[$^{13}C_8$]octanesulfonate	M8PFOS	n/a	529.9466	5.1 - 6.5	507 → 80 507 → 99	41.39 41.23	2.719	299	n/a	n/a

2. SYNTHESIS

2.1 Synthesis of Small Molecule and Oligomeric Starting Materials



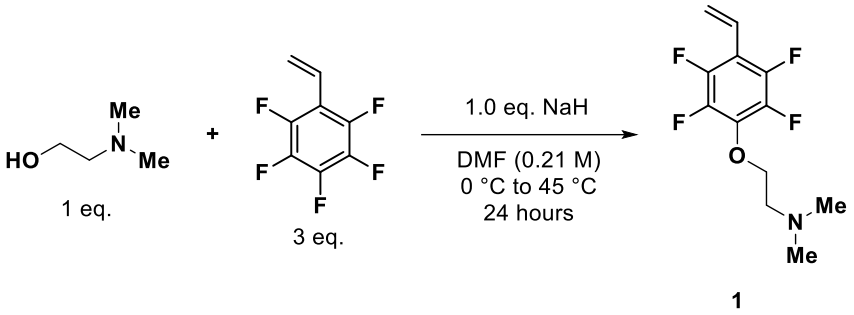
Scheme S1: Synthesis of perfluorostyrene-functionalized perfluoropolyether oligomers (PFS-PFPEs)

PFS-FTEG and **PFS-E10H** were prepared according to a modified literature procedure.[2]

For **PFS-FTEG:** To a 50 mL round-bottom flask was added 1H,1H,11H,11H-Perfluoro-3,6,9-trioxaundecane-1,11-diol (fluorinated tetraethylene glycol, FTEG) (2.00 g, 1.0 eq.), perfluorostyrene (2.84 g, 3.0 eq), potassium carbonate (2.02 g, 3.0 eq), and 18-crown-6 (0.05 eq, 62 mg). The reagents were dissolved in 10 mL N,N-dimethylacetamide. The mixture was sparged under N_2 for 10 minutes, then heated to 80 °C for 72 hours, followed by dilution in H_2O and liquid–liquid extraction with diethyl ether. The product was concentrated via rotary evaporation, followed by drying *in vacuo* to remove any additional perfluorostyrene. The product was collected as a yellow oil (2.0 g, 53%). ^{1}H NMR (400 MHz, Acetone) δ 6.68 (dd, *J* = 18.0, 11.9 Hz, 2H), 6.05 (dq, *J* = 18.1, 0.9 Hz, 2H), 5.76 (d, *J* = 11.9 Hz, 2H), 4.92 (t, *J* = 9.0 Hz, 4H). ^{19}F NMR (377 MHz, Acetone) δ -78.92 – -79.46 (m), -88.97 – -89.79 (m), -146.22 – -146.38 (m), -159.00 (dd, *J* = 20.5, 8.7 Hz). ^{13}C NMR (101 MHz, Acetone) δ 147.02, 144.55, 143.26, 140.80, 136.11, 125.51, 124.00, 122.73, 122.48, 119.96, 113.23 (t, *J* = 14.3 Hz), 72.43 (t, *J* = 33.0 Hz). **IR (neat, ATR, cm^{-1}):** 1628, 1458, 1432, 1410, 1503, 1489, 1271, 1183, 1141, 1109, 1088, 1020, 958, 973, 936, 912, 874.Size Exclusion Chromatography: FTEG: M_n = 400 g/mol, $Đ$ = 1.01. PFS-FTEG: M_n = 320 g/mol, $Đ$ = 1.01.

PFS-E10H was prepared in the same manner, however the PFPE was Fluorolink E10H. The product was precipitated directly into H_2O before drying *in vacuo*, and it was collected as a pale oil (2.8 g, 90%). **^{1}H NMR (600 MHz, Acetone)** δ 6.67 (dd, *J* = 18.0, 11.9 Hz, 2H), 6.01 (d, *J* = 18.1 Hz, 2H), 5.70 (d, *J* = 12.1 Hz, 2H), 4.47 (dd, *J* = 34.3, 5.9 Hz, 4H), 4.33 – 3.94 (m, 12H), 3.66 (d, *J* = 1.2 Hz, 17H). **^{19}F NMR (564 MHz, Acetone)** δ -52.29 (d, *J* = 254.4 Hz), -54.07, -55.45 (d, *J* = 408.4 Hz), -78.54, -80.71, -89.40 (d, *J* = 189.5 Hz), -90.87 (d, *J* = 436.4 Hz), -92.27 (d, *J* = 166.5 Hz), -147.17 (d, *J* = 40.0 Hz), -159.64. **^{13}C NMR (101 MHz, Acetone)** δ 147.13, 144.68, 143.38, 122.97, 122.74, 122.20, 121.44, 119.47, 118.72, 117.96, 117.04, 116.74, 116.00, 115.48, 115.09, 114.71, 114.61, 114.20, 112.23, 111.36, 75.05, 75.01, 73.62, 72.60, 72.29, 71.44, 71.28, 71.22, 70.97, 70.35, 61.95. **IR (CH_2Cl_2, ATR, cm^{-1}):** 1649, 1503, 1490, 1191,

1069, 971, 935, 844. **Size Exclusion Chromatography:** Fluorolink E10H: M_n = 1000 g/mol, $Đ$ = 1.06. PFS-E10H: M_n = 930 g/mol, $Đ$ = 1.08.



Scheme S2: Synthesis of Compound 1

1 was prepared according to literature procedures for similar compounds.[3]

In a flame-dried 200 mL round bottom flask, 2-(dimethylamino)ethanol (1 eq., 2.00 g) was diluted with N,N-Dimethylformamide (30mL) and cooled to 0 ºC. NaH in 40 mL DMF (1 eq., 538 mg) was added over 20 minutes. After H_2 was released completely, pentafluorostyrene (1 eq., 4.35g) in 20mL of DMF was added in over 10 min. The reaction mixture was heated to 45 ºC for 24 hours, cooled to room temperature, and subsequently quenched via slow addition of 50 mL saturated aqueous NH_4Cl. The organic products were extracted into diethyl ether, which was washed with water, brine, and dried using $MgSO_4$. The crude product was purified by Flash Chromatography (1:9 MeOH: DCM). After rotary evaporation, Compound **1** was dried *in vacuo* as a brown oil (3.8g, 64% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.63 (ddd, *J* = 18.0, 11.9, 1.5 Hz, 1H), 6.03 (d, *J* = 18.0 Hz, 1H), 5.63 (d, *J* = 11.9 Hz, 1H), 4.30 (t, *J* = 5.7 Hz, 2H), 2.73 (t, *J* = 5.6 Hz, 2H), 2.34 (d, *J* = 1.4 Hz, 6H). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -145.04 (dd, *J* = 20.9, 8.7 Hz), -145.41, -158.07 (dd, *J* = 20.7, 8.7 Hz). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 122.49, 122.41, 122.33, 122.25, 111.03, 99.18, 73.00, 58.81, 45.87. **IR (CH_2Cl_2, ATR, cm^{-1}):** 2951, 2778, 1647, 1502, 1487, 1429, 1407, 1367, 1265, 1209, 1145, 1120, 1080, 969, 932, 852. **HRMS (ES+)** Exact mass calculated for $C_{12}H_{13}F_4NO$ [M+H]+, 264.1006. Found 264.1009.

2.2 Synthesis of Ionic Fluorogels

An illustrative procedure for the synthesis of Ionic Fluorogel **IF-3** is given below:

Thermally-initiated copolymerizations:

To a 20 mL scintillation vial with green top cap equipped with magnetic stir bar was added **PFS-E10H** (0.4 g), **PFS-FTEG** (0.4 g), **1** (0.2 g), azobisisobutyronitrile (10 mg) and trifluoroethanol (1.0 g). The vial was closed, nitrogen was passed through the solution for 5 minutes, and the solution was heated at 70 °C overnight while stirring at 200-300 rpm. The resulting material was a brittle gel. After the reaction, the mixture was cooled to room temperature and the gel was ground to fine powder. The resulting powder was suspended in trifluoroethanol (5 mL) and iodomethane (1 mL), then stirred for 24 hours. The gel was transferred to a paper teabag and purified via Soxhlet extraction in ethanol for 24 hours. Finally, the gel was dried in a vacuum oven at 50 ºC for 48 hours. **IF-3** was collected as a pale yellow powder (0.65 g, 65% yield). The gel was passed through sieves, and particles from 75 – 125 μm were collected for use in PFAS remediation experiments. **IR (neat, ATR, cm^{-1}):** 2918, 1493, 1189, 1067, 959.

Other formulations of Ionic Fluorogels containing varied amounts of **PFS-E10H, PFS-FTEG,** and **1** were prepared by adding those amounts following the above procedure. For instance, **IF-1** was synthesized using 0.8 g **PFS-E10H,** 0 g **PFS-FTEG**, and 0.2 g **1**. Other Ionic Fluorogels including perfluorostyrene as a fourth comonomer were synthesized in the same fashion. These IF were named according to their monomer composition as IF-X-P-Y-Z, where X = wt % **PFS-E10H**, P = wt % **PFS**, Y = wt % **PFS-FTEG**, and Z = wt % **1**.

Photoinitiated copolymerizations:

To a 20mL scintillation vial was added **PFS-E10H** (200 mg, 40 wt%), **PFS-FTEG** (200 mg, 40 wt%), and **1** (50 mg, 20 wt%), 1-hydrocyclohexyl phenyl ketone (50 mg, 2 wt%) and trifluoroethanol (12 mg). The solution was vortexed 1 minute to ensure homogeneity. The solution was pipetted onto a glass slide which had been pre-treated with Rain-X, and washed with water, then acetone, and dried. The film was cured 1 hour under 365nm irradiation under N_2 atmosphere. The film was removed from the slide with a razor blade, then 8 mm discs were punched using 8 mm biopsy punches. The resulting **IF-3** gels were submerged in 2 M iodomethane in trifluoroethanol solution 24 hours. Then the discs were washed via soaking in 0.5 M aqueous NaCl.

IF-20+ was synthesized according to previous literature.[4]

3. CHARACTERIZATION OF IONIC FLUOROGELS

3.1 Swelling Ratio

Photocured discs of IF were swollen in DI H_2O 24 hours, massed, then dried under vacuum and massed again. This analysis was completed in triplicate for each IF formulation. Swelling of the IF was determined using the swelling ratio:

$$Swelling\ Ratio = \frac{mass\ of\ swollen\ disc}{mass\ of\ dried\ disc}$$

3.2 Thermogravimetric Analysis

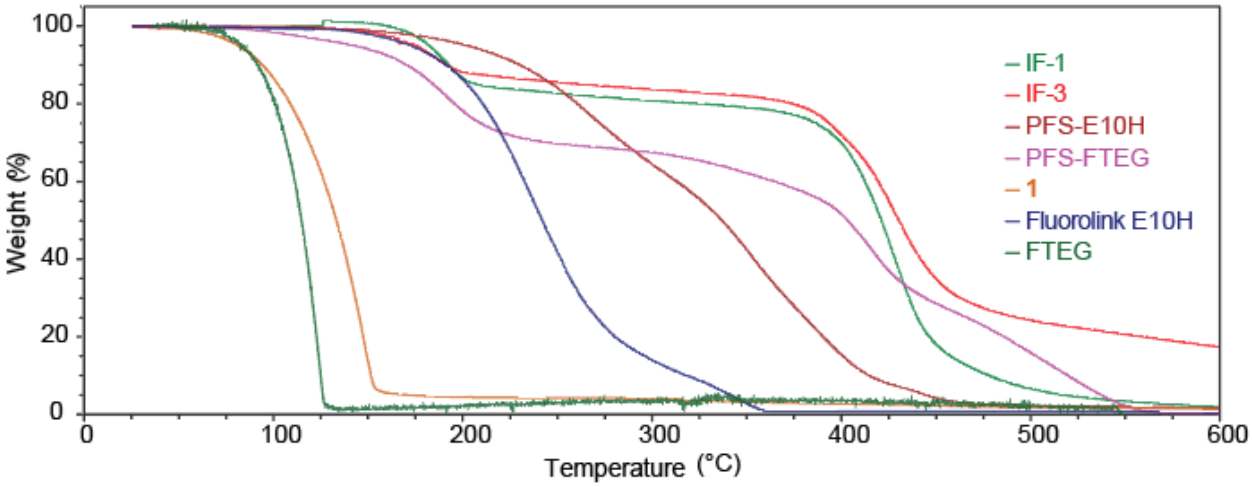


Figure S1: Thermogravimetric analysis (rate: 10º C/min) of Ionic Fluorogels, monomers, and perfluoropolyether starting materials.

3.3 Differential Scanning Calorimetry

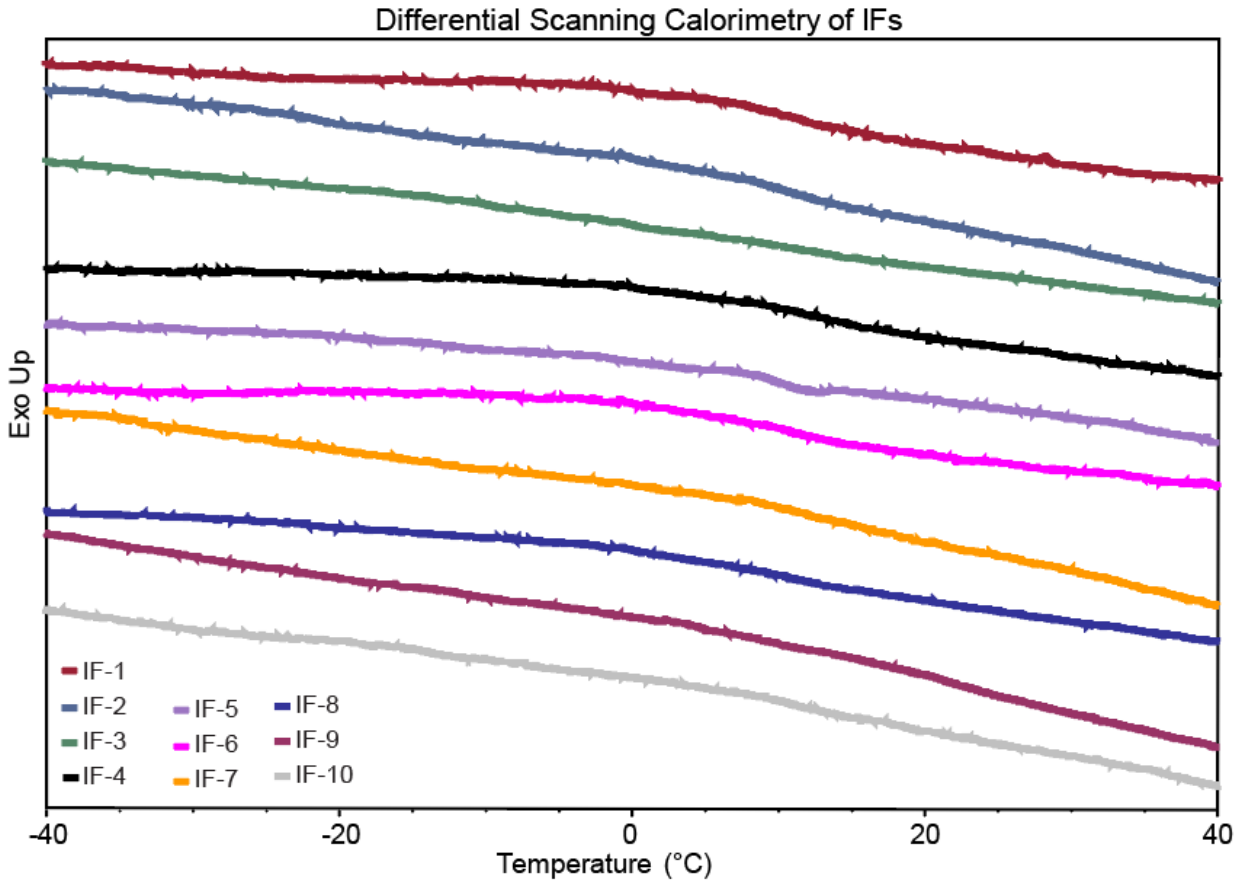


Figure S2: Differential Scanning Calorimetry (rate: 10 ºC/min, second heating cycle) of Ionic Fluorogels.

4. BATCH ADSORPTION STUDIES

4.1 Equilibrium Adsorption Studies

The batch adsorption studies of mixtures of PFAS (PFOA, PFHxA and GenX) were performed in a 1L polypropylene bottle equipped with a magnetic stir bar. The mixture was stirred on a stir plate at room temperature and at 700 revolution per minute (rpm).

To a 1L deionized water added sodium chloride (200 mg) and humic acid (Sigma-Aldrich®, Saint Louis, MO) (20 mg) and stirred overnight. To this mixture was added vacuum dried Ionic Fluorogel (10 mg L^{-1}) and stirred at room temperature for 3h. A stock solution of PFAS (100 μL, 10 μg/mL) was spiked to the mixture to create an initial concentration of 1 μg/L of each PFAS. This mixture was stirred for 21h after which an aliquot of about 10 mL was withdrawn and filtered through either 0.2 μm PTFE or 0.45 μm cellulose acetate filter. The first 5 mL was drained to avoid any electrostatic effect from the filter and the remaining 5 mL was collected for LCMS analysis. Control experiments to account for PFAS losses during handling were performed under identical conditions in the absence of sorbent. This batch experiment was performed in triplicate.

The efficiency of PFAS removal by sorbents was determined by the following equation

$$\% \text{ PFAS removal} = \frac{C_0 - C_t}{C_0} \times 100$$

C_0 (μg L^{-1}) = Initial concentration of PFAS

C_t (μg L^{-1}) = Residual concentration of PFAS

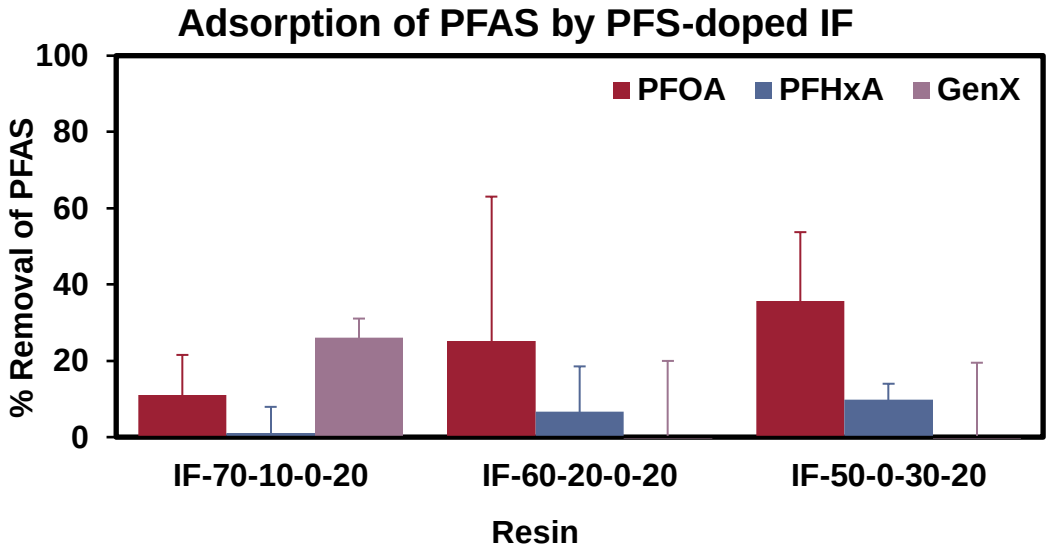


Figure S3: Equilibrium PFAS removal efficiency by various compositions of perfluorostyrene-doped IF. IFs denoted IF-X-P-Y-Z, where X = wt % PFS-E10H, P = wt % PFS, Y = wt % PFS-FTEG, and Z = wt % **1**. Water constituents: NaCl (200 ppm) and humic acid (20 ppm). PFAS: PFOA, PFHxA and GenX (each 1

μg/L). Sorbent dosage: 10 mg/L. Equilibrium time: 21 h. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

4.2 GenX Sorption Kinetics

High concentration (200 μg/L): The sorption kinetic experiments were performed in 125 mL polypropylene bottle equipped with a magnetic stir bar. The experiments were performed at room temperature on a multi-position stirrer at 500 rpm. The sorbent dose was set at 10 mg/L with total operating volume of 100 mL. The fluorogel and water mixture was stirred for 3 h with occasional sonication to disperse the sorbent before being spiked with GenX stock to create an initial concentration of 200 μg/L. About 1 mL aliquot was taken at each predetermined time intervals (0.5, 1, 5, 10, 30, 60, mins and 21, 48 and 72 h). The aliquots were centrifuged for 15 minutes and the supernatant was analyzed by LCMS to determine the residual GenX concentration. Control experiments to account for GenX losses during handling were performed under identical condition in the absence of sorbent. This batch kinetics experiment was performed in triplicate.

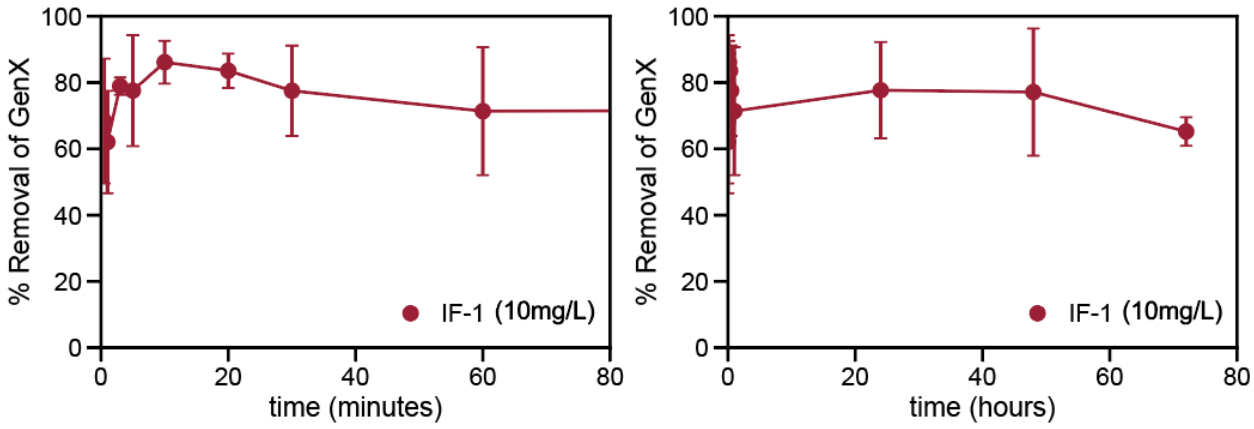


Figure S4: Kinetics of GenX (200 μg/L) sorption by IF-1 over 60 minutes (left) and 72 hours (right). Sorbent dosage: 10 mg/L. The data points in the figure are an average of 3 experiments. Error bars: standard deviation of 3 experiments.

Low concentration (1 μg/L): The sorbent dose was set to 10 mg/L with total operating volume of 100 mL. IF-1 was added to 100mL DI water in a polypropylene bottle. The mixture was stirred at 500 rpm for 3 h before being spiked with GenX stock to create an initial concentration of 1 μg/L. About 1 mL aliquot was taken at each predetermined time intervals (0.5, 1, 3, 5, 10, 20, 30, 60, 120, 240 mins and 21, 48 and 72 h). The aliquots were centrifuged for 15 minutes and the supernatant was analyzed by LCMS to determine the residual GenX concentration. Control experiments to account for GenX losses during handling were performed under identical condition in the absence of sorbent. This batch kinetics experiment was performed in triplicate.

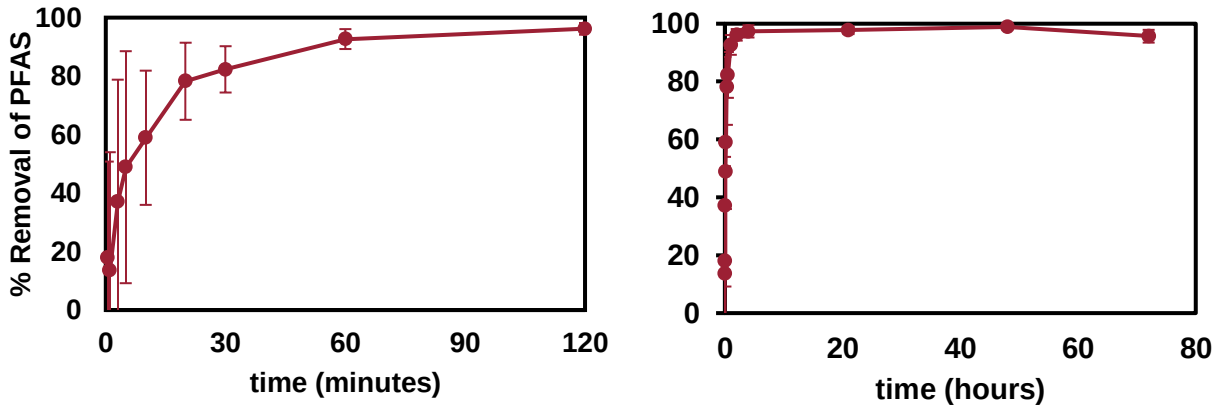


Figure S5: Kinetics of GenX (1 μg/L) sorption by IF-1 over 120 minutes (left) and 72 hours (right). Sorbent dosage: 10 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

The kinetics of sorption can be described with via the pseudo-second-order model below:[5]

$$q_t = \frac{1 k_2 q_e^2 t}{1 + k_2 q_e t}$$

q_t (mg g^{-1}) = Amount of GenX sorbed on the solid phase at time *t* (h)

k_2 (g mg^{-1} h^{-1}) = Rate of adsorption

q_e (mg g^{-1}) = Amount of GenX sorbed on the solid phase at equilibrium

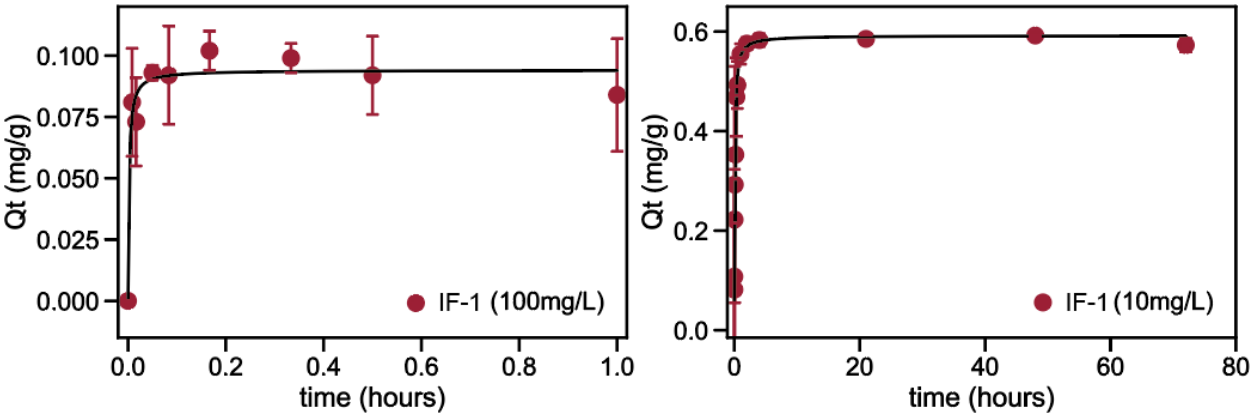


Figure S6: Pseudo-second-order sorption model of GenX ssorption by IF-1 at high (left) and low (right) concentrations. Left: [IF-1] = 100 mg/L, $[GenX]_0$ = 200μg/L. Right, [IF-1] = 10 mg/L, $[GenX]_0$ = 1μg/L.

Table S2: Pseudo-second-order sorption parameters for the sorption of GenX by IF-1.

[IF-1] (mg/L)	$[GenX]_0$ (μg/L)	q_e (mg/g)	k_2 (mg/g/h)	r^2
100	200	0.09 ± 0.03	5000 ± 2000	0.95
10	1	0.59 ± 0.01	22 ± 4	0.98

4.3 Binding Isotherm Studies

The batch isotherm studies were performed in 125 mL polypropylene bottles (100 mL operating volume) containing a magnetic stir bar on a multi-position stirrer at 23-25 °C at 500 rpm. The deionized water containing the ionic fluorogel sorbent (100 mg/L) was stirred for 3 h before the GenX addition. A stock solution of GenX was spiked to create initial concentrations of 0.2, 1, 5, 10, 20, 30 and 50 mg/L. The suspension was stirred for 21 h to reach equilibrium and an aliquot was taken in a centrifuge tube. The aliquots were centrifuged for 15 minutes and the supernatant from the top was taken for LCMS analysis. High concentration samples were serially diluted (5-10 mg/L diluted 20x and 20-50 mg diluted 100x) before LCMS analysis. Control experiments in the absence of sorbent were performed under identical conditions to account for handling losses. All the batch experiments were carried out in triplicate.

Langmuir sorption and Freundlich isotherm fits were generated by non-linear least square regression of the following equation.

Langmuir adsorption isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + C_e K_L}$$

q_e (mg g^{-1}) = Amount of PFAS sorbed on the solid phase at equilibrium
q_m (mg g^{-1}) = Maximum sorption capacity of sorbent at equilibrium
C_e (mg L^{-1}) = Residual PFAS concentration at equilibrium
K_L (L mg^{-1}) = Equilibrium constant

Freundlich adsorption isotherm:

$$q_e = K_F C_e^{\frac{1}{n}}$$

q_e (mg g^{-1}) = Amount of PFAS sorbed on the solid phase at equilibrium
C_e(mg^{-1} L^{-1}) = Residual PFAS concentration at equilibrium
K_F (mg g^{-1})(L mg^{-1})$^{1/n}$ = Freundlich constant.
n is the intensity of adsorption

Table S3: Langmuir and Freundlich parameters derived from nonlinear least-squares regression analysis of GenX binding to IF-1.

	Langmuir Fit			Freundlich Fit		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
IF-1	1.2 ± 0.5	280 ± 20	0.96	140 ± 20	4.2	0.90

5. SORPTION AND REGENERATION STUDIES

Ionic Fluorogel **IF-1** (20 mg) was suspended in 400mM ammonium acetate in 1:1 EtOH:H_2O (20 mL) followed by series of sonication and vortexing for 5 mins to disperse the adsorbent. The resulting suspension was passed through 20 mL syringe fitted with 0.45 μm PTFE filter (25 mm), additional water was used if necessary. This created a "packed bed" of IF-1 in the syringe filter.

Sorption experiment: A solution of GenX (10 mg L^{-1}, 20 mL) was passed through the filter over 2 mins and the resultant filtrate was collected in a polypropylene tube. The PTFE filter was washed by passing through deionized water (20 mL) to remove any trace of GenX solution. The change in GenX concentration in the filtrate was measured by LCMS.

Desorption experiment: The PTFE filter containing GenX was extracted by passing through 20 mL of a 1:1 EtOH:H_2O solution containing 400 mM ammonium acetate over 2 minutes. The concentration of extracted GenX was analyzed by LCMS. The PTFE filter was washed by passing through deionized water (20 mL) to remove any trace of methanolic solution left over and the residual deionized water was removed by vacuum suction.

The sorption-desorption cycle was extended to 5 cycles to demonstrate the recyclability of the ionic fluorogel without the loss of efficiency.

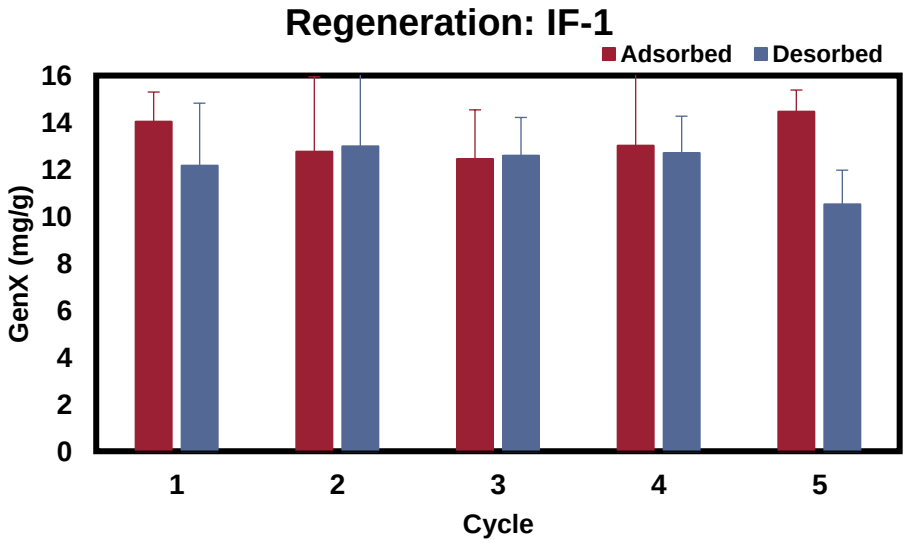


Figure S7: Regeneration and reuse of IF-1 with 400 mM ammonium acetate (1:1 EtOH:H_2O). Sorbent dosage: 20 mg; [GenX]: 10 mg/L, 20 mL. Extraction dosage: 20 mL.

6. DEGRADATION OF IONIC FLUOROGELS IN BASIC SOLUTION

6.1 Mass Loss Studies

Photocured discs of IF-1 and IF-20+[4] were prepared and dried 24h under vacuum. The average disc weight was 18.0 mg. The discs were pre-weighed and suspended in 2 mL alkaline solution for a defined period of time, then removed from the suspension, washed once with deionized H_2O, massed, dried, soaked in 400mM methanolic ammonium acetate solution over 2hr, washed with deionized H_2O, dried, and massed again. Discs were removed after 1, 2, 4, and 8 weeks. The alkaline solutions were composed of a glycine-$NaHCO_3$ buffer (pH 8.7) and a $NaHCO_3$-NaOH buffer (pH 11.7). Discs were incubated either at 23 ºC or 50ºC, and each experiment was run in triplicate. Swelling ratio was determined by the ratio of swollen to dried mass before washing with MeOH solution. % mass loss was determined from the initial and final (after MeOH wash) dry mass.

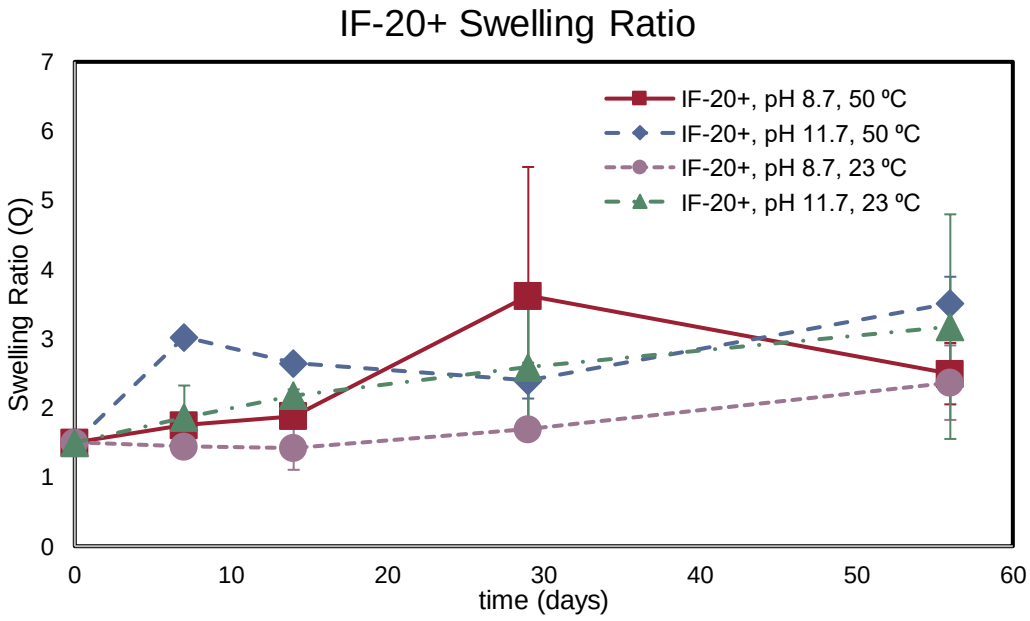


Figure S8. Swelling ratio (Q) of IF-20+ over 56 days. Discs were soaked either in pH 8.7 or 11.7 buffer. Error bars: standard deviation of 3 experiments.

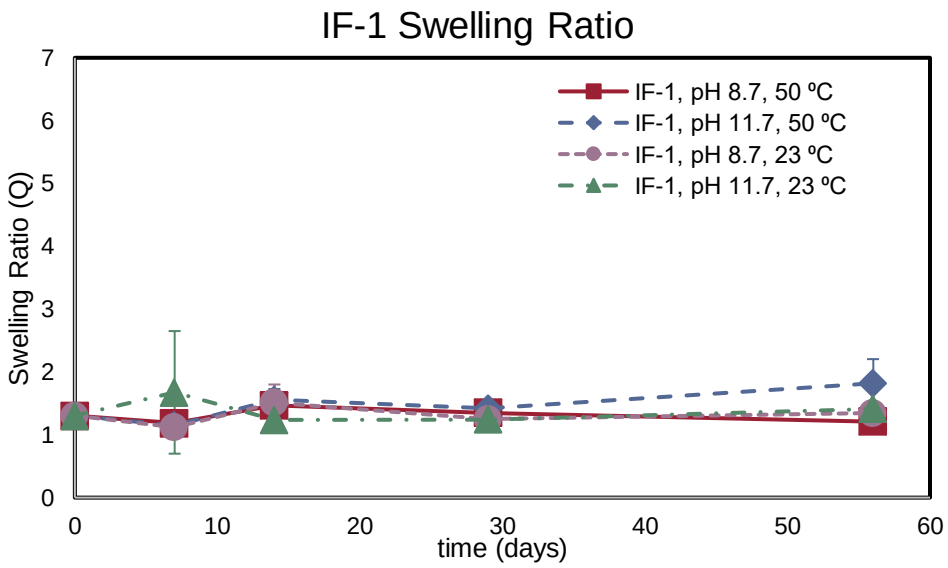


Figure S9. Swelling ratio (Q) of IF-1 over 56 days. Discs were soaked either in pH 8.7 or 11.7 buffer. Error bars: standard deviation of 3 experiments.

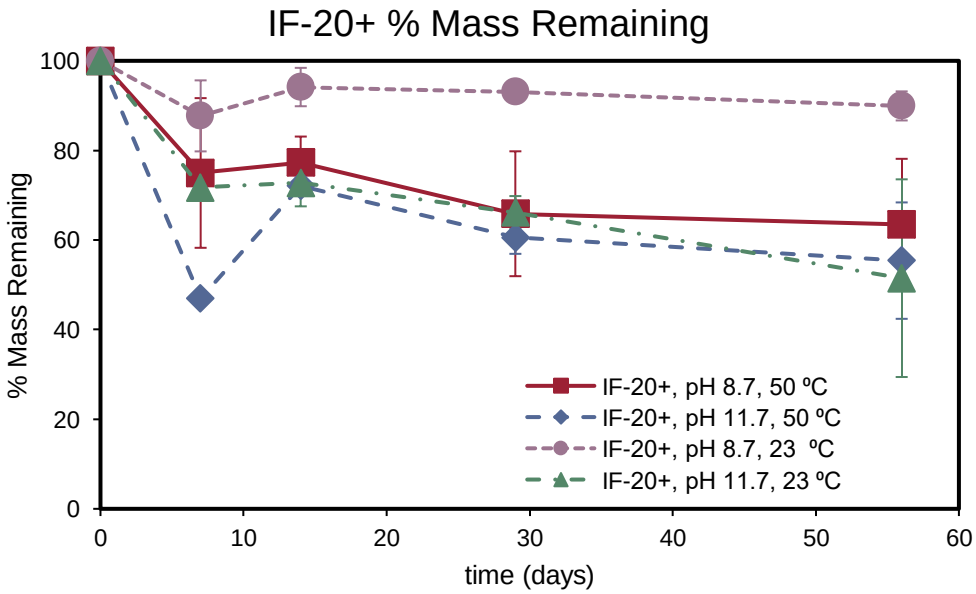


Figure S10. Mass loss over 56 days for IF-20+ after soaking in alkaline solutions. Error bars: standard deviation of 3 experiments.

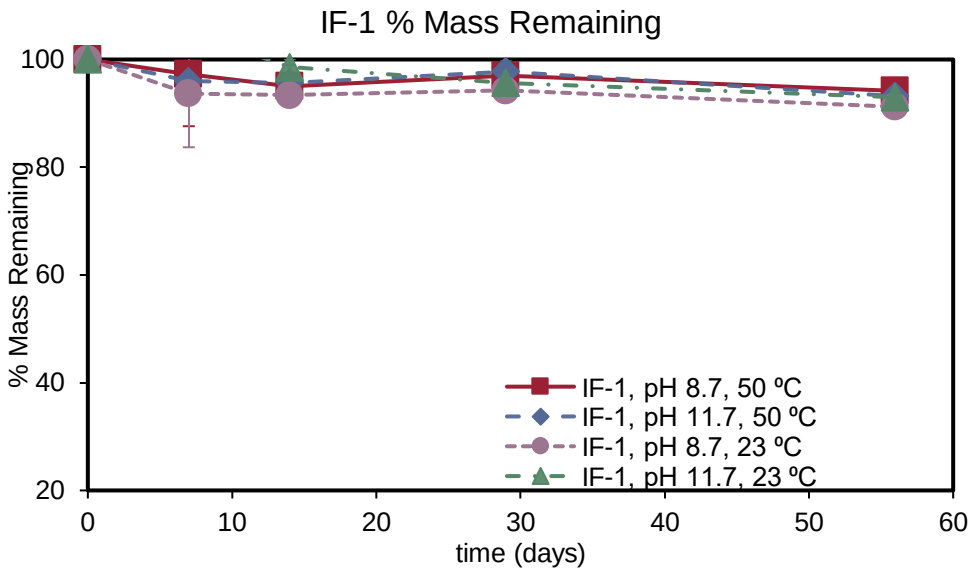


Figure S11. Mass loss over 56 days for IF-1 after soaking in alkaline solutions. Error bars: standard deviation of 3 experiments.

6.2 Nontargeted Analysis

The degradation media from the studies in **6.1** were submitted for nontargeted analysis to determine if any PFAS were leached upon resin degradation. Both the original degradation media (H_2O), and the extract upon methanol washing (MeOH) were submitted. Concurrently, Fluorolink MD700 was hydrolyzed to the resulting diol and submitted as a solution in MeOH to compare the resulting nontargeted analysis results.

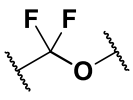
Fluorolink MD700 hydrolysis:
Fluorolink MD700 (500 mg) was dissolved in 2 mL trifluoroethanol in a 20 mL, PTFE-capped via. Then 1 mL NaOH (1M) was added. The reaction mixture was stirred overnight at 50 ºC. Upon cooling, more water was added to precipitate the hydrolyzed oligomer (Fluorolink MD700 – OH).

Nontargeted analyses (NTA) were performed using a Thermo Scientific Vanquish Flex coupled to a Thermo Scientific Orbitrap Fusion Tribrid Mass Spectrometer. Extract samples were analyzed in negative ion mode. Table S4 details Orbitrap parameters and acquisition settings.

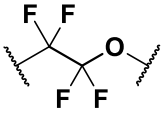
A reversed-phase separation occurred on a Waters ACQUITY UPLC BEH C18, 130Å, 1.7 µm, 2.1 mm X 50 mm column (Milford, MA) at 55 °C. Thermo Scientific Hypersil GOLD C18, 1.9 µm, 3 x 50 mm was used as a delay column. A binary gradient was used as shown in Table S5.

Duplicate extract samples and Fluorolink MD700 were collected and prepared in 1:3 methanol/deionzied water solution (v/v) in vials at a concentration of roughly 75 pg/µL. The first round of analyses with the extract samples (IF-20+ (H_2O), IF-20+ (MeOH), IF-1 (H_2O), and IF-1 (MeOH)) had an injection volume of 50 µL. The second round of analyses that compared IF-20+ (MeOH) to Fluorolink MD700-OH (MeOH) had an injection volume of 100 µL. Data from the analyses were processed in Thermo Scientific Compound Discoverer 3.2 software. Retention times were aligned, features merged, mass defect calculated, and gaps filled. Then results were filtered to include only masses with a mass defect greater than 0.80 (fractional mass). The final list of masses, their retention time, and peak areas were sorted in RStudio (Boston, MA) according to homologous series CF_2, CF_2O, and CF_2CF_2O.

Chemical Formula: $CF_2^{2\bullet}$
Exact Mass: 49.99



Chemical Formula: $CF_2O^{2\bullet}$
Exact Mass: 65.99



Chemical Formula: $C_2F_4O^{2\bullet}$
Exact Mass: 115.99

Figure S12: PFPE Repeat Units observed via Nontargeted analysis.

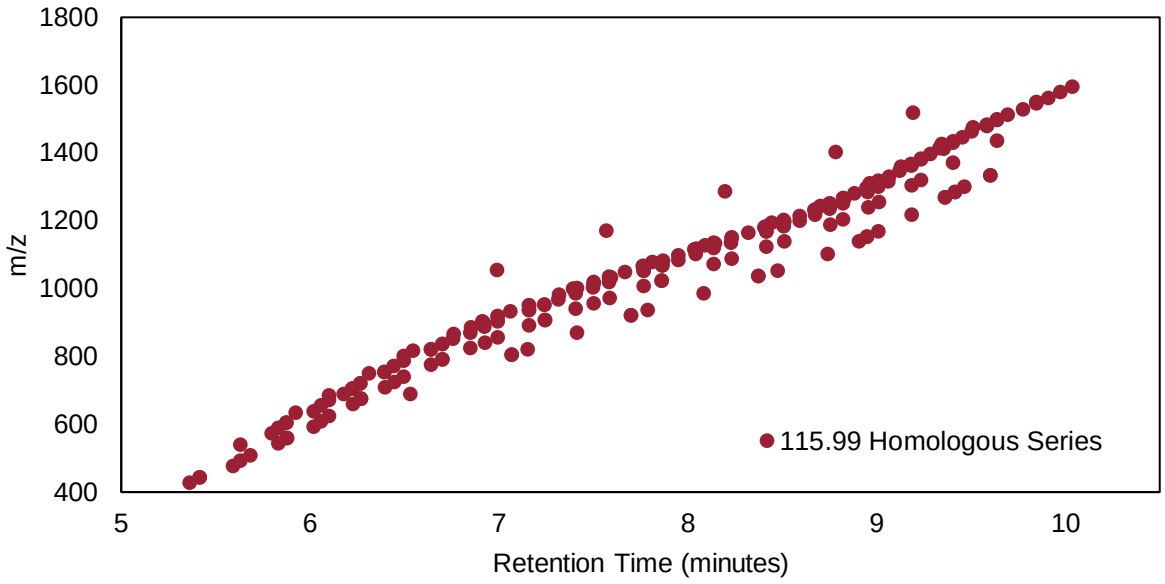


Figure S13. Identified Homologous Series varying by *m/z* = 115.99.

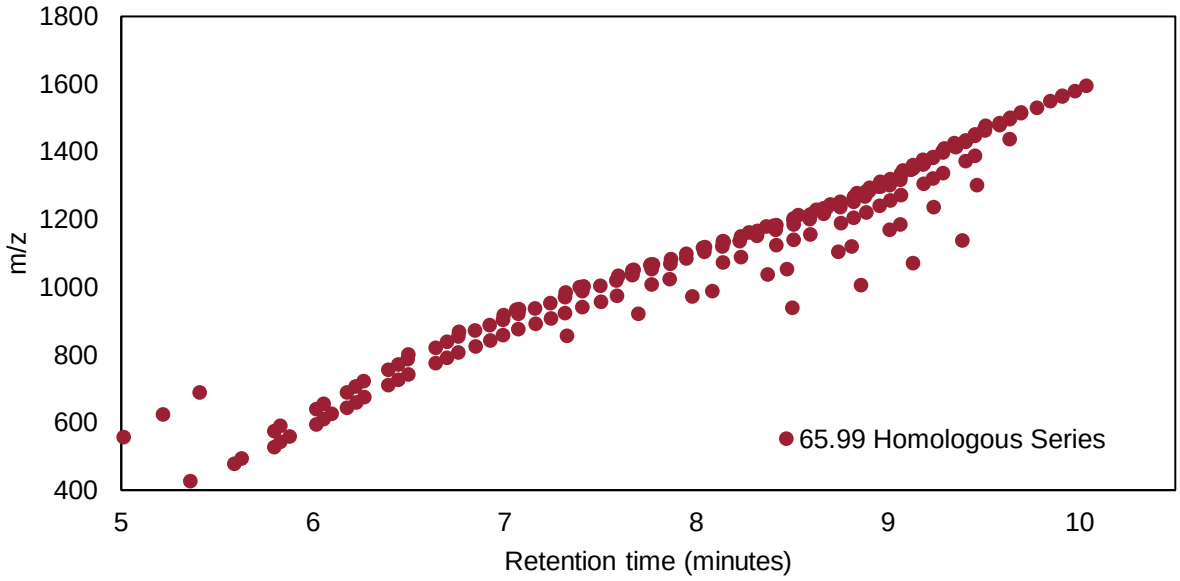


Figure S14: Identified Homologous Series varying by *m/z* = 65.99.

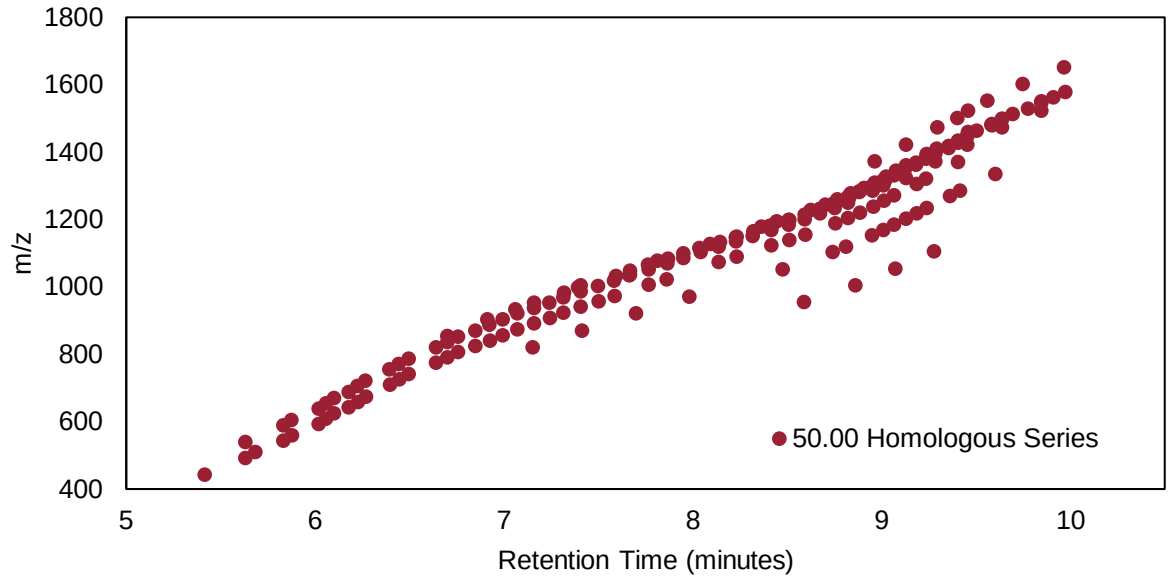


Figure S15: Identified Homologous Series varying by *m/z* = 50.00.

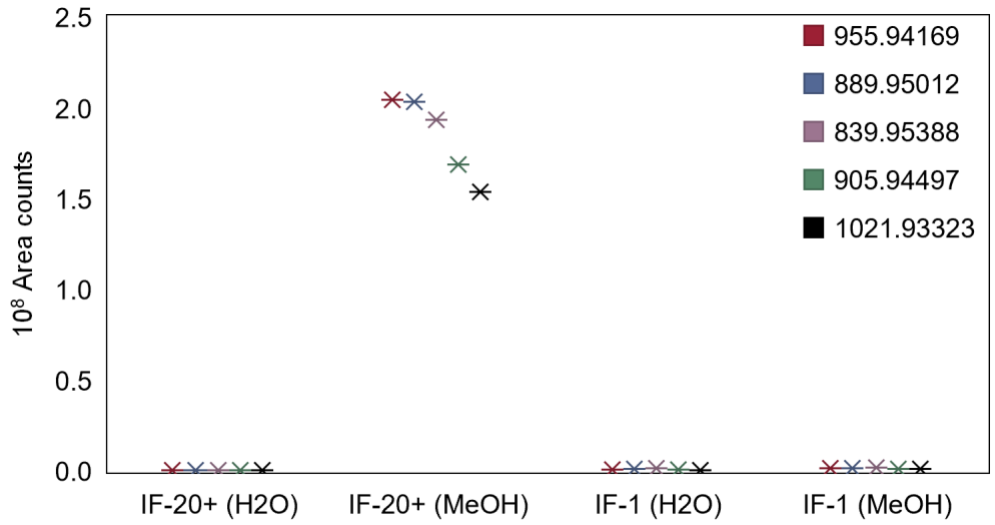


Figure S16: Comparison between averaged area counts of degradation media (H2O) and methanol extracts (MeOH) of IF-20+ and IF-1 subjected to nontargeted analysis. Duplicate samples.

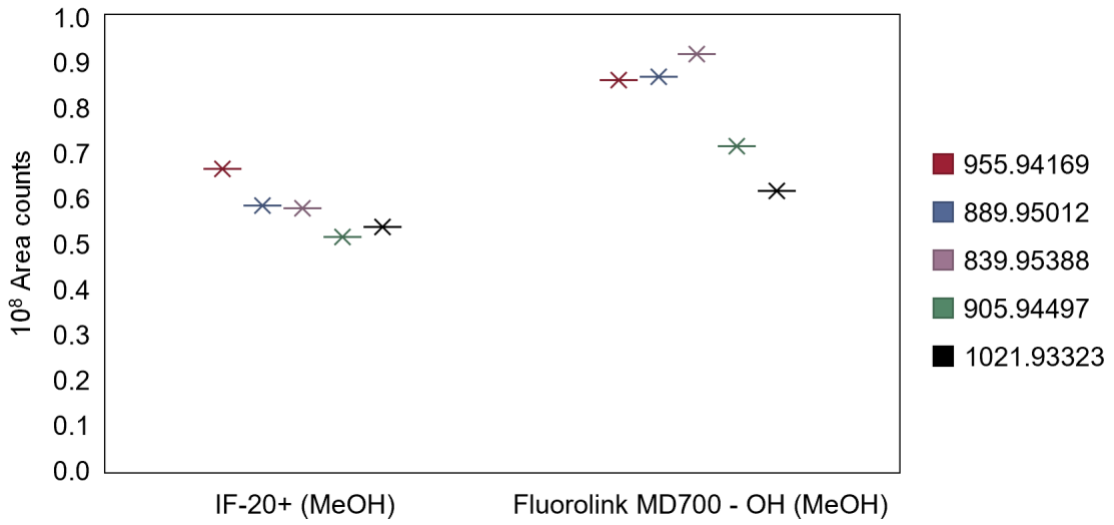


Figure S17: Comparison between averaged area counts of IF-20+ methanol extract versus Fluorolink MD700 – OH methanol extract. Duplicate samples.

Table S4: Orbitrap Parameters and Acquisition Settings for Nontargeted Analyses

Ion Source Type	H-ESI
Spray Voltage	Static
Negative Ion (V)	2000
Sheath Gas (Arb)	20
Aux Gas (Arb)	8
Sweep Gas (Arb)	4
Ion Transfer Tube Temp (°C)	325
Vaporizer Temp (°C)	100
Expected LC Peak Width (s)	8
Default Charge State	1
Internal Mass Calibration	EASY-IC™
External Mass Calibration	Pierce FlexMix Calibration Solution
Master Scan	Orbitrap (MS OT)
Cycle Time (sec)	0.35
Orbitrap Resolution	50000
Mass Range: Normal	Normal
Use Quadrupole Isolation	TRUE
Scan Range (*m/z*)	150-2000
RF Lens (%)	60
AGC Target	Standard
Maximum Injection Time Mode	Auto
Microscans	1

Data Type	Profile
Polarity	Negative
Filters	
Dynamic Exclusion	
Use Common Settings	TRUE
Exclude after n times	1
Exclusion duration (s)	6
Mass Tolerance	ppm
Low	10
High	10
Exclude Isotopes	TRUE
Perform dependent scan on single charge state per precursor only	TRUE
Exclude Within Cycle	TRUE
MIPS	
Apex Detection	
Expected peak width (FWHM, s)	8
Desired Apex Window (%)	30
Data Dependent Mode	Cycle Time
Time between Master Scans (sec)	0.35
Scan Event Type 1	ddMS^2 IT HCD
Intensity Threshold	5.00E+03
Scan Priority	2
Isolation Mode	Quadrupole
Allow earlier execution of lower priority scans when performed during parallelizable time	TRUE
Isolation Window (*m/z*)	1.6
Isolation Offset	Off
Activation Type	HCD
Collision Energy Mode	Assisted
HCD Assisted Collision Energies (%)	10, 25, 40
Detector Type	Ion Trap
Ion Trap Scan Rate	Normal
Mass Range	Normal
Scan Range Mode	Auto
AGC Target	Standard
Maximum Injection Time Mode	Auto
Microscans	1
Data Type	Profile

Scan Event Type 2	ddMS² OT HCD
Intensity Threshold	1.00E+06
Scan Priority	1
Isolation Mode	Quadrupole
Isolation Window (*m/z*)	1.6
Isolation Offset	Off
Activation Type	HCD
Collision Energy Mode	Assisted
HCD Assisted Collision Energies (%)	10, 25, 40
Detector Type	Orbitrap
Orbitrap Resolution	30000
Mass Range	Normal
Scan Range Mode	Auto
AGC Target	Standard
Maximum Injection Time Mode	Auto
Microscans	1
Data Type	Profile

Table S5: UHPLC Gradient Conditions

Time (min)	Flow (mL/min)	A% 95/5 Water/Acetonitrile + 2.5 mM Ammonium Acetate	B% 95/5 Acetonitrile/Water + 2.5 mM Ammonium Acetate	Curve
-1.5	Equilibration			
-1.5	0.5	100	0	5
-0.01	0.5	100	0	5
-0.01	0.35	100	0	5
0	0.35	100	0	5
1	0.35	100	0	5
2	0.35	90	10	5
5	0.35	20	80	5
8.5	0.35	0	100	5
9	0.5	0	100	5
9.99	0.5	0	100	5
10	0.5	100	0	5

7. BATCH EQUILIBRIUM SORPTION OF 21 PFAS IN SETTLED CONVENTIONAL WATER

The sorption kinetic experiments were performed in 100mL polypropylene bottles equipped with a magnetic stir bar. The experiments were performed at room temperature on magnetic stirrers. Settled conventional water (OWASA, Chapel Hill, NC, pH = 5.34, TOC ≤ 0.5 mg/L, conductivity 180 uS/cm) was spiked with a solution of 21 PFAS ($[PFAS]_0$ = 1 ug/L each). A 2 mL aliquot was taken immediately before adding 10 mg IF-1, and at time = 30, 60, 120, 240 minutes and 24 hours. The aliquots were filtered through a 0.45 um cellulose acetate syringe filter, then centrifuged 5 minutes. 1mL of supernatant was transferred to a clean 1.5mL snap-top tube, then analyzed by LCMS to determine the residual PFAS concentration. Controls were performed with either no PFAS, or no PFAS and no resin, just settled conventional water. This experiment was performed in triplicate. A double blank sample (75/25 deionized water/methanol, v/v) was analyzed between each set of triplicate or control sample.

All samples and calibration standards were spiked with mass-labelled standard solution for a final concentration of 1.1 pg/µL. A calibration curve was prepared with native standards in OWASA water at the following calibration points (pg of analyte per 100 µL): 0, 0.1, 0.25, 0.5, 1, 2, 5, 10, 25, 50, 100, 250. Table S1 provides the detection limits of each analyte. A 300 µL aliquot of sample or calibration standard combined with 100 µL of internal standard in methanol were prepared in vials for direct injection of 100 µL.

A reversed-phase separation occurred on a Waters ACQUITY UPLC BEH C18, 130Å, 1.7 µm, 2.1 mm X 50 mm column (Milford, MA) at 55 °C. Thermo Scientific Hypersil GOLD C18, 1.9 µm, 3 x 50 mm was used as a delay column. A binary gradient was used as shown in Table S5.

Targeted analyses of 21 PFAS were performed using a Thermo Vanquish Horizon ultra-high performance liquid chromatograph (UHPLC) coupled to a Thermo TSQ Quantis triple-quadrupole (QQQ) mass spectrometer. Twenty-one analytes and ten mass-labelled standards were monitored in negative ion mode. Table S1 lists analytes and their mass transitions. See Table S6 for additional QQQ parameters and acquisition settings.

Data were processed and peak areas integrated in Thermo Scientific Xcalibur Quan Browser 4.3. Native standard peak areas were matched against internal standard peak areas according to Table S1 and response ratios were calculated.

Table S6: QQQ Parameters and Acquisition Settings for Targeted Analyses

Ion Source Type	H-ESI
Spray Voltage	Static
Negative Ion (V)	3000

External Mass Calibration	Pierce Triple Quadrupole Calibration Solution Extended Mass Range
Sheath Gas (Arb)	50
Aux Gas (Arb)	10
Sweep Gas (Arb)	1
Ion Transfer Tube Temp (°C)	275
Vaporizer Temp (°C)	275
Mode	Selective Reaction Monitoring (SRM)
Polarity	Negative
Cycle Time (sec)	0.2
Use Calibrated RF Lens	False
Q1 Resolution (FWHM)	0.7
Q3 Resolution (FWHM)	1.2
CID Gas (mTorr)	1.5
Source Fragmentation	0
Chromatographic Peak Width (sec)	10

8. MINI-RAPID SMALL-SCALE COLUMN TESTS

Filtered settled conventional water (OWASA, Chapel Hill, NC, pH = 5.34, TOC ≤ 0.5 mg/L, conductivity 180 uS/cm) was spiked with PFHxA, PFOA, and GenX, each at a concentration of ~500 ng/L, and exposed to air at ambient temperature (~22ºC) overnight. Bench-scale mini-RSSCT experiments were performed in accordance with the protocols stipulated in ASTM 6586-03.[6] The respective mini-RSSCT columns were scaled from a representative pilot-scale column based on the constant diffusivity (CD) similitude approach in which intraparticle diffusivity is assumed constant with particle size. The CD approach has been validated for PFAS sorption via GAC[7–9] and IX[8,10] from PFAS-impacted waters with low levels of dissolved organic carbon, which is synonymous with the type of water used in this study. Four-channel, eight-roller peristaltic pumps (Cole-Parmer®, Vernon Hills, IL) with platinum-cured silicone tubing were used to distribute the influent and maintain a target flow rate of 3.5 mL/min throughout the duration of the experiments. Pulse dampeners were added before the columns to minimize pulsation. The columns were rinsed in an upflow configuration with methanol followed by laboratory-grade water (LGW) prior to operation.

The column-diameter-to-particle-size ratio was kept close to 50 to minimize channeling effects. Columns were PP with an inner diameter of 0.318 cm (Grainger, Lake Forest, IL). Granular sorbents were pulverized using a mortar and pestle, and sieved using U.S. standard testing sieves with mesh sizes of #200 and #230 (Sigma-Aldrich®, Saint Louis, MO) to obtain a desired mean particle diameter of 0.0685 mm. A predetermined amount of each sorbent was added into a PP centrifuge tube filled with LGW and sonicated for an hour. The sorbent was then loaded as a slurry into the column (1.353 cm bed depth) between two wetted pieces of glass wool (0.008 mm diameter, Fisher Scientific). The hydraulic loading rate (HLR) and empty bed contact time (EBCT) were 26.3 m/h and 0.03 min, respectively. Columns were operated in an upflow configuration. Effluent samples were collected in PP centrifuge tubes at predetermined intervals and stored at 4ºC prior to analysis. Experiments were performed in duplicate through ~150,000 bed volumes (BVs).

BVs were calculated using the parameters in Table S7 and the following equations.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p_{sc}}}{d_{p_{LC}}}\right]^2$$

$EBCT_{SC}$ (min): Empty-bed contact time in mini-RSSCT column

$EBCT_{LC}$ (min): Empty-bed contact time in pilot-scale column

$d_{p_{sc}}$ (mm): Mean particle diameter of sorbent in mini-RSSCT column

$d_{p_{LC}}$ (mm): Mean particle diameter of sorbent in pilot-scale column

$$\frac{V_{SC}}{V_{LC}} = \left[\frac{d_{p_{LC}}}{d_{p_{SC}}}\right] \times \frac{Re_{SC_{min}} \times Sc}{Re_{LC} \times Sc}$$

V_{SC} (m h^{-1}): Hydraulic loading rate (HLR) in mini-RSSCT column

V_{LC} (m h^{-1}): Hydraulic loading rate (HLR) in pilot-scale column

$Re_{SC_{min}}$(-): Reynolds number of flow in mini-RSSCT column

Re_{LC} (-): Reynolds number of flow in pilot-scale column

Sc (-): Schmidt number

Table S7: Summary of mini-RSSCT design parameters used in this study

Design Parameters	**Pilot-scale column**	**Mini-RSSCT column**
Mean particle diameter (mm)	0.675[a]	0.0685
Column diameter (cm), dia	366[b]	0.318
EBCT (min)	3[b]	0.03
HLR (m/h)	36.7[b]	26.3
Bed depth (cm), h = EBCT × HLR	183.5	1.353
Re (-)	5.13	0.56
Sc (-)	1,785	1,785
Re × Sc (-)	9,157	1,000
Bed volume (mL), BV = π × (dia/2)^2 × h	19,305,814	0.107
Flow rate (mL/min), Q = BV/EBCT	6,435,271	3.5
Bed volumes treated, n	180,000	180,000
Operating time (day) = (n × BV)/Q	375	3.86

[a] Based on Purolite's product data sheet

[b] Based on industrial standard

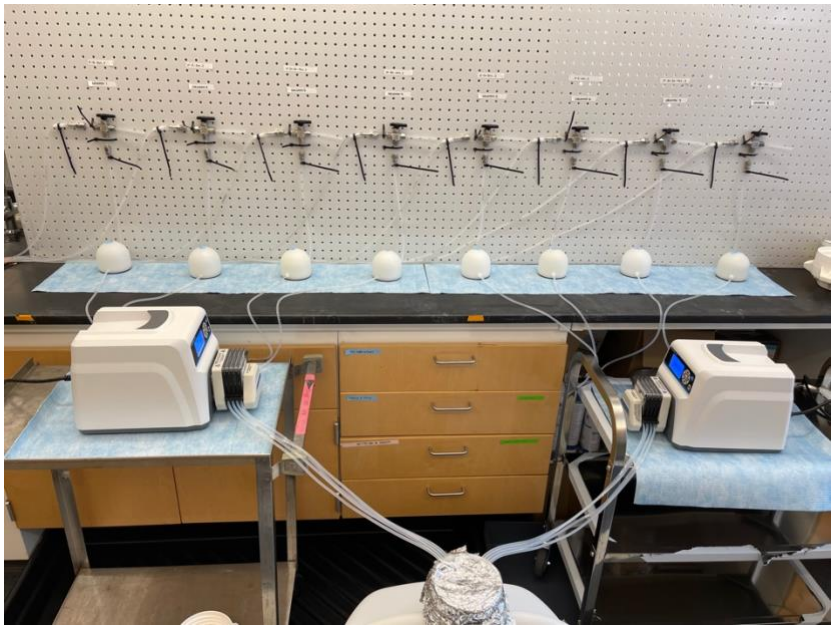


Figure S18: Mini-RSSCT experimental rig

9. SIZE EXCLUSION CHROMATOGRAMS

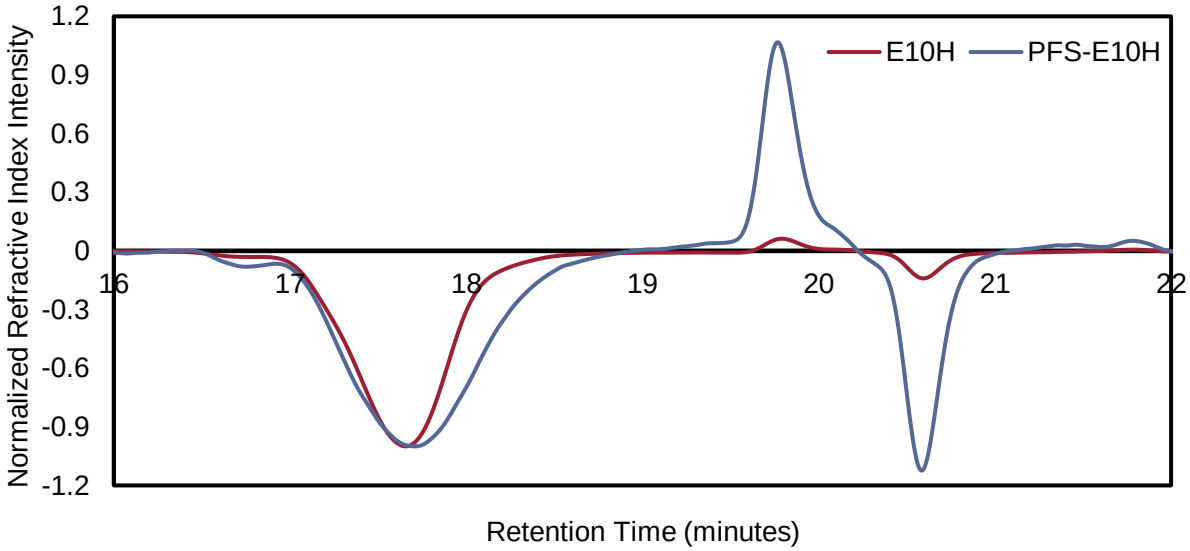


Figure S19: Size Exclusion Chromatography of Fluorolink E10H and PFS-E10H material in DMF. Starting material: M_n = 1000 g/mol, $Đ$ = 1.06. PFS-E10H: M_n = 930 g/mol, $Đ$ = 1.08.

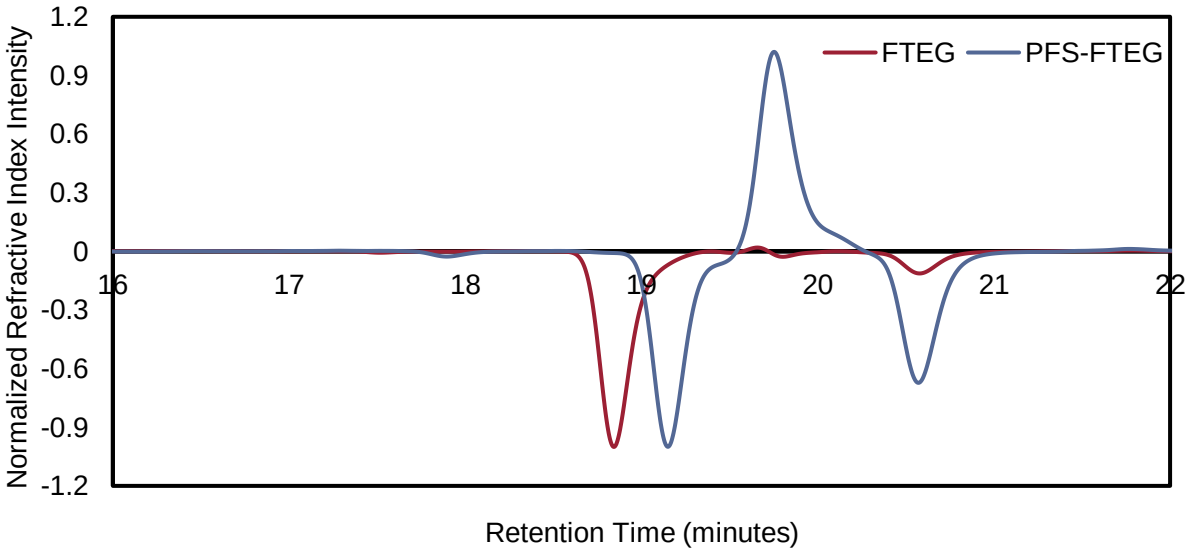


Figure S20: Size Exclusion Chromatogram of fluorinated tetraethylene glycol (FTEG) and PFS-FTEG material in DMF. Starting material: M_n = 400 g/mol, $Đ$ = 1.01. PFS-FTEG: M_n = 320 g/mol, $Đ$ = 1.01.

10. NMR SPECTRA OF NEW COMPOUNDS

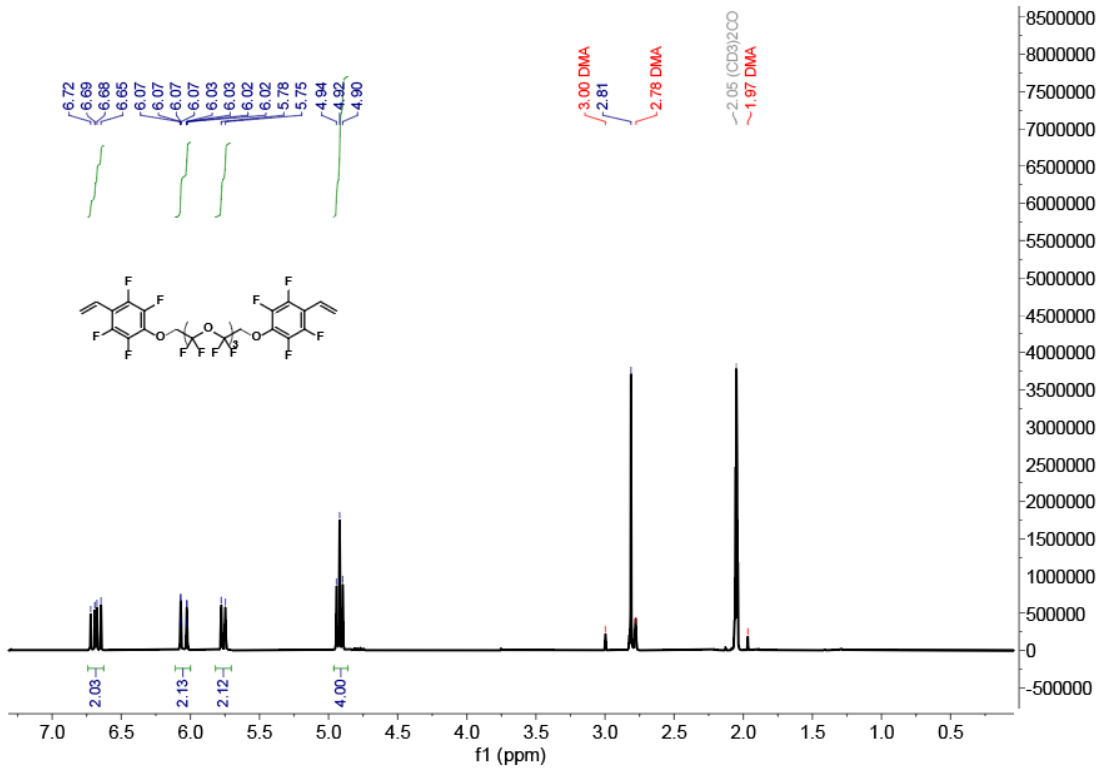


FIGURE S21: ^{1}H NMR of PFS-FTEG.

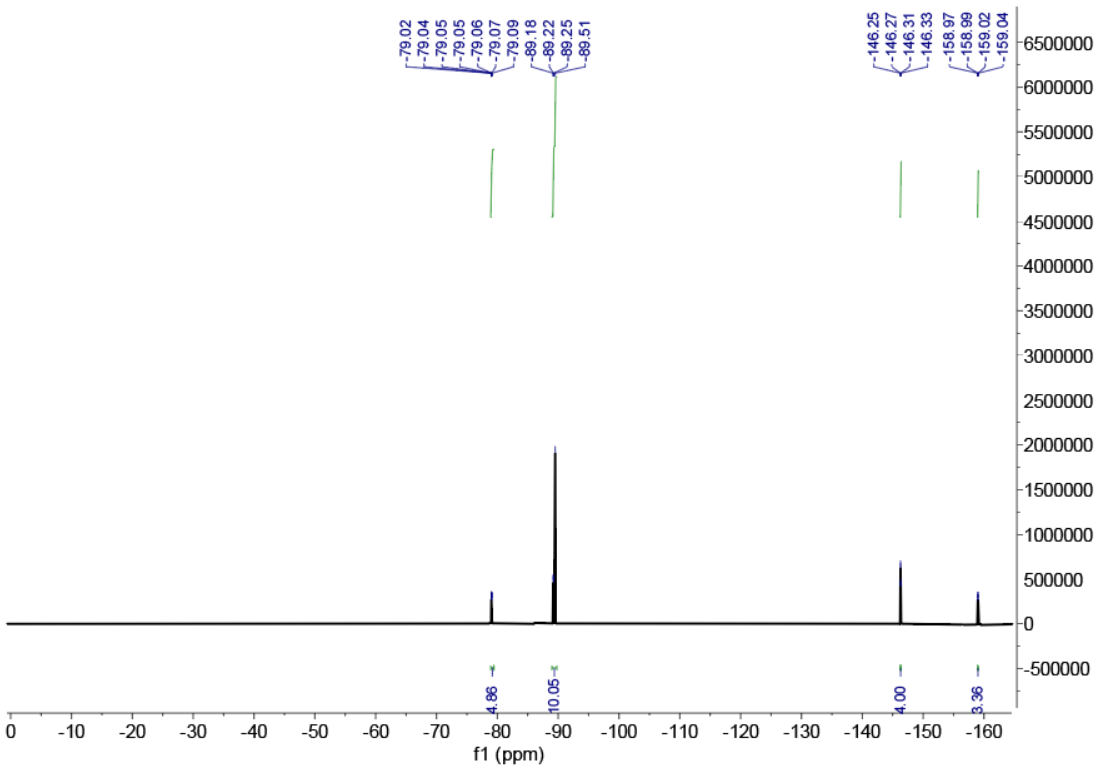


Figure S22: ^{19}F NMR of PFS-FTEG.

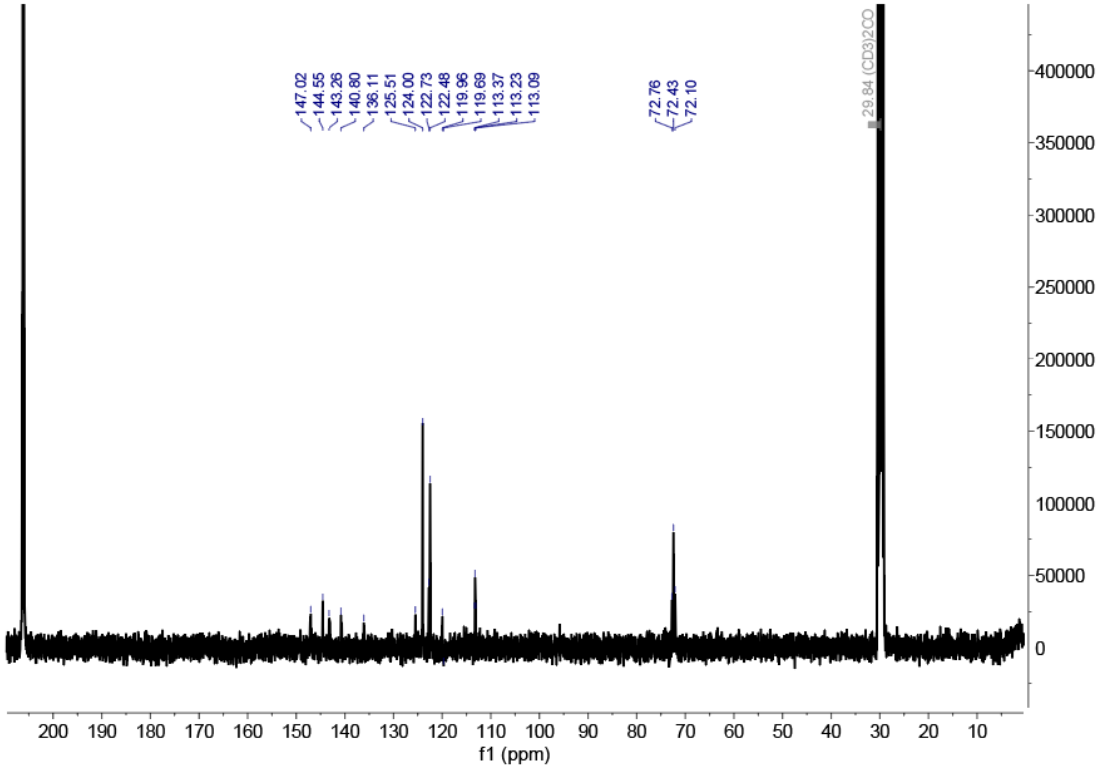


Figure S23: ^{13}C NMR of PFS-FTEG.

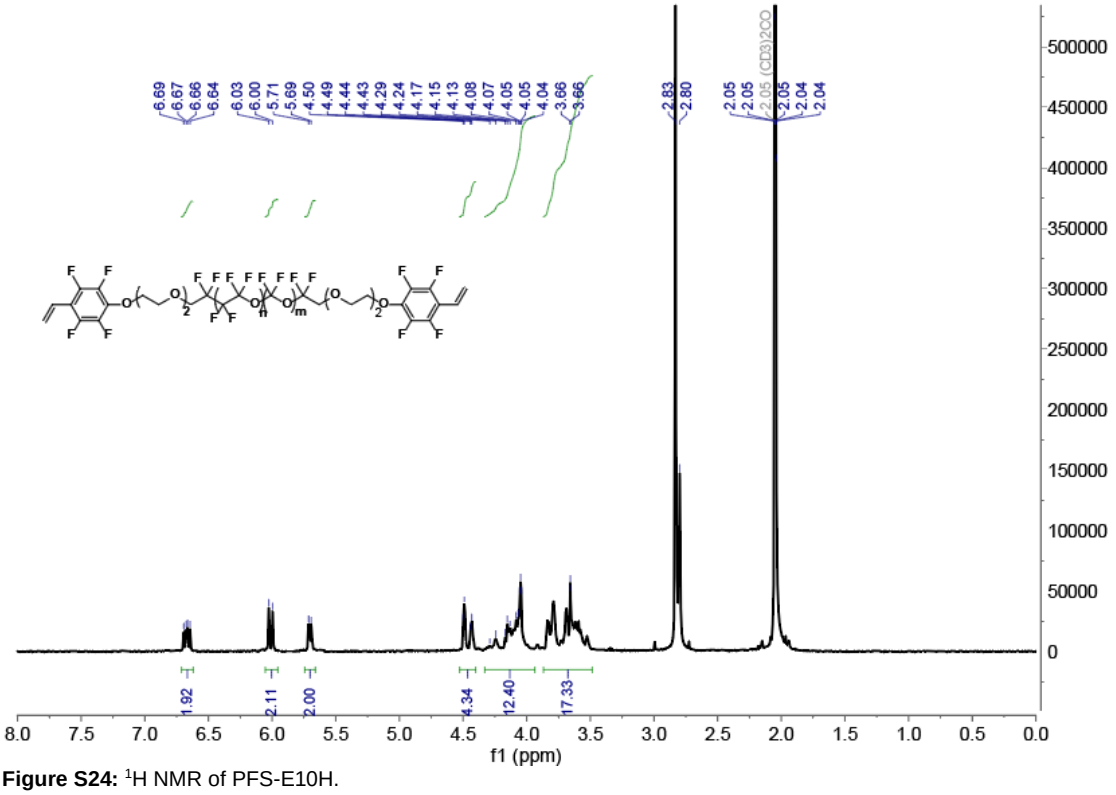


Figure S24: ^{1}H NMR of PFS-E10H.

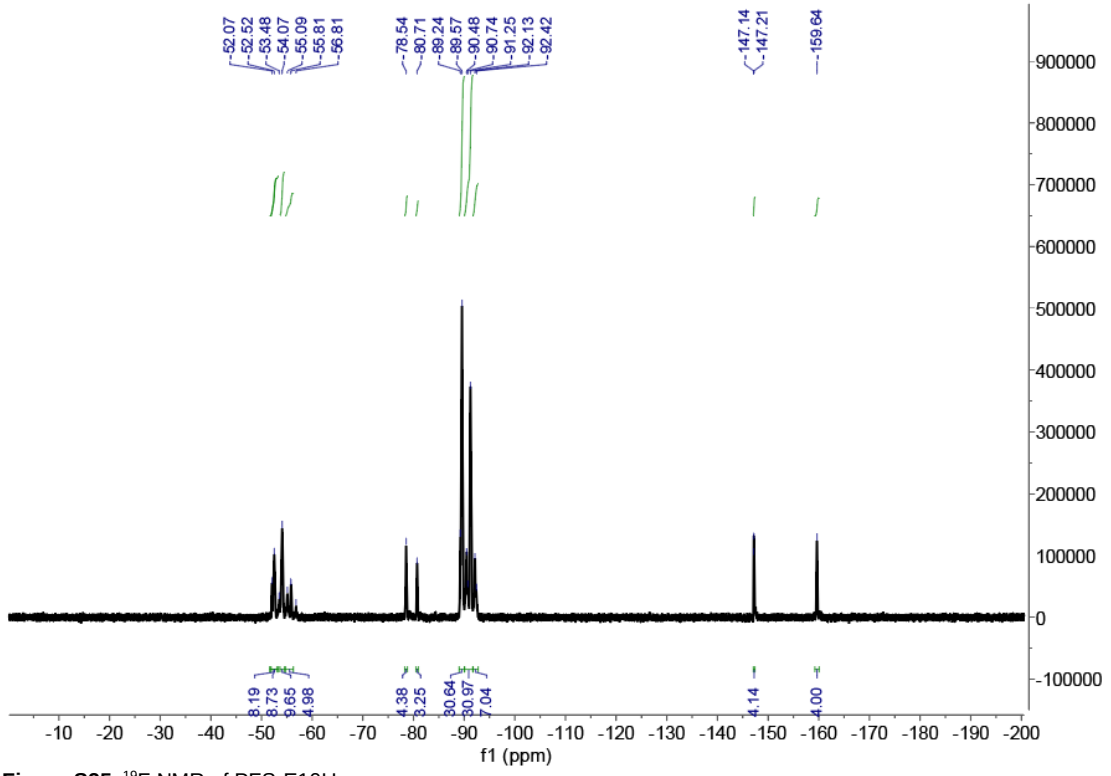


Figure S25: ^{19}F NMR of PFS-E10H.

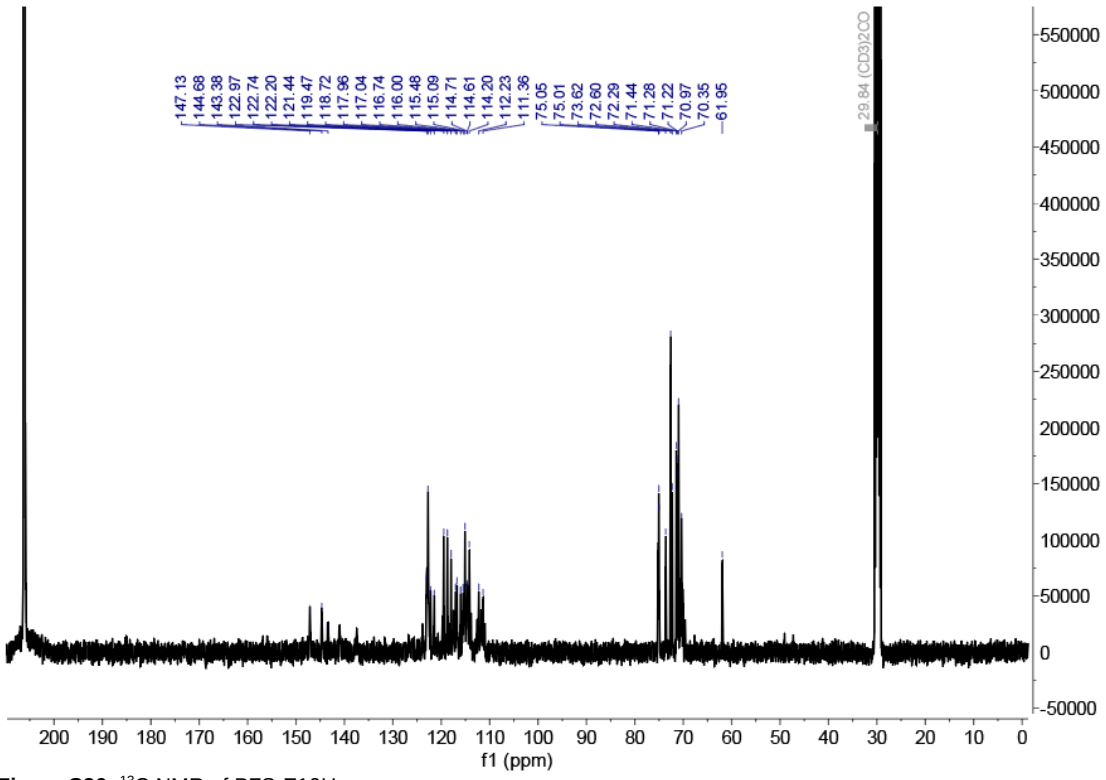


Figure S26: ^{13}C NMR of PFS-E10H.

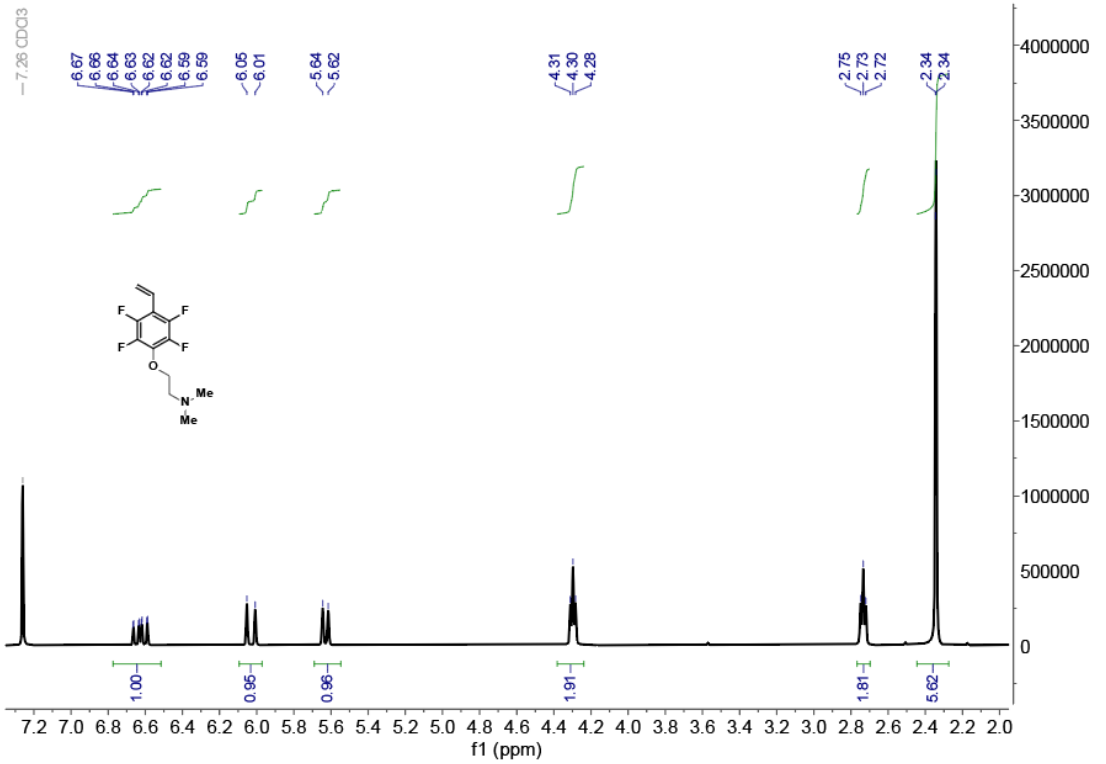


Figure S27: ^{1}H NMR of **1**.

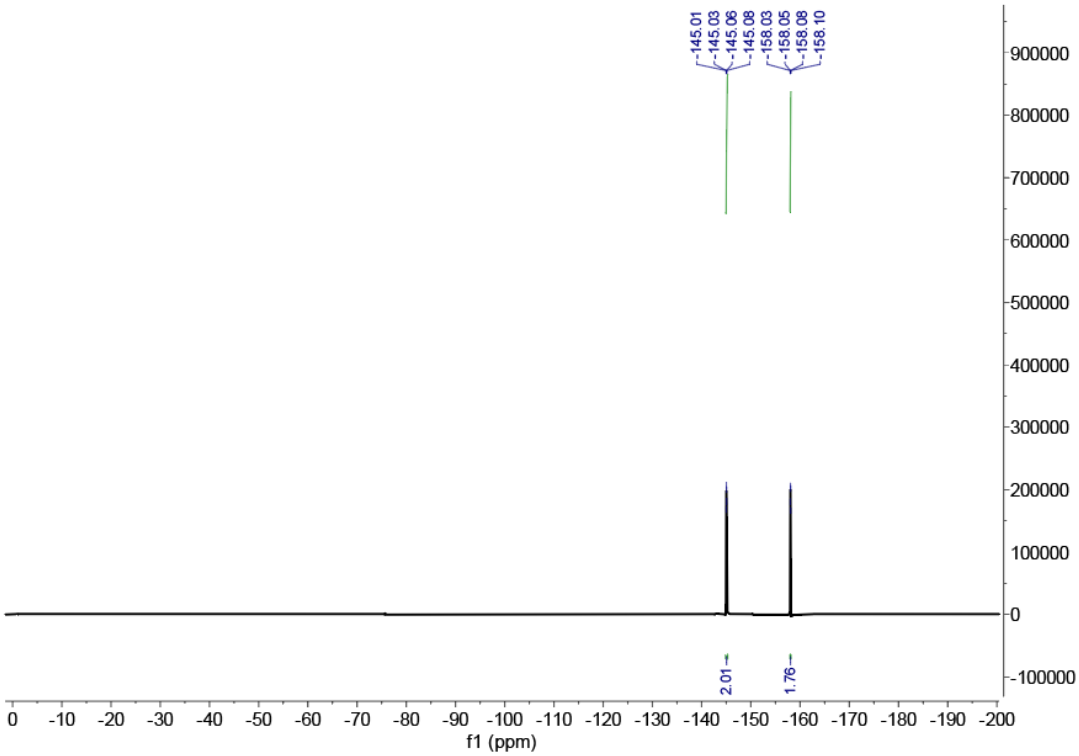


Figure S28: ^{19}F NMR of **1**.

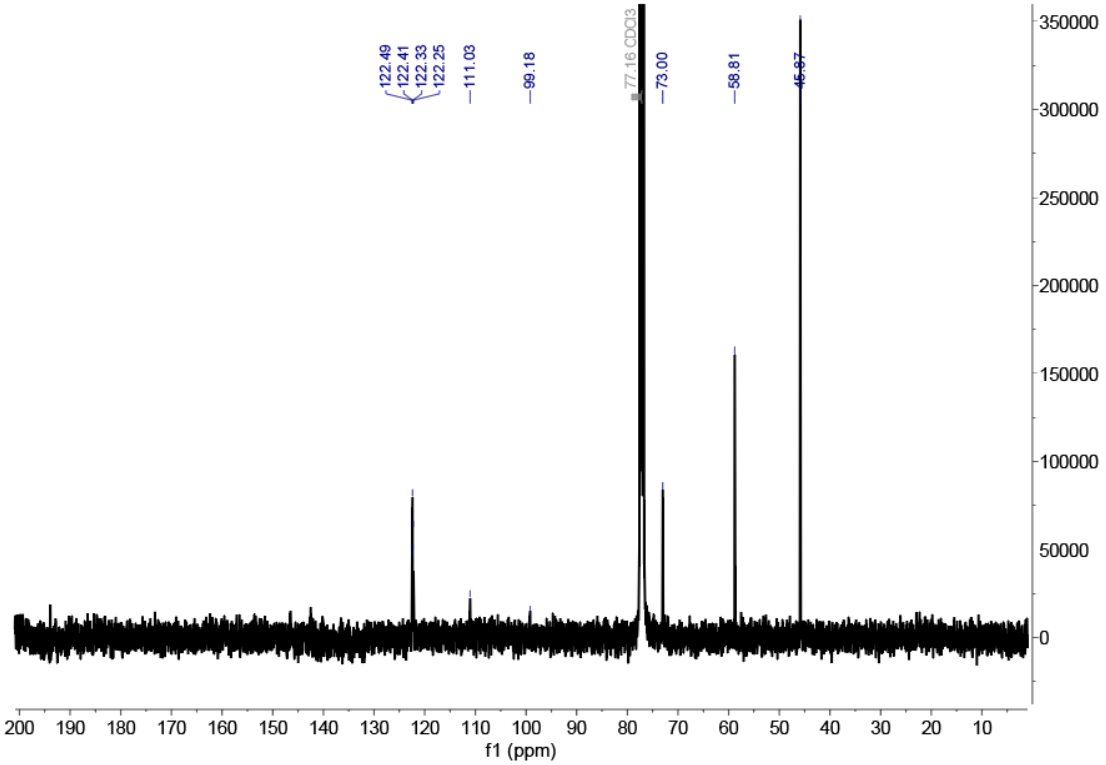


Figure S29: ^{13}C NMR of **1**.

11. Images of Ionic Fluorogels

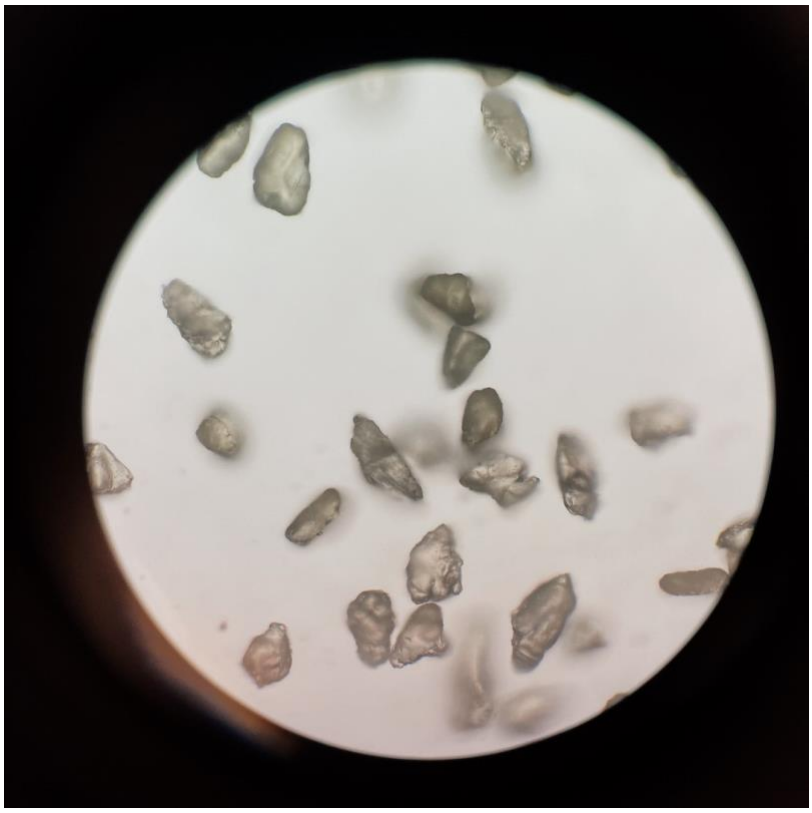


Figure S30. Light microscope image at 100x magnification of IF-8 showing the granular nature of the resin

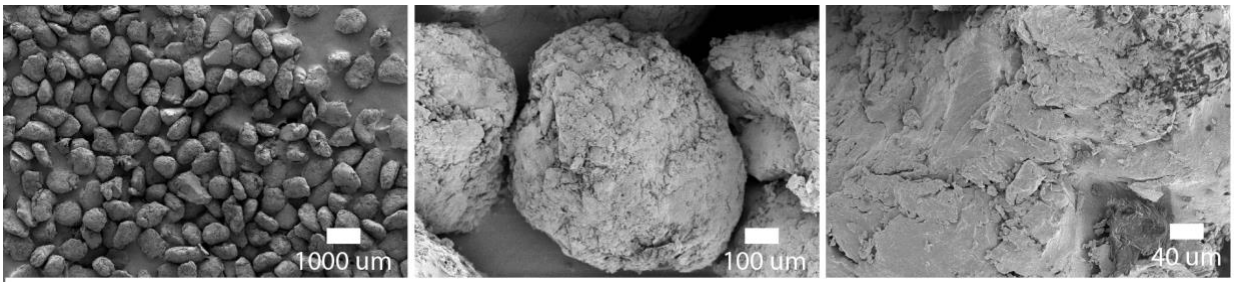


Figure S31. SEM images of IF-8 at 2.0 kV

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