

Supporting Information

Degradation of Perfluoroalkyl Ether Carboxylic Acids (PFECAs) with Hydrated Electrons: Structure-Reactivity Relationships and Environmental Implications

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Detailed Information on Materials and Methods

Chemicals and Preparation of PFAS Stock Solutions.

All PFAS chemicals were purchased from Alfa-Aesar, Fluorix Labs, Oakwood Chemicals, and SynQuest Laboratories. **Table A1** summarizes the name, purity, and CAS number of all PFECAs included in this study. All other chemicals and solvents were purchased from Fisher Chemical. Individual PFECAs were dissolved in either deionized (DI, produced by Milli-Q system) water or methanol as 10 mM stock solutions. For acid compounds in water solvent, the addition of 20 mM NaOH effectively facilitated the dissolution of long chain structures and prevented the volatilization of short chain structures. For long chain PFECAs that did not readily dissolve in water, methanol was used as the solvent. Methanol does not interfere with the PFAS defluorination with hydrated electrons. For example, preliminary experiments with 25 μ M HFPO-DA introduced with the water stock solution (1.5 mL into 600 mL final volume) and with the methanol stock solution (1.5 mL into 600 mL final volume, resulting in ~62 mM methanol in water) gave the same rate and extent of defluorination. All PFECA stock solutions were wrapped in Parafilm and stored at room temperature (20°C).

Table A1. Information of PFECAs Used in This Study.

Entry	Chemical Name	<i>n</i>	Purity	CAS#
CF₃CF₂–[CF₂–O–CF(CF₃)]_n–COOH				
A1	Perfluoro(2-methyl-3-oxahexanoic) acid	1	97%	13252-13-6
A2	Perfluoro(2,5-dimethyl-3,6-dioxanonanoic) acid	2	95%	13252-14-7
A3	Perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoic) acid	3	97%	65294-16-8
CF₃O–[CF₂]_n–COOH (or salt)				
B1	Perfluoro(2-methoxyacetate) sodium salt	1	98%	21837-98-9
B2	Perfluoro(3-methoxypropanoic) acid	2	98%	377-73-1
B3	Perfluoro(4-methoxybutanoic) acid	3	-	863090-89-5
CF₃O–[CF₂CF₂O]_n–CF₂–COOH				
C1	Perfluoro(3,6-dioxahexanoic) acid	1	98%	151772-58-6
C2	Perfluoro(3,6,9-trioxadecanoic) acid	2	98%	151772-59-7
CF₃CF₂CF₂CF₂O–[CF₂CF₂O]_n–CF₂–COOH				
D1	Perfluoro(3,6-dioxadecanoic) acid	1	97%	137780-69-9
D2	Perfluoro(3,6,9-trioxatridecanoic) acid	2	98%	330562-41-9
Special structures				
-	Trifluoropyruvic acid CF₃–CO–COOH	-	97%	1081801-99-1
-	2-(trifluoromethoxy)acetic acid CF₃O–CH₂–COOH	-	97%	69105-00-6

Measurement of PFAS Parent Compound Decay and Transformation Products.

Quantification of PFAS Parent Compounds. The concentrations of PFAS parent compounds were measured by a high-performance liquid chromatography–triple quadrupole mass spectrometry system (HPLC–MS/MS, Agilent 1200 HPLC, and Sciex 5500 QTRAP MS) as previously described,¹ but with a slight modification. Briefly, a 1-μL sample was loaded onto a Zorbax SB-Aq column (particle size 5μm, 4.6×50 mm, Agilent) and eluted with 350 μL min⁻¹ of 10 mM ammonia formate (A) and methanol (B), at a linear gradient as follows: 100% A for 0–1 min, 2% A for 2–15 min, and 100% A for 16–21 min. The mass spectra were obtained from a negative ionization mode. The ion spray voltage was set to –4500 V, the source temperature was set to 450°C, and the curtain gas, ion source gas 1, and ion source gas 2 were 30, 50, and 60, respectively. Multiple reaction monitoring (MRM) was used for quantification, and the MRM transition was listed in Table A2. The limit of quantification (LOQ) for each compound was determined as the lowest concentration with a detection variation <20% (Table A2).

Transformation Products Identification. To identify the transformation products (TPs), samples were first analyzed by liquid chromatography coupled to a high-resolution quadrupole orbitrap mass spectrometer (LC-HRMS/MS) (Q Exactive, Thermo Fisher Scientific). As described in our previous study,¹ the TPs were detected in full scan negative ionization mode on HRMS at a resolution of 70,000 at m/z 200 and a scan range of m/z 50–750. The software Xcalibur (Thermo Fisher Scientific) was used for data acquisition and analysis. Suspect screening was carried out to identify the TPs of selected PFASs, which was conducted on software TraceFinder 4.1 EFS (Thermo Fisher Scientific). The TP suspect lists were compiled using an automatic product mass prediction script, which considered all possible reactions including chain shortening, H/F exchange, and C–O bond cleavage. Plausible TPs were identified based on the following criteria: (i) mass accuracy tolerance < 5 ppm; (ii) isotopic pattern score > 70%; (iii) peak area > 10⁵; (iv) peak area showing an increasing trend over time, or a first increase then followed by a decrease. For the identified TPs with the reference compounds available, their concentrations were further determined by the liquid chromatography–triple quadrupole mass spectrometer (HPLC–MS/MS) as above described.

Table A2. MRM Transition and LOQ.

Entry	Chemical Name	<i>n</i>	MRM Transition (m/z)	LOQ (nM)
CF₃CF₂–[CF₂–O–CF(CF₃)]_n–COOH				
A1	Perfluoro(2-methyl-3-oxahexanoic) acid	1	329.0/185.0	1
A2	Perfluoro(2,5-dimethyl-3,6-dioxanonoic) acid	2	495.0/185.0	1
A3	Perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoic) acid	3	661.0/185.0	25
CF₃O–[CF₂]_n–COOH (or salt)				
B2	Perfluoro(3-methoxypropanoic) acid	2	229.0/85.0	25
B3	Perfluoro(4-methoxybutanoic) acid	3	279.0/85.0	0.1
CF₃O–[CF₂CF₂O]_n–CF₂–COOH				
C1	Perfluoro(3,6-dioxaheptanoic) acid	1	295.0/135.0	25
C2	Perfluoro(3,6,9-trioxadecanoic) acid	2	411.0/317.0	2
CF₃CF₂CF₂CF₂O–[CF₂CF₂O]_n–CF₂–COOH				
D1	Perfluoro(3,6-dioxadecanoic) acid	1	445.0/169.0	2
D2	Perfluoro(3,6,9-trioxatridecanoic) acid	2	561.0/467.0	2

Ion Chromatography Analysis of Small Parent Compounds and Transformation Products. Analysis was performed using a Dionex ICS-5000 ion chromatography system equipped with a conductivity detector and suppressor (AERS 4 mm). Ion separation was executed with an IonPac AS11-HC analytical column (4 × 250 mm) in line with an AG11-HC guard column (4 × 50 mm). The column temperature was maintained at 30°C. The isocratic NaOH mobile phase was provided by a Dionex ICS-6000 EG eluent generator. Specific methods for each target analyte are below:

- Perfluoro(2-methoxy)acetate (**BI**) and oxalate: 20 mM NaOH, 1.0 mL min⁻¹;
- Trifluoromethoxyacetate (TFMOA, CF₃-O-CH₂-COOH): 10 mM NaOH, 1.0 mL min⁻¹;
- Trifluoropyruvate (TFPy): 20 mM NaOH, 1.5 mL min⁻¹ / 15 mM NaOH, 1.0 mL min⁻¹;
- Trifluoroacetic acid (TFA): 10 mM NaOH, 1.0 mL min⁻¹.

Tables S1 to S9 Referred in the Main Text

Table S1. Concentrations and Peak Areas of the Parent Compound and Transformation Product (TP) Suspects from Perfluoro(2-methyl-3-oxahexanoate) [A1, HPFO-DA] Degradation.

Time(h)	HPFO-DA (A1) ^a			
	^{b,c} C ₆ F ₁₁ O ₃ ⁻	^c C ₆ F ₁₀ HO ₃ ⁻	^c C ₅ F ₇ H ₂ O ₃ ⁻	
0	25.0	1.03E+07	ND	ND
1	23.4	9.67E+06	5.34E+05	ND
2	20.3	8.32E+06	1.51E+06	ND
4	7.2	5.80E+06	3.54E+06	ND
8	6.3	2.62E+06	5.36E+06	ND
12	3.5	1.44E+06	5.71E+06	ND
24	1.2	4.59E+05	5.38E+06	ND
48	0.4	1.73E+05	4.02E+06	ND

^aProducts with the same chain length are assumed to be H/F and H/CF₃ exchange derivatives from the corresponding branched PFCEA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

Table S2. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(2,5-dimethyl-3,6-dioxanonoate) [A2, HFPO-TrA] Degradation.

Time(h)	HFPO-TrA (A2) ^a			HFPO-DA (A1) ^a		
	^{c,d} C ₉ F ₁₇ O ₄ ⁻	^c C ₉ F ₁₆ HO ₄ ⁻	^c C ₈ F ₁₃ H ₂ O ₄ ⁻	^b C ₆ F ₁₁ O ₃ ⁻	^c C ₆ F ₁₀ HO ₃ ⁻	^c C ₅ F ₇ H ₂ O ₃ ⁻
0	4.05E+05	ND	ND	2.53	ND	ND
1	3.10E+05	9.10E+04	ND	4.06	6.87E+04	ND
2	2.12E+05	1.43E+05	ND	4.18	2.79E+05	ND
4	1.37E+05	6.63E+05	ND	5.95	1.40E+06	ND
8	7.18E+04	1.00E+06	3.28E+04	6.57	3.64E+06	ND
12	1.27E+05	1.10E+06	8.78E+04	5.58	4.93E+06	ND
24	ND	1.85E+06	1.09E+05	3.79	7.87E+06	ND
48	ND	1.85E+06	1.61E+05	2.61	7.98E+06	ND

^aProducts with the same chain length are assumed to be H/F and H/CF₃ exchange derivatives from the corresponding branched PFCEA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

^dNot stable under the ionization condition used for both MS detection methods. Only the small peak areas by HRMS are shown. Note the significant concentration of HFPO-DA detected in the t=0 sample.

Table S3. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoate) [A3, HFPO-TeA] Degradation.

Time(h)	HFPO-TeA (A3) ^a			HFPO-TrA (A2) ^a			HFPO-DA (A1) ^a		
	^{b,c} C ₁₂ F ₂₃ O ₅ ⁻	^c C ₁₀ F ₁₅ H ₄ O ₅ ⁻	^b C ₉ F ₁₇ O ₄ ⁻	^c C ₉ F ₁₆ HO ₄ ⁻	^c C ₈ F ₁₅ H ₂ O ₄ ⁻	^c C ₈ F ₁₃ H ₂ O ₄ ⁻	^b C ₆ F ₁₁ O ₃ ⁻	^c C ₆ F ₁₀ HO ₃ ⁻	^c C ₅ F ₇ H ₂ O ₃ ⁻
0	25.0	ND	0.27	ND	ND	ND	0	ND	ND
1	23.4	ND	2.02	ND	ND	ND	0.04	ND	ND
2	14.2	ND	3.57	ND	ND	ND	0.27	ND	ND
4	13.0	ND	6.45	2.86E+05	4.78E+04	ND	1.22	ND	ND
8	6.9	ND	7.93	8.60E+05	1.99E+05	7.13E+04	2.97	2.93E+06	6.61E+05
12	4.9	6.37E+04	7.49	1.13E+06	1.08E+06	5.77E+04	3.71	3.69E+06	4.16E+05
24	3.1	2.42E+05	4.80	1.70E+06	2.61E+06	1.00E+05	3.46	6.71E+06	1.16E+06
48	2.9	4.86E+05	2.17	1.90E+06	4.61E+06	1.09E+05	2.45	7.23E+06	1.06E+06

Time(h)	PFPrA ^d		
	^b C ₃ F ₅ O ₂ ⁻	^b C ₃ F ₄ HO ₂ ⁻	^b C ₃ F ₃ H ₂ O ₂ ⁻
0	ND	ND	ND
1	ND	ND	ND
2	ND	0.19	ND
4	ND	0.47	ND
8	0.35	0.81	ND
12	0.62	0.93	ND
24	0.70	0.96	ND
48	0.71	0.80	ND

^aProducts with the same chain length are assumed to be H/F and H/CF₃ exchange derivatives from the corresponding branched PFCEA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

^dProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding PFCEA.

^eNot stable under the ionization condition used for HRMS detection.

Table S4. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(3-methoxypropanoate) [**B2**] Degradation.

Time (h)	Perfluoro(3-methoxypropanoate) (B2) ^a				Perfluoro(2-methoxyacetate)
	^{b,c} C ₄ F ₇ O ₃ ⁻	^c C ₄ F ₆ HO ₃ ⁻	^c C ₄ F ₅ H ₂ O ₃ ⁻		^c C ₃ F ₅ O ₃ ⁻
0	25.0	7.26E+08	1.15E+06	ND	1.02E+05
1	20.3	5.91E+08	3.71E+06	ND	4.54E+05
2	15.2	4.42E+08	7.01E+06	ND	9.75E+05
4	6.3	1.83E+08	9.23E+06	ND	7.14E+05
8	0.6	1.75E+07	6.30E+06	3.74E+04	2.65E+05
12	0.2	6.35E+06	3.99E+06	4.86E+04	1.77E+05
24	0.2	5.61E+06	1.76E+06	1.02E+05	8.92E+04
48	0.1	5.52E+06	1.01E+06	1.39E+05	2.04E+05

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFECA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

Table S5. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(4-methoxybutanoate) [**B3**] Degradation.

Time (h)	Perfluoro(4-methoxybutanoate) (B3) ^a			Perfluoro(3-methoxypropanoate) (B2) ^a		Perfluorosuccinate
	^{b,c} C ₅ F ₉ O ₃ ⁻	^c C ₅ F ₈ HO ₃ ⁻	^c C ₅ F ₇ H ₂ O ₃ ⁻	^b C ₄ F ₇ O ₃ ⁻	^c C ₄ F ₆ HO ₃ ⁻	^b C ₄ F ₄ O ₄ ²⁻
0	25.0	6.74E+08	2.23E+06	ND	0.23	4.39E+06
1	13.9	5.16E+08	4.50E+07	ND	0.83	9.08E+06
2	8.9	3.44E+08	7.96E+07	1.21E+05	0.81	8.35E+06
4	2.8	1.71E+08	1.03E+08	3.57E+05	0.40	4.04E+06
8	0.3	2.89E+07	9.19E+07	8.72E+05	0.08	6.89E+05
12	ND	3.94E+06	7.40E+07	6.12E+05	0.05	4.18E+05

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFECA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

Table S6. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(3,6-dioxaheptanoate) [**C1**] Degradation.

Time(h)	Perfluoro(3,6-dioxaheptanoate) (C1) ^a			Perfluoro(2-methoxyacetate)
	^{b,c} C ₅ F ₉ O ₄ ⁻	^c C ₅ F ₈ HO ₄ ⁻	^c C ₅ F ₇ H ₂ O ₄ ⁻	^c C ₃ F ₅ O ₃ ⁻
0	25.6	6.91E+07	2.03E+06	ND
1	20.7	5.60E+07	1.82E+06	2.41E+07
2	17.4	4.69E+07	4.55E+06	3.85E+07
4	10.6	2.86E+07	6.63E+06	4.37E+07
8	4.4	1.18E+07	5.56E+06	3.57E+07
12	2.5	6.75E+06	4.24E+06	2.50E+07

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFECA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

Table S7. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(3,6,9-trioxadecanoate) [**C2**] Degradation.

Time(h)	Perfluoro(3,6,9-trioxadecanoate) (C2) ^a			Perfluoro(3,6-dioxaheptanoate) (C1) ^a	
	^{b,c} C ₇ F ₁₃ O ₅ ⁻	^c C ₇ F ₁₂ HO ₅ ⁻	^c C ₇ F ₁₁ H ₂ O ₅ ⁻	^b C ₅ F ₉ O ₄ ⁻	^c C ₅ F ₈ HO ₄ ⁻
0	25.0	1.26E+07	ND	ND	ND
1	23.6	9.17E+06	1.90E+06	2.4	2.24E+05
2	20.1	8.14E+06	5.19E+06	4.6	7.11E+05
4	12.7	5.66E+06	1.01E+07	6.5	2.55E+06
8	3.8	3.36E+06	9.55E+06	5.2	4.85E+06
12	1.8	1.98E+06	6.89E+06	2.9	4.45E+06

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFECA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

Table S8. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(3,6-dioxadecanoate) [**D1**] Degradation.

Time(h)	Perfluoro(3,6-dioxadecanoate) (D1) ^a			Perfluoro(3-oxaheptanoate) ^a			PFBA
	^{b,c} C ₈ F ₁₅ O ₄ ⁻	^c C ₈ F ₁₄ HO ₄ ⁻	^c C ₈ F ₁₃ H ₂ O ₄ ⁻	^c C ₆ F ₁₁ O ₃ ⁻	^c C ₆ F ₁₀ HO ₃ ⁻	^{c,d} C ₅ F ₆ H ₃ O ₃ ⁻	
0	26.7	6.83E+06	5.73E+05	ND	5.39E+06	ND	ND
1	20.6	5.27E+06	3.92E+06	3.50E+04	1.05E+07	5.18E+05	ND
2	20.6	5.28E+06	7.86E+06	1.63E+05	1.32E+07	1.99E+06	5.57E+04
4	12.7	3.24E+06	1.13E+07	8.99E+05	1.32E+07	4.88E+06	6.77E+05
8	6.9	1.78E+06	8.14E+06	1.29E+06	8.04E+06	5.58E+06	1.76E+06
12	3.3	8.36E+05	4.74E+06	1.87E+06	4.87E+06	3.70E+06	2.94E+06

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFCEA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

^dProduct assigned as the product after *DHEH*.

Table S9. Concentrations and Peak Areas of the Parent Compound and TP Suspects from Perfluoro(3,6,9-trioxatridecanoate) [**D2**] Degradation.

	Perfluoro(3,6,9-trioxatridecanoate) (<i>D2</i>) ^a				Perfluoro(3,6-dioxadecanoate) (<i>D1</i>) ^a			Perfluoro(3-oxaheptanoate) ^a	
Time(h)	^{b,c} C ₁₀ F ₁₉ O ₅ ⁻		^c C ₁₀ F ₁₈ HO ₅ ⁻	^{c,d} C ₉ F ₁₄ H ₃ O ₅ ⁻	^b C ₈ F ₁₅ O ₄ ⁻	^c C ₈ F ₁₄ HO ₄ ⁻	^c C ₈ F ₁₃ H ₂ O ₄ ⁻	^c C ₆ F ₁₁ O ₃ ⁻	^c C ₆ F ₁₀ HO ₃ ⁻
0	25.0	1.43E+06	3.54E+05	2.22E+05	0.02	<i>ND</i>	<i>ND</i>	1.27E+06	<i>ND</i>
1	22.7	1.44E+06	3.66E+06	2.13E+05	5.0	4.77E+05	<i>ND</i>	2.48E+06	<i>ND</i>
2	17.9	9.28E+05	7.64E+06	1.00E+06	10.2	1.49E+06	<i>ND</i>	4.53E+06	2.69E+05
4	14.0	8.33E+05	8.96E+06	4.39E+06	14.4	4.16E+06	<i>ND</i>	7.24E+06	1.11E+06
8	7.0	5.09E+05	7.19E+06	1.71E+07	13.2	9.76E+06	1.15E+06	1.03E+07	3.85E+06
12	3.5	1.64E+05	3.64E+06	2.78E+07	11.0	1.02E+07	9.30E+05	9.22E+06	4.99E+06

PFBA	
Time(h)	^b C ₄ F ₇ O ₂ ⁻
0	ND
1	ND
2	0.1
4	0.4
8	1.3
12	1.4

^aProducts with the same chain length are assumed to be H/F exchange derivatives from the corresponding linear PFCEA and PFCA.

^bQuantified by LC-MS/MS with standards (in μM).

^cObserved by HRMS analysis without standards for quantification (in peak area).

^dProduct assigned as the product after *DHEH*.

Figures S1 to S13 Referred in the Main Text

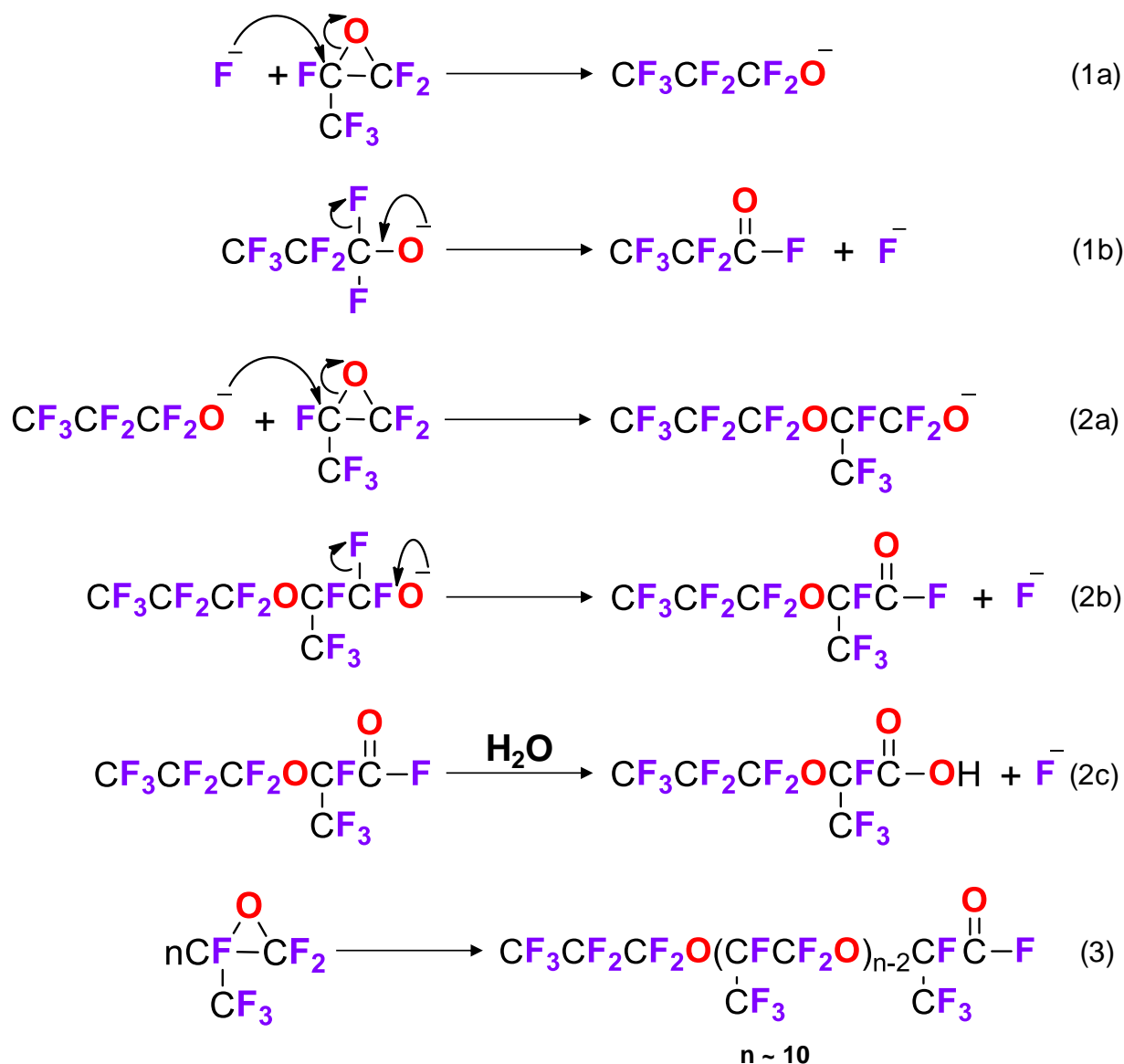


Figure S1. Polymerization of hexafluoropropylene oxide (HFPO).² A fluoride ion opens the epoxide ring to generate n-perfluoroalkoxide (**1a**). This structure can undergo rearrangement to generate perfluoroacyl fluoride (**1b**). Alternatively, n-perfluoroalkoxide can attack another epoxide monomer to generate the branched perfluoroalkoxide dimer (**2a**). The dimer can undergo rearrangement to form the dimer acyl fluoride (**2b**). Subsequent hydrolysis yields the carboxylic acid (i.e., HFPO-DA or “GenX” in this example) (**2c**). Following this reaction scheme, a variety of branched perfluoroalkyl ether oligomers and polymers can be synthesized (**3**).

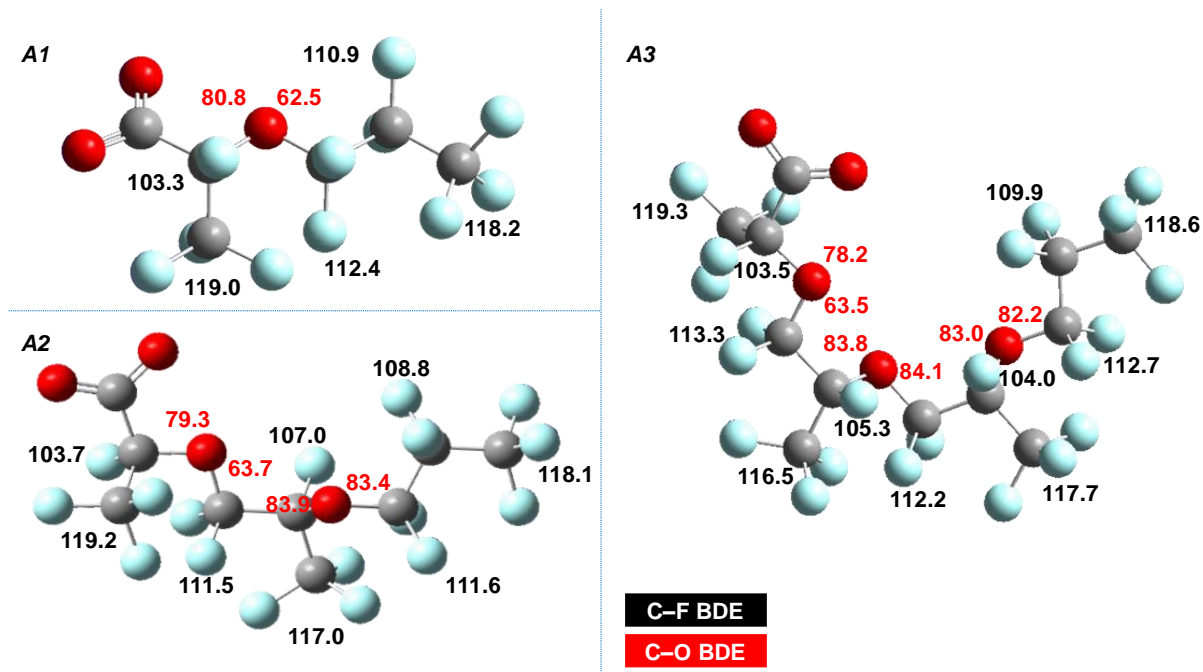


Figure S2. Calculated C-F and C-O BDEs (kcal mol⁻¹) for branched HFPO oligomers.

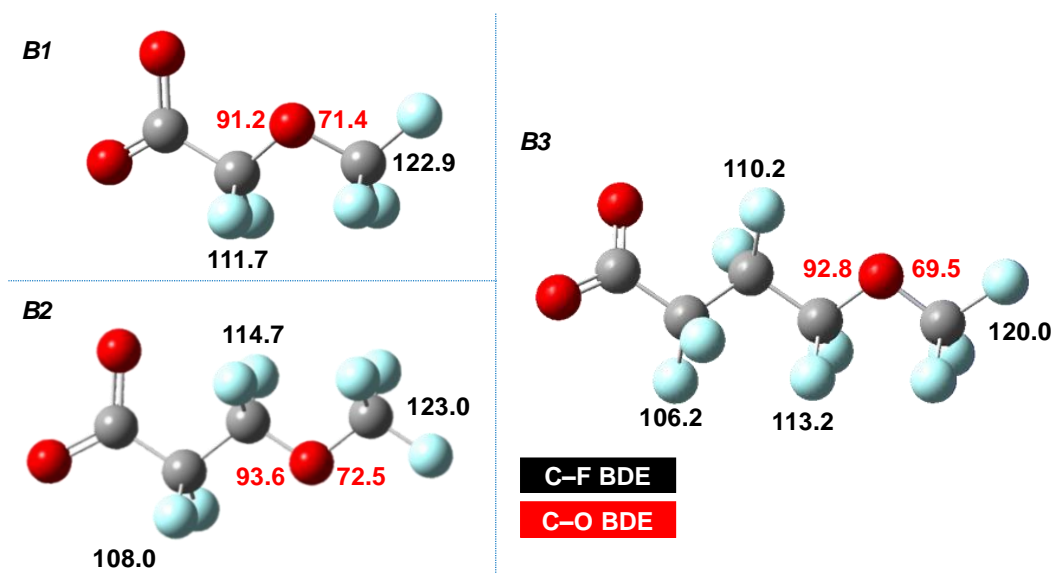


Figure S3. Calculated C-F and C-O BDEs (kcal mol⁻¹) for mono-ethers with the CF₃O- head group.

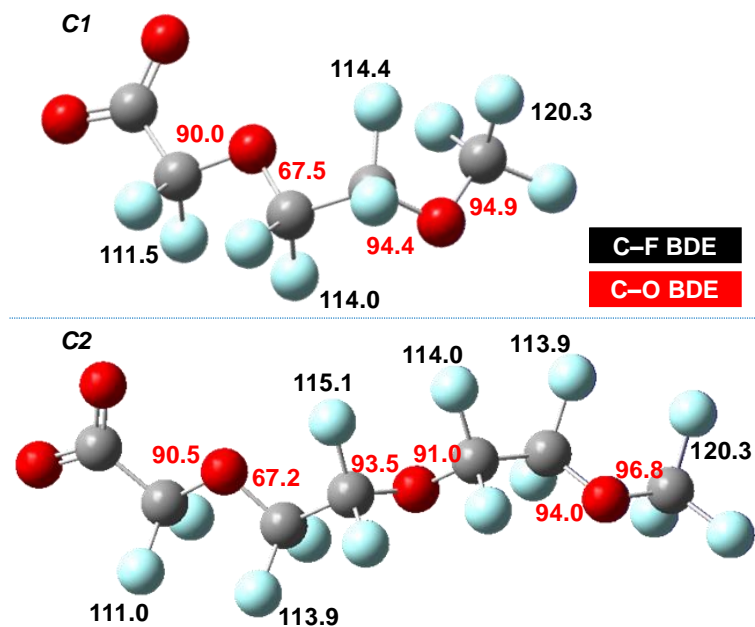


Figure S4. Calculated C-F and C-O BDEs (kcal mol⁻¹) of TFEO oligomers with the CF₃O- head group.

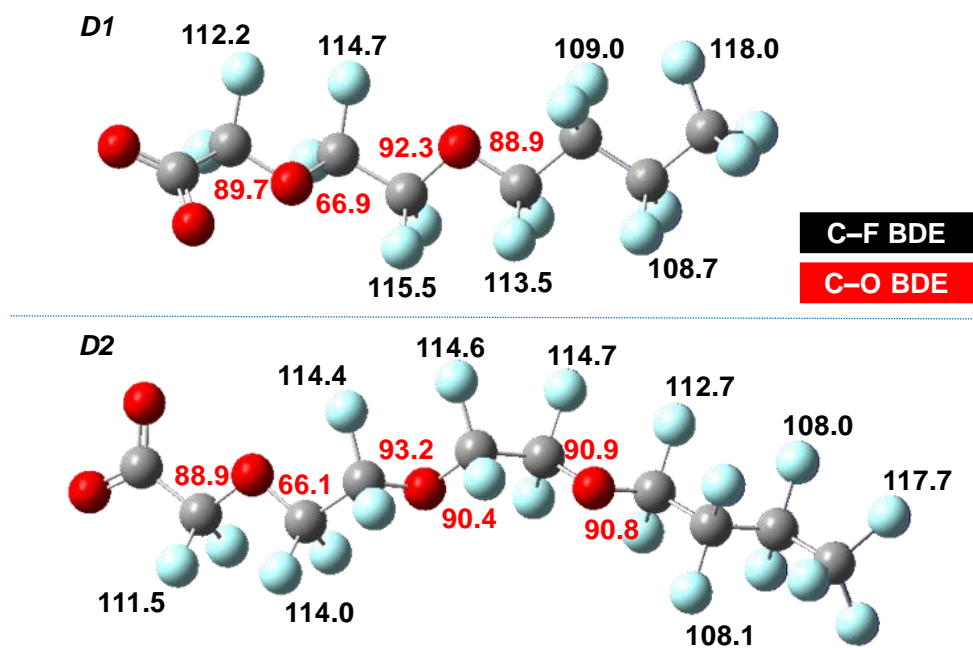


Figure S5. Calculated C-F and C-O BDEs (kcal mol⁻¹) for TFEO oligomers with the C₄F₉O- head group.

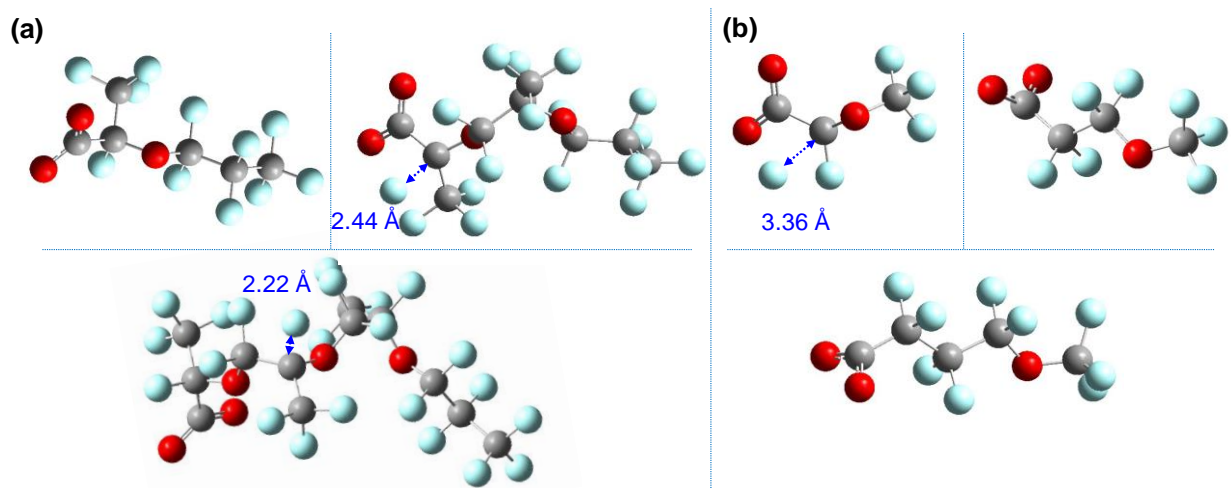


Figure S6. Geometry-optimized $[R_F\text{-COO}]^{\bullet 2-}$ structures from (a) *A1-A3* and (b) *B1-B3* at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory, showing C-F bond stretching.

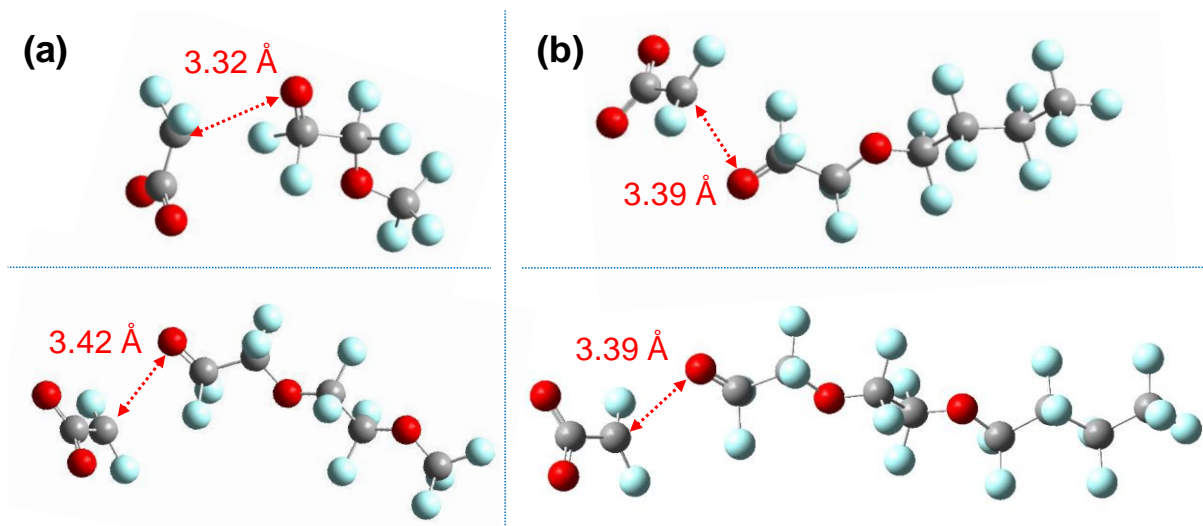


Figure S7. Geometry-optimized $[R_F\text{-COO}]^{\bullet 2-}$ structures of (a) *C1-C2* and (b) *D1-D2* at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory, showing C-O bond stretching.

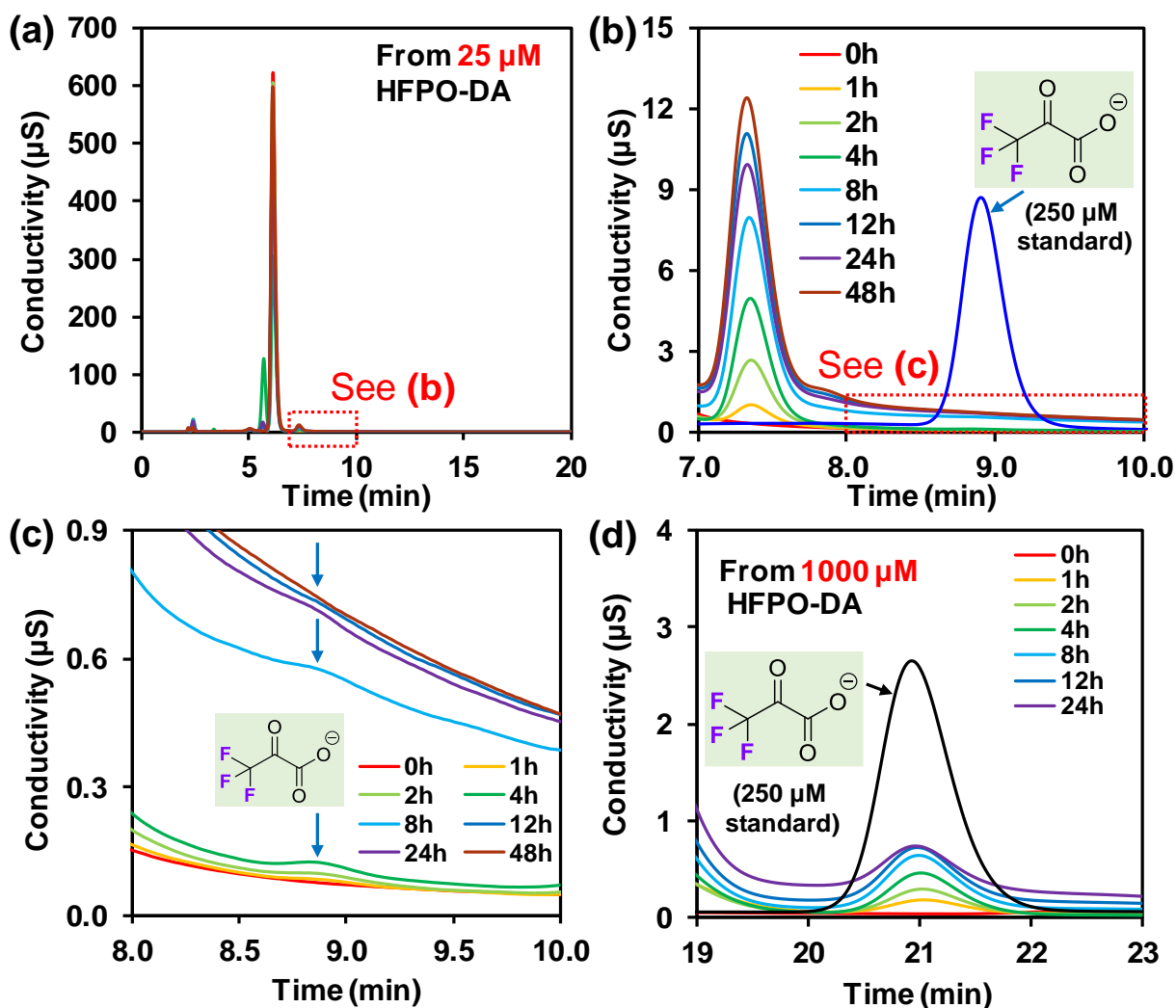


Figure S8. Ion-chromatography analysis for the generation of trifluoropyruvate (TFPy) from the degradation of HFPO-DA (**A1**). The chromatograph from the reaction mixture (**a**) is magnified in panels (**b**) and (**c**). Reaction conditions: **A1** (0.025 mM), Na_2SO_3 (10 mM), carbonate buffer (5 mM, pH adjusted to 9.5), 600 mL solution, 254 nm irradiation (18 W low-pressure Hg lamp) at 20°C. The formation of TFPy was observed in panel (**c**), but the quantification was difficult due to the interference of another unknown species in a much higher intensity. However, as shown in panel (**d**), the elevated concentration of **A1** (1 mM) generated more TFPy, and the peak separation was also improved by adjusting the eluent flow rate of the ion chromatography. Separation conditions: AS11-HC column (4 mm \times 250 mm, 4 μm) with AG-11 guard column at 30°C; isocratic eluent with 20 mM NaOH at a flow rate of 1.5 mL min⁻¹ for (**a**)–(**c**) and with 15 mM NaOH at a flow rate of 1.0 mL min⁻¹ for (**d**).

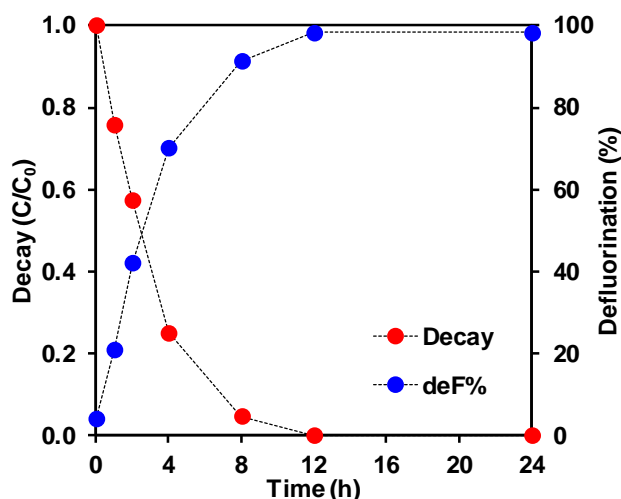


Figure S9. Time profiles of parent compound decay and defluorination percentage for trifluoropyruvate (TFPy). Reaction conditions: $\text{CF}_3\text{-CO-COO}^-$ (0.025 mM), Na_2SO_3 (10 mM), carbonate buffer (5 mM, pH adjusted to 9.5), 600 mL solution, 254 nm irradiation (18 W low-pressure Hg lamp) at 20°C.

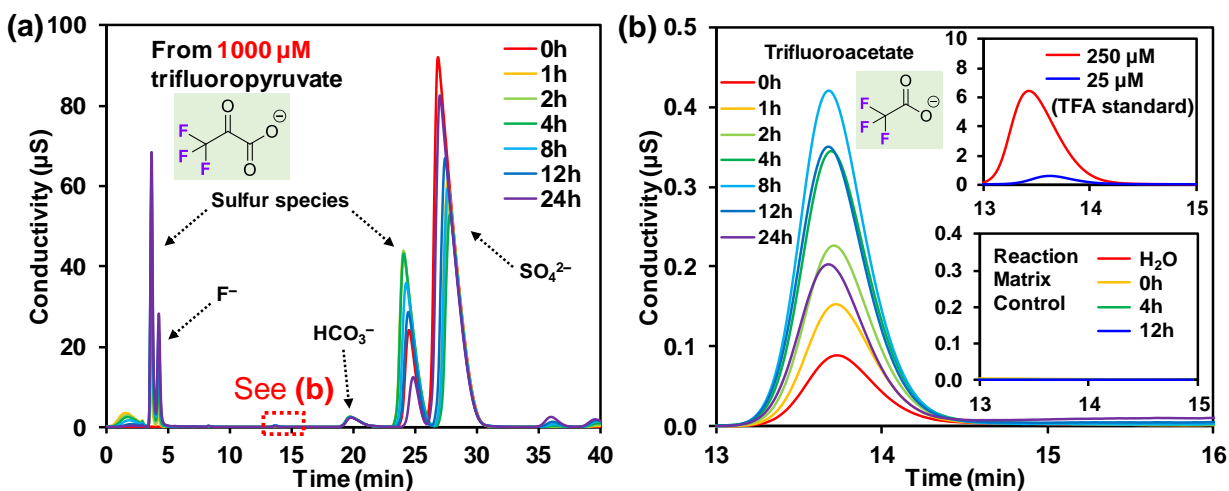


Figure S10. Ion-chromatography analysis for the generation of trifluoroacetate (TFA) from the degradation of trifluoropyruvate (TFPy). The chromatograph from the reaction mixture (a) is magnified in panel (b). The top small panel in (b) shows the peaks of two TFA standards. The bottom panel shows the lack of this TFA peak in the reaction matrix control where TFPy was not added. Reaction conditions: TFPy (1 mM), Na_2SO_3 (10 mM), carbonate buffer (5 mM, pH adjusted to 9.5), 600 mL solution, 254 nm irradiation (18 W low-pressure Hg lamp) at 20°C. The high concentration of TFPy was used because the amount of TFA generated from 25 μM TFPy was too small (similar to **Figure S8c**). The maximum concentration of TFA generated at 8 h was 19 μM (i.e., 1.9% of the initial TFPy). Separation conditions: AS11-HC column (4 mm \times 250 mm, 4 μm) with AG-11 guard column at 30°C; isocratic eluent with 10 mM NaOH at a flow rate of 1.0 mL min^{-1} .

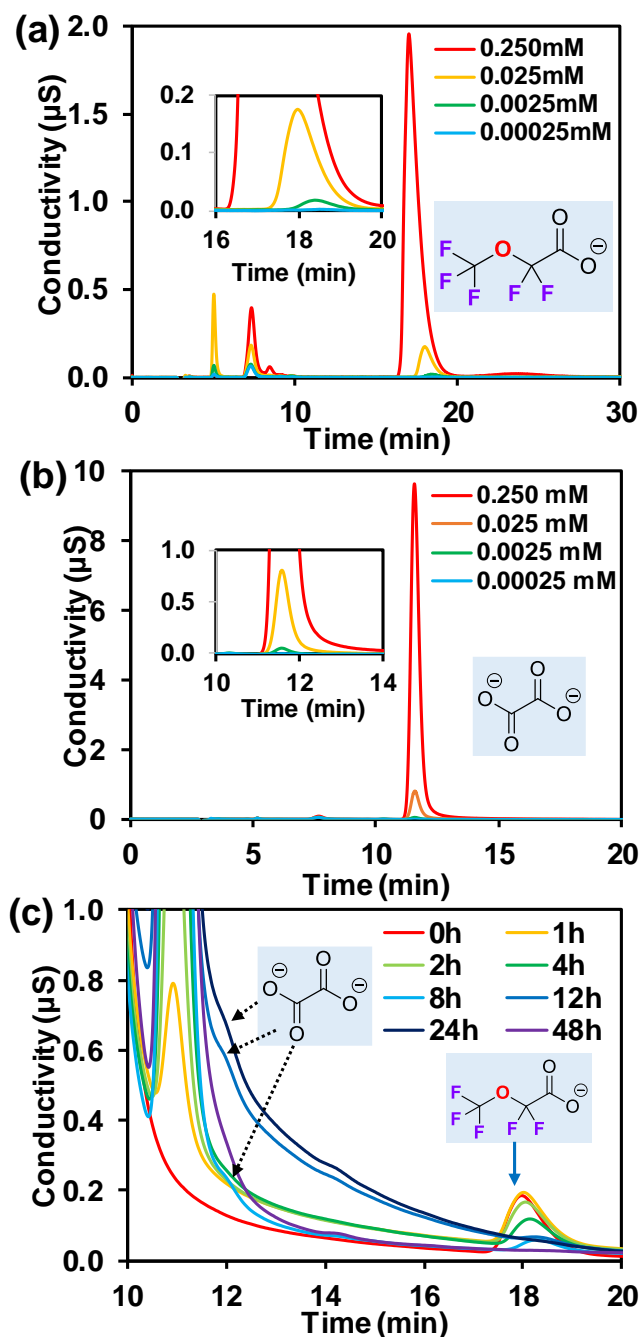


Figure S11. Ion-chromatography analysis for the generation of oxalate from the degradation of **BI**. The peaks for (a) compound **BI** and (b) oxalate are verified with four standard calibrating concentrations. The magnified chromatograph for the reaction mixture is shown in panel (c). Reaction conditions: **BI** (0.025 mM), Na_2SO_3 (10 mM), carbonate buffer (5 mM, pH adjusted to 9.5), 600 mL solution, 254 nm irradiation (18 W low-pressure Hg lamp) at 20°C . The quantification of oxalate was difficult due to the interference of another unknown species in a much higher intensity. Separation conditions: AS11-HC column (4 mm \times 250 mm, $4\mu\text{m}$) with AG-11 guard column at 30°C ; isocratic eluent with 20 mM NaOH at a flow rate of 1.0 mL min^{-1} .

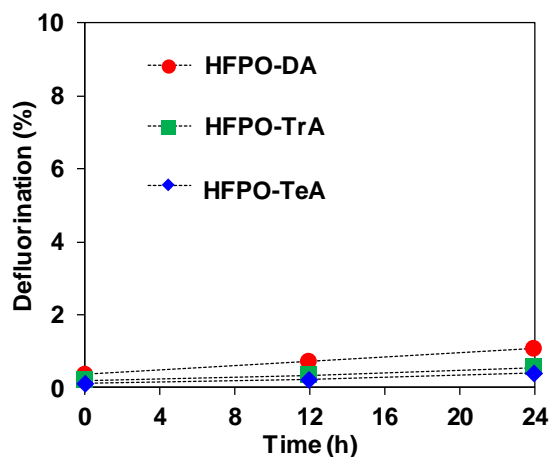


Figure S12. Defluorination percentages of the three HFPO oligomer acids without adding sulfite. Note that the y-axis range is 0–10%. Reaction conditions: individual PFECA (0.025 mM), carbonate buffer (5 mM), 254 nm irradiation (a 18 W low-pressure Hg lamp for 600 mL solution) at pH 9.5 and 20°C.

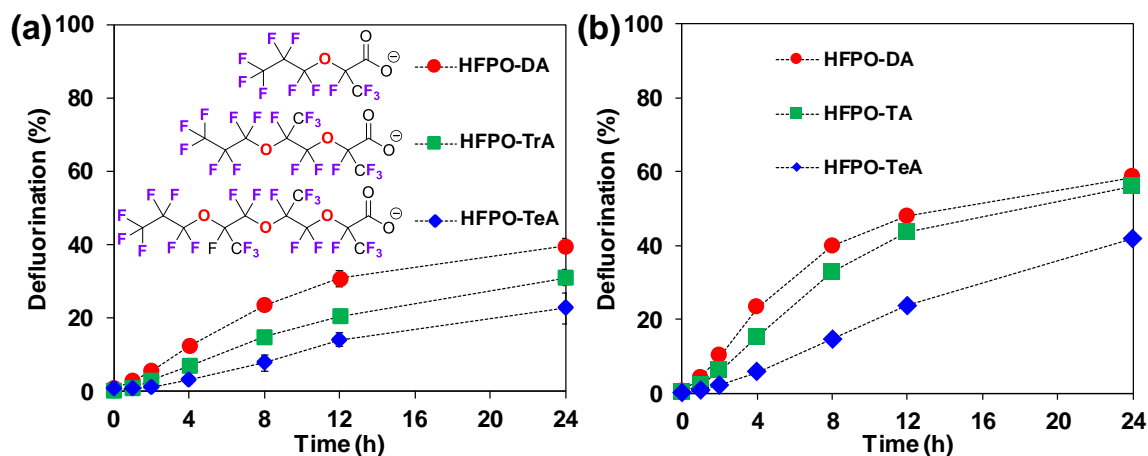
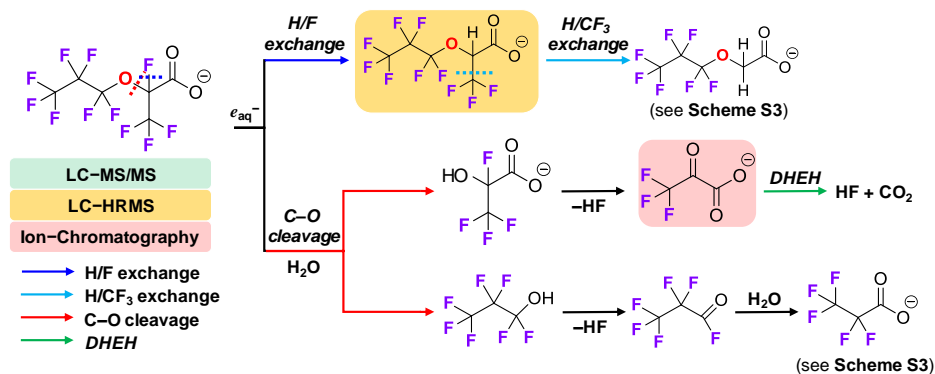
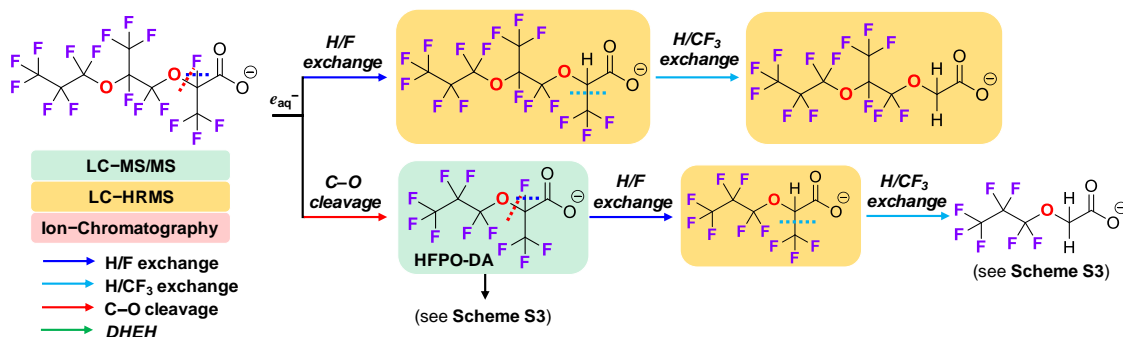


Figure S13. Comparison of defluorination percentages of the three HFPO oligomer acids with (a) 10 mM Na₂SO₃ at pH 9.5 and (b) 20 mM Na₂SO₃ at pH 10.0. Common reaction conditions: individual PFECA (0.025 mM), carbonate buffer (5 mM), 254 nm irradiation (a 18 W low-pressure Hg lamp for 600 mL solution) at 20°C.

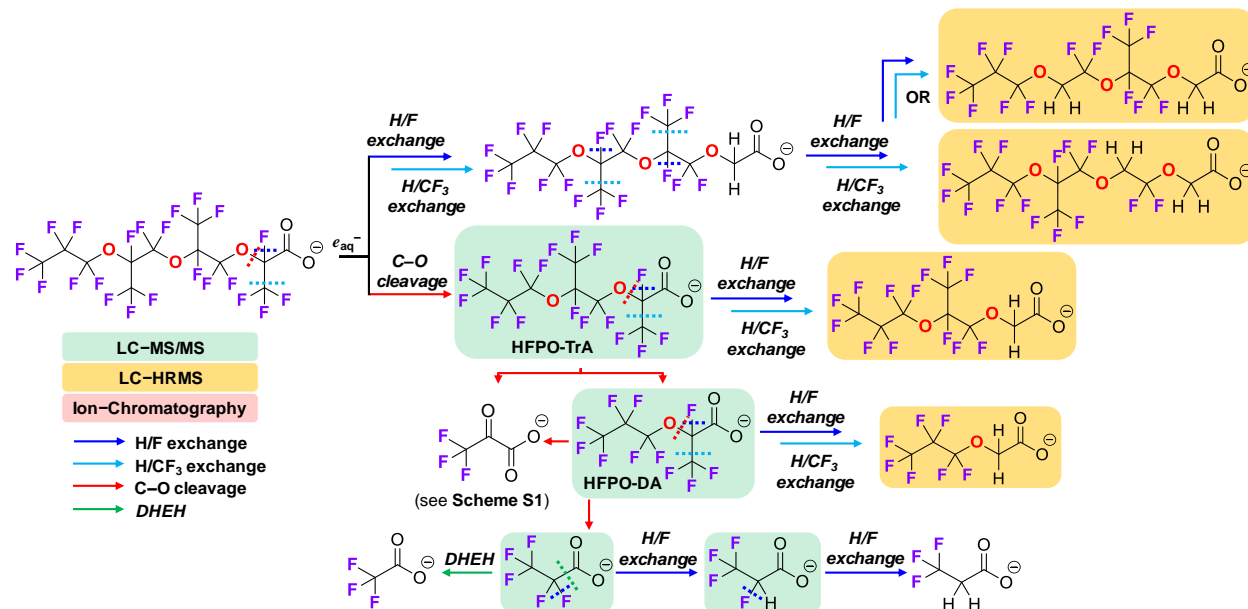
Schemes S1 to S10 Referred in the Main Text



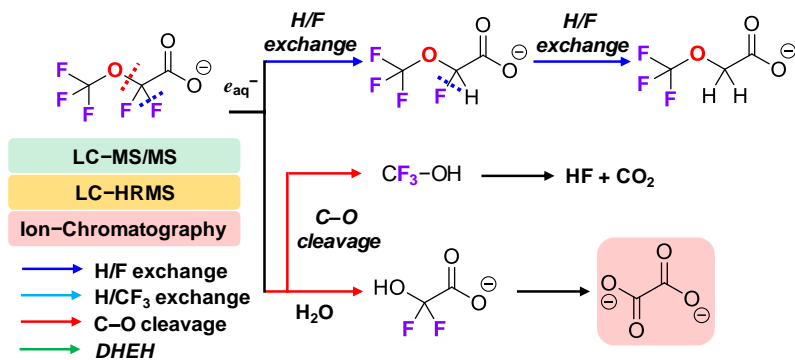
Scheme S1. Proposed degradation mechanism for perfluoro(2-methyl-3-oxahexanoate) [A1, HPFO-DA].



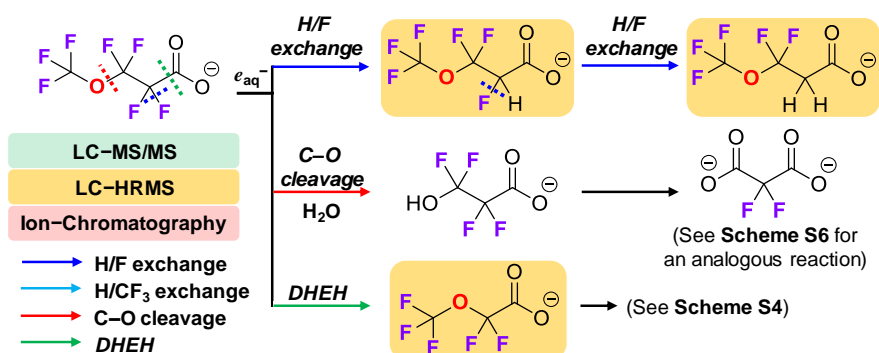
Scheme S2. Proposed degradation mechanism for perfluoro(2,5-dimethyl-3,6-dioxanonanoate) [A2, HFPO-TrA].



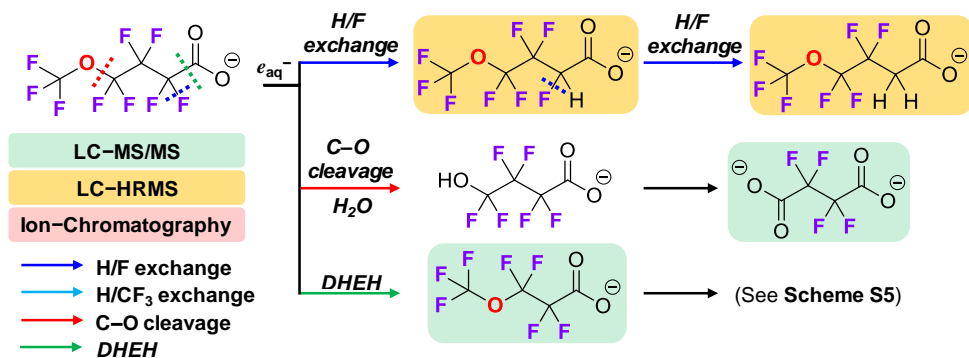
Scheme S3. Proposed degradation mechanism for perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoate) [A3, HFPO-TeA].



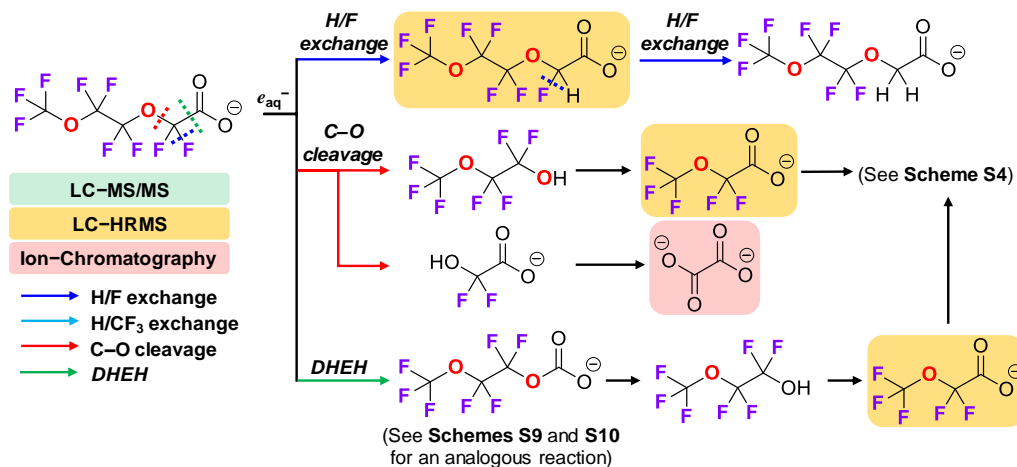
Scheme S4. Proposed degradation mechanism for perfluoro(2-methoxyacetate) [B1].



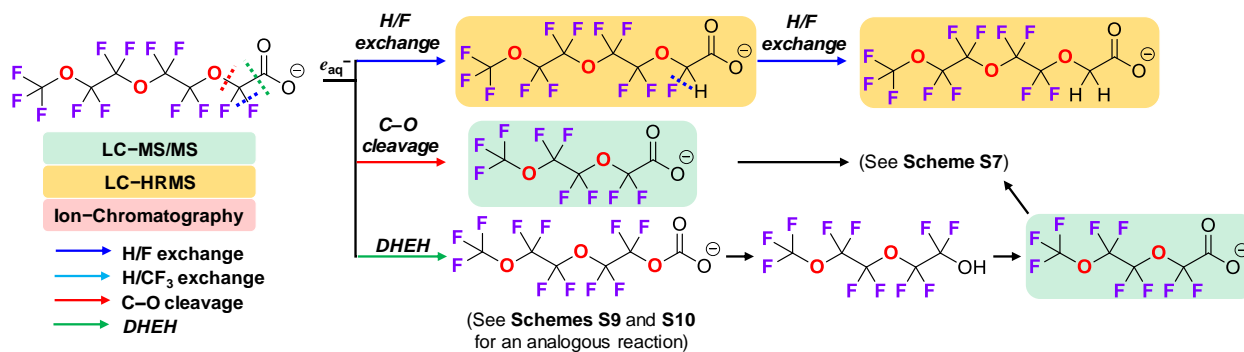
Scheme S5. Proposed degradation mechanism for perfluoro(3-methoxypropanoate) [B2].



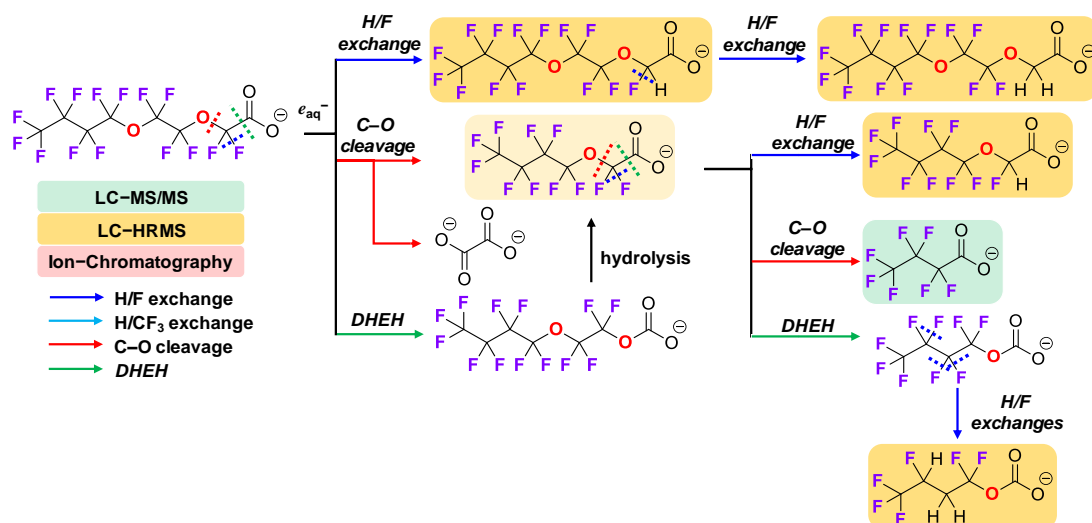
Scheme S6. Proposed degradation mechanism for perfluoro(4-methoxybutanoate) [B3].



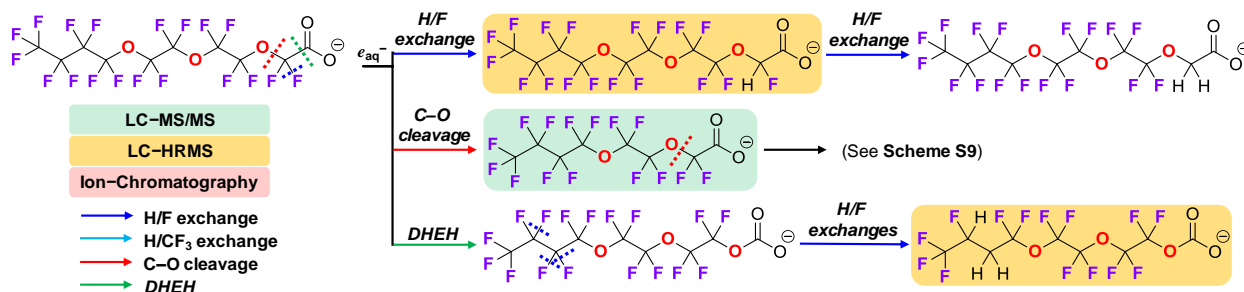
Scheme S7. Proposed degradation mechanism for perfluoro(3,6-dioxaheptanoate) [C1].



Scheme S8. Proposed degradation mechanism for perfluoro(3,6,9-trioxadecanoate) [C2].



Scheme S9. Proposed degradation mechanism for perfluoro(3,6-dioxadecanoate) [**D1**].



Scheme S10. Proposed degradation mechanism for perfluoro(3,6,9-trioxatridecanoate) [**D2**].

References

1. Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Defluorination of per- and polyfluoroalkyl substances (PFASs) with hydrated electrons: Structural dependence and implications to PFAS remediation and management. *Environ. Sci. Technol.* **2019**, 53 (7), 3718-3728.
2. Hill, J. T., Polymers from hexafluoropropylene oxide (HFPO). *J. Macromol. Sci. Chem.* **1974**, 8 (3), 499-520.