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Fluorinated sulfonate surfactants

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Dedicated to Professor Wei-Yuan Huang on the occasion of his 90th birthday.

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ABSTRACT

New classes of fluorinated sulfonate surfactants were synthesized in which a perfluoroalkyl chain is interrupted either by an ether oxygen (–O–), or by methylene (–CH_2–) units. Both classes of molecules involve multi-step syntheses. The fluoroether sulfonates ($RfOCF_2CF_2CH_2CH_2SO_3H$, Rf = C_2F_5, C_3F_7) were achieved in four steps including fluoroiodonation of perfluorovinyl ethers (RfCF = CF_2), ethylation, chlorination and hydrolysis. The methylene interrupted fluorosulfonates ($RfCH_2CF_2CH_2CH_2SO_3H$, Rf = C_4F_9, C_6F_{13}) were also prepared in four steps involving vinylidene fluoride insertion of fluoroalkyl iodides, ethylene insertion, chlorination and hydrolysis. All intermediates and final products were well characterized by ^1H and ^{19}F NMR. These new fluorinated surfactants were compared to a commercially available fluorosulfonate ($C_6F_{13}CH_2CH_2SO_3H$) for surface activity. These materials match the surface tensions of commercial fluorosurfactant yet are more efficient because they have lower fluorine content.

1. Introduction

Fluorinated surfactants are surface active agents comprised mainly of two structural components, a hydrophobic and oleophobic perfluorinated carbon chain (e.g., $F(CF_2)_n$–) and a hydrophilic component. The latter part is functionalized for selective applications and characterized as anionic, cationic, amphoteric or non-ionic [1].

Fluorinated surfactants can reduce surface tension energy much more than that achievable with hydrocarbon or silicone surfactants due to the unique properties of the fluorine atom. The high electron density and electronegativity of fluorine atoms reduce the polarizability of the surfactants, and therefore they are not as susceptible to the London dispersion forces that are the foundation of lipophilicity. The use of fluorine as opposed to hydrogen atoms in the surfactant backbone dramatically changes the nature of the surfactant and tends to drive the surfactant to the liquid-air interface. In contrast, hydrocarbon surfactants are more concentrated at condensed phases. In addition, many fluorinated surfactants are well-suited for use under high temperature and pressure conditions where low surface energy performance is critical due to the stability of carbon–fluorine bond [2]. They can also distinguish themselves by their exceptional chemical stability in corrosive media such as basic or acidic environments [2].

The application of fluorinated surfactants may not be familiar to many of us even though we come in contact with them during our everyday life. They can be used as anti-blocking additives for interior paints and coatings, wetting and leveling agent for floor finishes, aqueous fire fighting foams to put out fires, cleaner for hard surfaces, emulsifying and dispersing aid for olefin polymerization, etc. [3–9].

Fluorinated sulfonic acids are in the category of ionic surfactants. They are able to reduce the surface tension of aqueous solutions to very low levels, and can be used as an antistat in films [10]. They also possess outstanding chemical stability in corrosive media and, in particular, very acidic solutions. Fluorinated sulfonic acids impart additional properties that may prove useful to any formulation based on aggressive (highly acidic, oxidizing, or reducing) media [11–13]. For example, in chrome plating baths, they aid wetting of the components to be treated and promote the formation of a foam layer on the bath surface, reducing dangerous chromic acid mist generation. In metal treatment [14], they are used for cleaning, descaling and pickling purposes.

Here, we describe the syntheses of some novel fluorinated sulfonates in which the fluorinated carbon chains are interrupted either by methylene (–CH_2) units or by an ether (e.g., –O–) linkage. Their surface activities are also discussed.

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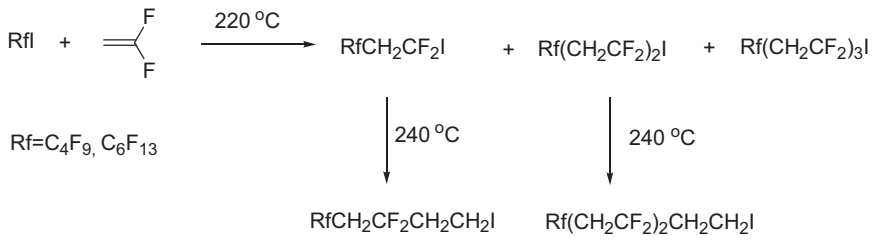
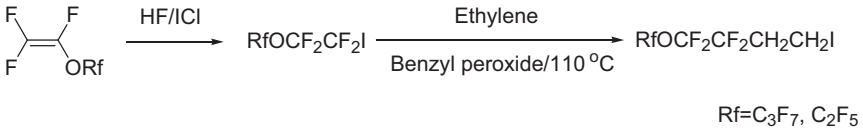


Scheme 1.

Table 1
Product distribution and physical properties of fluorinated Iodides prepared by VDF and ethylene insertion.

Rf	Yields (%)			
	VDF insertion		Ethylene insertion	
	1VDF	2VDF	1VDF	2VDF
C_4F_9	60 (**IA**) (b.p. 118–122 °C)	9 (**IIA**) (b.p. 188–191 °C)	75 (**IB**) (m.p. 41–43 °C).	70 (**IIB**) (m.p. 43–45 °C)
C_6F_{13}	57 (**IIIA**) (b.p. 170–172 °C)	13 (**IVA**) (b.p. 250–257 °C)	65 (**IIIB**) (m.p. 65–68 °C)	77 (**IVD**) (m.p. 68–72 °C)



Scheme 2.

2. Results and discussion

2.1. Fluorinated iodides incorporating vinylidene fluoride and ethylene

Thermal or redox-initiated vinylidene fluoride (VDF) insertion of fluoroalkyl iodides has been studied extensively by Ameduri et al. [15–18]. Considering the lengthy reaction time (48 h) and organic solvent (CH_3CN) used in redox-initiated VDF insertion reaction [15,19], thermal insertion is a much more attractive option due to its simple and solvent free condition. VDF was thermally inserted into perfluoroalkyl iodides to obtain a mixture of 1VDF, 2VDF and 3VDF insertion products at 220 °C. The 3VDF insertion product is formed only in trace amount (<3 wt% by GC), while the single VDF insertion dominates (Scheme 1 and Table 1). At 210–220 °C, 1VDF insertion selectivity between head to tail adduct ($RfCH_2CF_2I$) and head to head adduct ($RfCF_2CH_2I$) exceeds 95%, while 2VDF insertion selectivity of head to tail adduct $RfCH_2CF_2CH_2CF_2I$ vs head to head adduct $RfCH_2CF_2CF_2CH_2I$ is about 90%. The oligomers are readily separated by fractional distillation but the isomers could not be separated.

Ethylation of fluoroalkyl iodides can be achieved either by thermal or radical initiation [19–23]. The thermal insertion is preferred for ethylating VDF iodides because it selectively adds one ethylene to the head to tail VDF adducts $Rf(CH_2CF_2)_nI$ whereas the head to head adducts $RfCF_2CH_2I$ and $RfCH_2CF_2CF_2CH_2I$ are unreactive. Therefore the final reaction mixture can be separated by vacuum distillation. For example, in the absence of air the VDF fluorinated iodides prepared above were treated with an excess of ethylene at 240 °C for 12 h. Under this condition, a single ethylene inserted into head to tail structured VDF iodides $Rf(CH_2CF_2)_nI$ to form ethylated products $Rf(CH_2CF_2)_nCH_2CH_2I$. The product was purified by separating unreacted starting material from the final product through distillation. In addition, the distillation removed the unreacted head to head adducts $RfCF_2CH_2I$ or $RfCH_2CF_2CF_2CH_2I$ carried over from VDF insertion step since they did not get ethylated. We obtained satisfactory yields up to 75% using about 2.7 mol of ethylene per mole of VDF perfluoalkyl iodide.

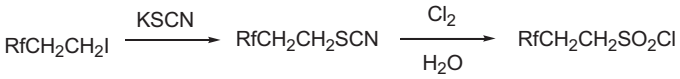
It is interesting to note that although the boiling points of the double VDF inserted iodides are 60–80 °C higher than single VDF inserted iodides, there is only marginal difference in melting points for the ethylene adducts. The boiling point is related to the molecular weight while melting point is related to the solid state forces. Increasing the number of VDF units increases the molecular weight but apparently has only a small impact on solid state interactions.

2.2. Perfluoralkylether ethyl iodides

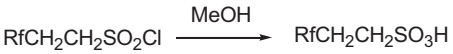
The starting perfluoroalkyl vinyl ether iodides were made by reacting fluorinated vinyl ethers with ICl and HF in the presence of BF_3 [24] (Scheme 2 and Table 2). This chemistry may also be effected by reacting perfluoroalkyl vinyl ether with I_2/IF_5 [25] or I_2/LiI [26]. Purification was achieved by phase separation of unreacted starting material and product, followed by distillation. The ethylation of the fluoroether may be accomplished by either thermal insertion or radical initiated insertion. However, radical initiation is preferred in the case of $C_2F_5OCF_2CF_2I$ (b.p. 67 °C, est. $T_c < 240$ °C) due to its high vapor pressure at the 240 °C temperature required for thermal insertion. Therefore, $C_2F_5OCF_2CF_2I$ was reacted with an excess of ethylene at 110 °C in the presence of benzoyl peroxide for 24 h (Scheme 2 and Table 2). Other peroxides such as isobutyryl peroxide, propionyl peroxide, or acetyl peroxide can be employed in this reaction as well. $C_3F_7OCF_2CF_2I$ (boiling point: 90 °C) is ethylated in thermal way. Both products can be purified by distilling unreacted starting material away from the final product.

Table 2
Yield and physical properties of fluoroalkyether ethyl iodides.

Rf	Yield (%)	
	Fluoroether iodide	Fluoroether ethylene Iodide
C_3F_7	92 (**VA**) (b.p. 89–91 °C)	85 (**VB**) (b.p. 56–60 °C at 25 Torr)
C_2F_5	90 (**VIA**) (b.p. 66–68 °C)	64 (**VIB**) (b.p. 70–72 °C at 60 Torr)



Scheme 3.



Scheme 4.

Table 3
Yields and physical properties of fluorinated thiocyanates and sulfonyl chlorides.

Rf	Yield (%)/(°C/Torr)	
	Thiocyanates	Sulfonyl chlorides
$C_4F_9CH_2CF_2$	91 (**IC**) (b.p. 112–115 °C at 1.5 Torr)	83 (**ID**)
$C_4F_9(CH_2CF)_2$	94 (**IIC**) (b.p. 129–133 °C at 1 Torr)	86 (**IID**)
$C_6F_{13}CH_2CF_2$	91 (**IIIC**) (b.p. 112–115 °C at 1.5 Torr)	83 (**IIID**)
$C_3F_7OCF_2CF_2$	99 (**VC**) (b.p. 73–74 °C at 2 Torr)	90 (**VD**)
$C_2F_5OCF_2CF_2$	92 (**VIC**) (b.p. 63–65 °C at 2 Torr)	84 (**VID**)

Table 4
Yields of fluorosulfonic acids.

Fluorosulfonic acids	Yield (%)
$C_4F_9CH_2CF_2CH_2CH_2SO_3H$ (**IE**)	97
$C_4F_9(CH_2CF)_2CH_2CH_2SO_3H$ (**IIE**)	98
$C_6F_{13}CH_2CF_2CH_2CH_2SO_3H$ (**IIIE**)	100
$C_3F_7OCF_2CF_2CH_2CH_2SO_3H$ (**VE**)	97.5
$C_2F_5OCF_2CF_2CH_2CH_2SO_3H$ (**VIE**)	100

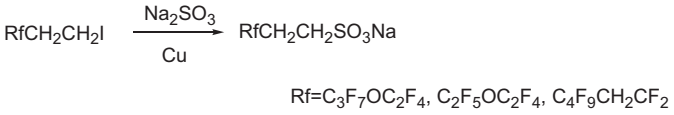
2.3. Fluorinated sulfonates

The sulfonyl chloride route is applied to obtain fluorosulfonic acids. Fluorinated sulfonyl chlorides are important intermediates and can be made via several methods. One common route is to react fluorinated ethylene iodide with thiourea, followed by oxidation with $KMnO_4$ [27] or chlorine gas [28] to provide corresponding sulfonyl chloride. Here, we adapted the fluorinated thiocyanate route in which fluoroethylene iodides are converted into fluorinated thiocyanates by reacting with potassium thiocyanates in the presence of a phase transfer catalyst in high yields [29], followed by chlorination to generate fluorinated sulfonyl chlorides (Scheme 3 and Table 3). Fluoroethylene iodides are converted into fluorinated thiocyanates by reacting with potassium thiocyanates in water in the presence of Aliquatt® 336 in high yields. It was found that double the amount of phase transfer catalyst reduced reaction time by almost half from 36 h to less than 20 h. Chlorination of these thiocyanates generated the fluorinated sulfonyl chloride. In general, 3–5% starting material remained after 10 h under 10 psi pressure, and excess chlorine had to be added to drive the reaction to 100% conversion. Slightly higher pressure (17 psi) seemed more effective, and 100% conversion is achieved after 10 h.

Fluorinated sulfonyl chlorides were treated with methanol to form the corresponding fluorinated sulfonic acids (Scheme 4 and Table 4).

Fluorosulfonates can also be made by reaction of fluoroethylene iodide with sodium sulfite in the presence of copper. The reaction is sluggish and the conversion of this reaction is moderate after 7 days (Scheme 5 and Table 5). The solubility of these sodium fluorosulfonates in water is poor and generally lower than 1% at room temperature. This property is used for product purification, as the reaction mixed is filtered at 75 °C, and the filtered solution is cooled to precipitate out the desired sodium fluorosulfonate in high purity.

It is worth noting that the structure difference of **IF** ($C_4F_9CH_2CF_2CH_2CH_2SO_3Na$) and **VF** ($C_3F_7OCF_2CF_2CH_2CH_2SO_3Na$) is a methylene vs an oxygen, however, it leads to nearly a 50 °C



Scheme 5.

Table 5
Yields and physical properties of sodium fluorosulfonates.

Sodium fluorosulfonates	Yield (%)	m.p. (°C)	Solubility in water at rt
$C_4F_9CH_2CF_2CH_2CH_2SO_3Na$	84 (**IF**)	225–227	≤1%
$C_3F_7OCF_2CF_2CH_2CH_2SO_3Na$	41 (**VF**)	180	<1%
$C_2F_5OCF_2CF_2$ $CH_2CH_2SO_3Na$	62 (**VIF**)	135–137	≤1%

melting point difference between these two molecules. Apparently the oxygen linkage interferes with inter molecular interaction in the solid state structure of these molecules.

Unlike sodium fluorinated sulfonates the acid forms of these sodium fluorosulfonates have excellent solubility in water. The above fluorinated sulfonic acids were diluted into water at different concentrations for surface tension measurement (Table 6 and Fig. 1).

Normal surface tension of deionized water is 72 dyn/cm. When the above fluorosulfonic acids were added at a specified rate, the surface tension of each aqueous solution was reduced significantly. As shown in Table 6 and Fig. 1, all fluorosulfonic acids exhibited excellent surface tension reduction. Surfactant **IIIE** ($C_6F_{13}CH_2CF_2CH_2CH_2SO_3H$) showed lower surface tension than $C_6F_{13}CH_2CH_2SO_3H$ at all concentrations for the same fluorine content. While at a lower fluorine content, surfactant **IIE** ($C_4F_9(CH_2CF_2)_2CH_2CH_2SO_3H$) has also better surface tension reduction than $C_6F_{13}CH_2CH_2SO_3H$. In addition, surfactants **IE**, **VE** and **VIE** demonstrated comparable performance to $C_6F_{13}CH_2CH_2SO_3H$ even all of them possess lower fluorine contents (Table 7 and Fig. 2).

Sodium fluorosulfonates frequently have higher room temperature surface tensions than their corresponding acids. For example when measured at 0.5 wt% in water, surfactant **VF** ($C_3F_7OCF_2CF_2CH_2CH_2SO_3Na$) has a surface tension ~41.5 dyn/cm vs

Table 6
Aqueous surface tensions of fluorosulfonic acids (dyn/cm).

Surfactants	F%	Concentration (wt% of surfactant)							
		1%	0.5%	0.2%	0.1%	0.05%	0.01%	0.005%	0.001%
$C_6F_{13}CH_2CH_2SO_3H$	57.7	22.8	22.1	27.4	32.1	50.6	64.4	68.4	72.5
$C_4F_9CH_2CF_2CH_2CH_2SO_3H$	53.3	17.4	21.7	32.6	42.0	49.8	69.2	71.2	72.9
$C_4F_9(CH_2CF_2)_2CH_2CH_2SO_3H$	54.2	20.5	22.3	29.8	40.7	43.5	52.5	56.0	64.3
$C_6F_{13}CH_2CF_2CH_2CH_2SO_3H$	57.9	19.1	19.5	24.2	32.8	35.2	46.8	51.8	66.2
$C_3F_7OCF_2CF_2CH_2CH_2SO_3H$	53.0	15.5	18.7	24.3	34.2	45.9	65.3	68.4	72.4
$C_2F_5OCF_2CF_2CH_2CH_2SO_3H$	49.7	19.2	27.4	37.7	45.0	51.2	62.9	71.5	73.2

The average of 10 replicates is reported; the standard deviation was <1 dyn/cm.

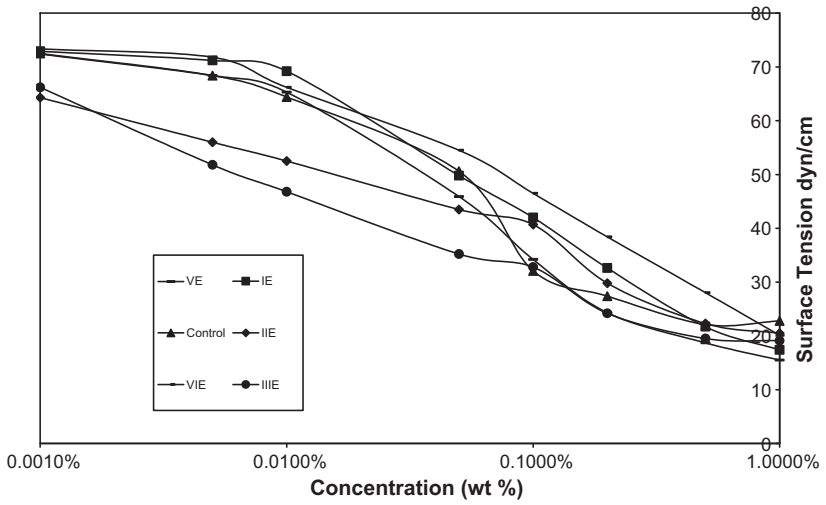


Fig. 1. Aqueous surface tensions of polyfluorosulfonic acids.

Table 7
Aqueous surface tensions of sodium fluorosulfonates (dyn/cm).

Surfactants	Concentration (wt% of surfactant)							
	1%	0.5%	0.2%	0.1%	0.05%	0.01%	0.005%	0.001%
$C_3F_7OCF_2CF_2CH_2CH_2SO_3Na$		41.5	51.7	58.5	62.6	69.7	70.9	72.3
$C_2F_5OCF_2CF_2CH_2CH_2SO_3Na$	46.4	54.5	62.8	67.0	69.1	71.6	71.8	72.8
$C_4F_9CH_2CF_2CH_2CH_2SO_3Na$	42.3	50.7	60.1	65.4	68.4	71.6	71.9	72.6

The average of 10 replicates is reported; the standard deviation was <1 dyn/cm.
$C_3F_7OCF_2CF_2$ $CH_2CH_2SO_3Na$ is not soluble in water at 1% at rt.

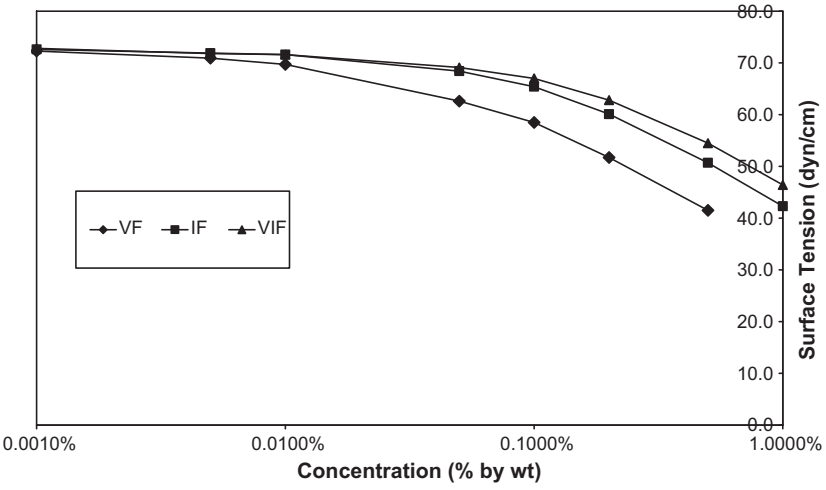


Fig. 2. Aqueous surface tensions of sodium polyfluorosulfonates.

18.7 dyn/cm for the corresponding free acid, **VE** ($C_3F_7OCF_2CF_2CH_2CH_2SO_3H$). The ability of sodium fluorosulfonates to lower surface tension is often limited by their relatively poor solubility.

3. Conclusions

In this paper, we describe the syntheses of two classes of partially fluorinated sulfonate surfactants: fluoroether sulfonate ($RfOCF_2CF_2CH_2CH_2SO_3H$, Rf = C_2F_5, C_3F_7) and the methylene interrupted fluorosulfonate ($RfCH_2CF_2CH_2CH_2SO_3H$, Rf = C_4F_9, C_6F_{13}). Both classes of sulfonates were prepared in multiple steps in good yields. Compared to perfluoroethyl sulfonic acid surfactant ($C_6F_{13}CH_2CH_2SO_3H$), these novel fluorosulfonates have lower fluorine content and therefore they are more fluorine efficient. The surface activities of the new fluorosulfonates were tested, and it is found that fluorine chains containing an ether oxygen or methylene units performed as well as perfluorinated ethyl sulfonic acid in surface tension reduction.

4. Experimental

4.1. General

Nonfluorinated starting materials and solvents were obtained from Sigma–Aldrich, Inc., St. Louis, MO, EMD Chemicals, Inc.

(Merck KGaA, Darmstadt, Germany) and Alfa Aesar, Ward Hill, MA. Perfluoroalkyl iodides, perfluorovinyl ether, vinylidene fluoride, hydrogen fluoride are from E.I. du Pont de Nemours. All reagents were used without further purification.

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded using a Bruker Avance DRX® (400 MHz) and fluorine-19 nuclei using a Bruker Avance DRX® (376 MHz). Abbreviations for coupling patterns are as follows: s (singlet), d (doublet), t (triplet), tt (triplet of triplets), q (quartet), p (pentuplet) and m (multiplet). Elemental analysis was performed by Micro Analysis, Inc., Wilmington, DE 19808. Mass spectra (MS) were obtained using an Agilent Technologies 5973Network mass selective detector coupled to an Agilent Technologies 6890N Network GC System.

Surface tension was measured according to the American Society for Testing and Materials ASTM # D1331-56, using the Wilhelmy plate method on a KRUSS K11 Version 2.501 tensiometer (KRUSS USA, Matthews, NC) in accordance with instructions with the equipment. A vertical plate of known perimeter was attached to a balance, and the force due to wetting was measured. Each example to be tested was added to deionized water by weight based on solids of the additive in deionized water. Several different concentrations were prepared. Ten replicates were tested of each dilution, and the following machine settings were used:

Method: Plate Method SFT;
Interval: 1.0 s;
Wetted length: 40.2 mm;
Reading limit: 10;
Min standard deviation: 2 dyns/cm;
Gr. acc.: 9.80665 m/s^2.

Results were in dyns/cm (mN/m) with a standard deviation of less than 1 dyn/cm. The tensiometer was used according to the manufacturer's recommendations.

4.2. 1,1,1,2,2,3,3,4,4,6,6-Undecafluoro-6-iodo-hexane (IA) and 1,1,1,2,2,3,3,4,4,6,6,8,8-tridecafluoro-8-iodo-octane (IIA)

VDF (70.3 g, 1.1 mol) was introduced to an 400 mL autoclave charged with C_4F_9I (316 g, 0.91 mol), and the reactor heated at 210 °C for 16 h. The pressure was raised up to 1500 psi as temperature was increasing, followed by dropping back to 150 psi, which indicated the consuming VDF to form VDF adducts. The products were transferred out of the autoclave and isolated by vacuum distillation to recover 10% starting material and provide 225 g $C_4F_9CH_2CF_2I$ (**IA**) (b.p. 45 °C/25 Torr) in 60% yield and 39 g $C_4F_9(CH_2CF_2)_2I$ (**IIA**) (b.p. ~80 °C/25 Torr) in 9% yield. **IA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.34 (2H, p, J = 15.2 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −40.45 (2F, p, J = 13.6 Hz), −83.59 (3F, tt, J_1 = 9.3 Hz, J_2 = 3.0 Hz), −114.89–115.13 (2F, m), −126.71–126.88 (2F, m), −128.26–128.40 (2F, m). **IIA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.31 (2H, p, J = 14.8 Hz), 2.74 (2H, p, J = 15.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −39.19–39.36 (2F, m), −81.76 (3F, tt, J_1 = 9.5 Hz, J_2 = 3.2 Hz), −88.65–88.89 (2F, m), −113.09 (2F, s), −125.00 (2F, s), −126.67–126.52 (2F, m). The NMR spectra of **IA** and **IIA** are consistent with literature reported values [15].

4.3. 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-Pentadecafluoro-8-iodo-octane (IIIA) and 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8,10,10-heptadecafluoro-10-iodo-decane (IVA)

VDF (15 g) was introduced to a 400 mL autoclave charged with $C_6F_{13}I$ (100 g), and the reactor heated at 220 °C for 16 h. The pressure was raised up to 300 psi as temperature was increasing, followed by dropping back to 40 psi, which indicated the consuming VDF to form VDF adducts. The products were transferred out of the autoclave isolated by vacuum distillation to recover starting material (14.3 g, 12.25%) and provide 63.7 g $C_6F_{13}CH_2CF_2I$ (**IIIA**) (b.p. 62–64 °C/28 Torr) in 60% yield and 14.4 g $C_6F_{13}(CH_2CF_2)_2I$ (**IVA**) (b.p. 95–96 °C/28 Torr) in 12.65% yield. **IIIA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.34 (2H, p, J = 15.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −38.54 (2F, p, J = 13.7 Hz), −81.54 (3F, tt, J_1 = 10.1 Hz, J_2 = 2.3 Hz), −112.73–113.02 (2F, m), −122.28 (2F, m), −123.41 (2F, s), −123.97 (2F, s), −126.65–126.82 (2F, m). **IVA**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.32 (2H, p, J = 14.8 Hz), 2.75 (2H, p, J = 16.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −39.12–39.29 (2F, m), −81.38 (3F, tt, J_1 = 9.8 Hz, J_2 = 2.4 Hz), −88.51–88.76 (2F, m), −112.61–112.89 (2F, m), −122.18 (2F, m), −123.31 (2F, s), −123.94 (2F, s), −126.53–126.70 (2F, m). The NMR spectra of **IIIA** and **IVA** are consistent with literature reported values [30].

4.4. Synthesis of 1,1,1,2,2,3,3,4,4,6,6-undecafluoro-8-iodo-octane (IB)

Ethylene (25 g, 0.53 mol) was introduced to an 400 mL autoclave charged with $C_4F_9CH_2CF_2I$ (217 g, 0.87 mol) and D-(+)-limonene (1 g), and then the reactor was heated at 240 °C for 12 h. The pressure was raised up to 1000 psi as temperature was increasing, followed by dropping back to 200 psi, which indicated the consumption of ethylene to form ethylated product. The product was transferred out of the autoclave, and 144 g $C_4F_9CH_2CF_2CH_2CH_2I$ (**IB**) was obtained via vacuum distillation 81–91 °C at 19–24 Torr in 62% yield. m.p. 41–43 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.16 (2H, t, J = 8.2 Hz), 2.73–2.50 (2H, m), 1.45 (2H, s). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.45 (3F, tt, J_1 = 9.4 Hz, J_2 = 3.2 Hz), −94.09–94.33 (2F, m), −113.10–113.37 (2F, m), −124.74 (2F, s), −126.13–126.27 (2F, m). MS (PCI): 438 (M^+). $C_8F_{11}H_6I$ (437.93). Calc. C 21.92, H 1.38; Found C 21.71, H 1.24.

4.5. Synthesis of 1,1,1,2,2,3,3,4,4,6,6,8,8-tridecafluoro-10-iodo-decane (IIB)

Ethylene (18 g, 0.64 mol) was introduced to an 400 mL autoclave charged with $C_4F_9(CH_2CF_2)_2I$ (181 g, 0.64 mol) and D-(+)-limonene (1 g), and then the reactor was heated at 240 °C for 12 h. The pressure was raised up to 650 psi as temperature was increasing, followed by dropping back to 150 psi, which indicated the consumption of ethylene to form ethylated product. The product was transferred out of the autoclave, and 134 g $C_4F_9(CH_2CF_2)_2CH_2CH_2I$ (**IIB**) was obtained via vacuum distillation 95–98 °C at 9 Torr in 70% yield. m.p. 43–45 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15 (2H, t, J = 8.6 Hz), 2.77 (2H, p, J = 16.0 Hz), 2.68–2.44 (2H, m), 1.45 (2H, s). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.48 (3F, tt, J_1 = 9.8 Hz, J_2 = 3.3 Hz), −88.41 to 88.69 (2F, m), −96.23 to 96.48 (2F, m), −112.85 to 113.13 (2F, m), −124.82 (2F, s), −126.17 to 126.31 (2F, m). MS (PCI): 502 (M^+). $C_{10}F_{13}H_8I$ (501.95). Calc. C 23.91, H 1.61; Found C 23.80, H 1.32.

4.6. Synthesis of 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluoro-10-iodo-decane (IIIB)

Ethylene (15 g, 0.53 mol) was introduced to an 400 mL autoclave charged with $C_6F_{13}CH_2CF_2I$ (170 g, 0.33 mol) and D-(+)-limonene (1 g), and then the reactor was heated at 240 °C for 12 h. The pressure was raised up to 680 psi as temperature was increasing, followed by dropping back to 220 psi, which indicated the consumption of ethylene to form ethylated product. The product was transferred out of the autoclave, and 121 $C_6F_{13}CH_2CF_2CH_2CH_2I$ (**IIIB**) was obtained via vacuum distillation in 68% yield b.p. 102–105 °C at 20–17 Torr. m.p. 65–68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.16 (2H, t, J = 8.4 Hz), 2.74–2.50 (2H, m), 1.45 (2H, s). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −83.19 (3F, tt, J_1 = 10.0 Hz, J_2 = 2.5 Hz), −96.06 to 96.31 (2F, m), −114.84 to 115.12 (2F, m),

−124.04 (2F, s), −125.19 (2F, m), −125.77 (2F, m), −128.39 to 128.54 (2F, m). MS (PCI): 538 (M^+). $C_{10}F_{15}H_6I$ (537.93). Calc. C 22.31, H 1.12; Found C 22.18, H 1.06 F 53.00. The NMR spectra of **IIIB** are consistent with literature reported values [19].

4.7. Synthesis of 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8,10,10-heptadecafluoro-12-iodo-dodecane (IVB)

Ethylene (56 g, 2.0 mol) was introduced to an 1300 mL autoclave charged with $C_6F_{13}(CH_2CF_2)_2I$ (714 g, 1.24 mol) and D-(+)-limonene (3.2 g), and then the reactor was heated at 240 °C for 12 h. The pressure was raised up to 800 psi as temperature was increasing, followed by dropping back to 240 psi, which indicated the consumption of ethylene to form ethylated product. The product was transferred out of the autoclave, and 627 g $C_6F_{13}(CH_2CF_2)_2CH_2CH_2I$ (**IVB**) was obtained in 84% yield after vacuum distillation (b.p. 124–128 °C at 12–9 Torr). m.p. 68–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15 (2H, t, J = 8.4 Hz), 2.77 (2H, p, J = 15.9 Hz), 2.68–2.45 (2H, m), 1.45 (2H, s). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.25 (3F, tt, J_1 = 10.0 Hz, J_2 = 2.5 Hz), −88.40 to 88.68 (2F, m), −96.23 to 96.48 (2F, m), −112.62 to 112.89 (2F, m), −122.11 (2F, s), −123.23 (2F, m), −123.89 (2F, m), −126.43 to 126.62 (2F, m). MS (PCI): 602 (M^+). $C_{12}F_{17}H_8I$ (601.94). Calc. C 23.92, H 1.34, F 53.66; Found C 23.83, H 1.15, F 54.37.

4.8. Synthesis of 1,1,1,2,2,3,3-heptafluoro-3-(1,1,2,2-tetrafluoro-2-iodo-ethoxy)-propane (VA)

The reactor was charged with iodine monochloride (200 g, 1.23 mol), HF (406 g, 20.3 mol), perfluoropropyl vinylether (PPVE) (327 g, 1.23 mol) and BF_3 (20 g, 0.29 mol) were introduced after cool evacuation. The reaction mixture was heated at 50 °C for 20 h. 250 mL ice cold water was introduced into the reactor. The mixture was transferred into a Teflon® separatory funnel and the organic layer was separated. After drying over anhydrous $MgSO_4$, the iodide $C_3F_7OCF_2CF_2I$ (**VA**) was obtained as a pink liquid (448 g, 88%). b.p. 89 °C. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −65.66 (2F, t, J = 6.0 Hz), −81.89 (3F, t, J = 7.3 Hz), −85.17 to 85.33 (2F, m), −86.17 to 86.28 (2F, m), −130.50 (2F, s). The NMR spectra of **VA** are consistent with literature reported values [24].

4.9. Synthesis of 1,1,1,2,2,3,3-heptafluoro-3-(1,1,2,2-tetrafluoro-2-iodo-ethoxy)-propane (VIA)

The reactor was charged with iodine monochloride (200 g, 1.23 mol), HF (407 g, 20.4 mol), perfluoroethyl vinylether (PEVE) (264 g, 1.22 mol) and BF_3 (15 g, 0.22 mol) were introduced after cool evacuation. The reaction mixture was heated at 50 °C for 20 h. 250 mL ice cold water was introduced into the reactor. The mixture was transferred into a Teflon® separatory funnel and the organic layer was separated. After drying over anhydrous $MgSO_4$, the iodide $C_2F_5OCF_2CF_2I$ (**VIA**) was obtained as a pink liquid (354 g, 89.7%). b.p. 63 °C. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −65.70 (2F, t, J = 5.5 Hz), −86.55 to 86.64 (2F, m), −87.83 (3F, t, J = 7.1 Hz), −89.68 (2F, t, J = 12.2 Hz). MS (PCI): 363 (M^++1).

4.10. Synthesis of 1,1,2,2-tetrafluoro-1-heptafluoropropyloxy-4-iodo-butane (VB)

The reactor was charged with $C_3F_7OCF_2CF_2I$ (590 g, 1.43 mol) and D-(+)-limonene under nitrogen. A series of three vacuum/N_2 gas purging sequences were then executed at −20 °C, and ethylene (64 g, 2.29 mol) was introduced. The reaction mixture was heated at 240 °C for 12 h. The pressure was raised up to 800 psi as temperature was increasing, followed by dropping back to 380 psi, which indicated the consumption of ethylene to form ethylated product. The autoclave was then cooled to 0 °C and opened after degassing. The product was collected, and vacuum distillation of the product yielded 385 g (61.2%) of $C_3F_7OCF_2CF_2CH_2CH_2I$ (**VB**). b.p. 57–58 °C/25 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.24–3.20 (2H, m), 2.70–2.58 (2H, m). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.83 (3F, t, J = 7.0 Hz), −84.96 to 85.09 (2F, m), −88.05 to 88.12 (2F, m), −119.37 (2F, t, J = 17.0 Hz), −130.42 (2F, s). MS (PCI): 440 (M^+). $C_7F_{11}H_4OI$ (439.91). Calc. C 19.09, H 0.92; Found C 18.84, H 0.89.

4.11. Synthesis of 1,1,2,2-tetrafluoro-1-heptafluoropropyloxy-4-iodo-butane (VIB)

$C_2F_5OCF_2CF_2I$ (488 g, 1.35 mol) and benzoyl peroxide (13 g) were charged under nitrogen in a reactor. A series of three vacuum/N_2 gas purging sequences were then executed at −50 °C, after which ethylene (101 g, 3.6 mol) was introduced. The vessel was heated for 24 h at 110 °C. The pressure was raised up to 1000 psi as temperature was increasing, followed by dropping back to 600 psi, which indicated the consumption of ethylene to form ethylated product. The autoclave was cooled to 0 °C and opened after degassing. Then the product was collected. Three runs were combined and the product was distilled giving 780 g of $C_2F_5OCF_2CF_2CH_2CH_2I$ (**VIB**) in 69% yield. b.p. 63–65 °C/60 Torr; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.26 (2H, t, J = 8.0 Hz), 2.69 (2H, tt, J_1 = 17 Hz, J_2 = 8.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −87.10 (3F, s), −88.08 to 88.15 (2F, m), −88.94 to 89.01 (2F, m), −117.99 (2F, t, J = 17 Hz). MS (PCI): 390 (M^++1). $C_4F_9H_4OI$ (365.92). Calc. C 18.48, H 1.03; Found C 18.38, H 0.68.

4.12. Synthesis of 1,1,1,2,2,3,3,4,4,6,6-undecafluoro-8-thiocyanato-octane (IC)

The flask was charged with $C_4F_9CH_2CF_2CH_2CH_2I$ (200 g, 0.457 mol), potassium thiocyanate (88.4 g, 0.910 mol) and trioctylmethylammonium chloride (Aliquat® 336) (1.84 g, 0.00455 mol) under nitrogen. De-ionized water (200 g, 11.1 mol) was added and the reaction mixture was heated to 90 °C for 18 h. A second addition of KSCN (potassium thiocyanate) (1 g, 0.0103 mol) was then added and the reaction continued for a further 3 h. The organic layer was separated in a glass separating funnel and washed with hot (70 °C) de-ionized water. The product was distilled on a high vacuum system giving 153.5 g (91.0%) of $C_4F_9CH_2CF_2CH_2CH_2SCN$ (**IC**). b.p. 112–115 °C/1.5 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.09 (2H, t, J = 8.0 Hz), 2.78–2.62 (2H, m), 2.50 (2H, tt, J_1 = 16.7 Hz, J_2 = 6.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.49 (3F, tt, J_1 = 10.0 Hz, J_2 = 3.0 Hz), −92.76 to 93.91 (2F, m), −113.09 (2F, s), −124.68 to 124.78 (2F, m), −126.16 to 126.77 (2F, m). MS (PCI): 370 (M^++1). $C_9F_{11}H_6SN$ (369.00). Calc. C 29.27, H 1.64; Found C 29.09, H 1.50.

4.13. Synthesis of 1,1,1,2,2,3,3,4,4,6,6,8,8-tridecafluoro-10-thiocyanato-decane (IIC)

The flask was charged with $C_4F_9(CH_2CF_2)_2CH_2CH_2I$ (500 g, 0.996 mol), potassium thiocyanate (194 g, 1.99 mol) and trioctylmethylammonium chloride (Aliquat® 336) (4.02 g, 0.00995 mol) under nitrogen. De-ionized water (500 g, 27.8 mol) was added and the reaction mixture was heated to 90 °C for 18 h. The organic layer was separated in a glass separating funnel and washed with hot (70 °C) de-ionized water. The product was distilled on a high vacuum system giving 407 g (94.3%) of $C_4F_9(CH_2CF_2)_2CH_2CH_2SCN$ (**IIC**). b.p. 129–133 °C/1.0 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.07 (2H, t, J = 7.9 Hz), 2.96–2.84 (2H, m), 2.84–2.64 (2H, m), 2.54 (2H, tt, J_1 = 16.7 Hz, J_2 = 7.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.90 (3F, tt, J_1 = 9.5 Hz, J_2 = 3.2 Hz), −89.33 to 89.56 (2F, m), −95.81 to 96.05 (2F, m), −113.23 (2F, s), −125.10 (2F, m), −126.47 to 126.62

(2F, m). MS (PCI): 434 (M^++1). $C_{11}F_{13}H_8SN$ (433.02). Calc. C 30.48, H 1.86; Found C 30.25, H 1.79.

4.14. Synthesis of 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluoro-10-thiocyanato-decane (IIIC)

The flask was charged with $C_6F_{13}CH_2CF_2CH_2CH_2I$ (500 g, 0.929 mol), potassium thiocyanate (180.6 g, 1.86 mol) and trioctylmethylammonium chloride (Aliquat® 336) (3.75 g, 0.00929 mol) under nitrogen. De-ionized water (500 g, 27.8 mol) was added and the reaction mixture was heated to 90 °C for 18 h. The organic layer was separated in a glass separating funnel and washed with hot (70 °C) de-ionized water. The product was distilled on a high vacuum system giving 386 g (88.6%) of $C_6F_{13}CH_2CF_2CH_2CH_2SCN$ (**IIIC**). b.p. 104–106 °C/0.75–0.50 Torr. m.p. 35–39 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.09 (2H, t, J = 7.9 Hz), 2.71 (2H, p, J = 15.0 Hz), 2.51 (2H, tt, J_1 = 16.9 Hz, J_2 = 8.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.23 (3F, tt, J_1 = 10.1 Hz, J_2 = 2.5 Hz), −93.67 to 93.90 (2F, m), −112.82 (2F, s), −121.94 to 122.18 (2F, m), −123.21 (2F, m), −123.76 (2F, m), −126.41 to 126.59 (2F, m). MS (PCI): 470 (M^++1). $C_{11}F_{15}H_6SN$ (469.00). Calc. C 28.15, H 1.29; Found C, 27.78 H 1.29.

4.15. Synthesis of 1,1,2,2-tetrafluoro-1-heptafluoropropyloxy-4-thiocyanato-butane (VC)

The flask was charged with $C_3F_7OCF_2CF_2CH_2CH_2I$ (200 g, 0.455 mol), potassium thiocyanate (88.4 g, 0.910 mol) and trioctylmethylammonium chloride (Aliquat® 336) (1.84 g, 0.00455 mol) under nitrogen. De-ionized water (200 g, 11.1 mol) was added and the reaction mixture was heated to 90 °C for 18 h. The organic layer was separated in a glass sep funnel and washed with hot (70 °C) de-ionized water. The product was distilled on a high vacuum system giving 167.6 g (99.0%) of $C_3F_7OCF_2CF_2CH_2CH_2SCN$ (**VC**). b.p. 73–74 °C/2.0 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.10–3.07 (2H, m), 2.58–2.46 (2H, m). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.71 (3F, t, J = 7.5 Hz), −84.84 to 84.97 (2F, m), −87.96 to 88.03 (2F, m), −118.29 (2F, t, J = 17.0 Hz), −130.29 (2F, s). MS (PCI): 372 (M^+). $C_8F_{11}H_4ONS$ (370.98). Calc. C 25.88, H 1.09; Found C 25.75, H 1.02, F 56.12.

4.16. Synthesis of 1,1,2,2-tetrafluoro-1-pentafluoroethyloxy-4-thiocyanato-butane (VIC)

The flask was charged with $C_2F_5OCF_2CF_2CH_2CH_2I$ (300 g, 0.769 mol), potassium thiocyanate (150 g, 1.54 mol) and trioctylmethylammonium chloride (Aliquat® 336) (3.11 g, 0.00769 mol) under nitrogen. De-ionized water (300 g, 16.7 mol) was added and the reaction mixture was heated to 90 °C for 18 h. The organic layer was separated in a separating funnel and washed with hot (70 °C) de-ionized water. The product was distilled on a high vacuum system giving 227.4 g (92.0%) of $C_2F_5OCF_2CF_2CH_2CH_2SCN$ (**VIC**). b.p. 63–65 °C/2.0 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.09 (2H, t, J = 8.0 Hz), 2.53 (2H, tt, J_1 = 16.8 Hz, J_2 = 8.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −87.29 (3F, s), −88.21 (2F, p, J = 13.7 Hz), −89.11 (2F, t, J = 13.0 Hz), −118.30 (2F, t, J = 17.0 Hz). MS (PCI): 433 (M^+). $C_7F_9H_4ONS$ (320.99). Calc. C 26.17, H 1.26; Found C 25.96, H 1.04.

4.17. Synthesis of 3,3,5,5,6,6,7,7,8,8,8-undecafluoro-octanesulfonyl chloride (ID)

An autoclave was charged with $C_4F_9CH_2CF_2CH_2CH_2SCN$ (230 g, 0.62 mol) and acetic acid (130 g, 2.17 mol) under nitrogen and heated to 45–50 °C. Chlorine gas (132 g, 1.86 mol) and de-ionized water were fed for 10 h. After feeding, the reaction was left to stir at 45–50 °C for 2 h. A second addition of chlorine gas (20 g, 0.282 mol) was fed over 1.5 h at 45–50 °C and continued to stir for 1 h. The crude product was heated at 70 °C and washed with de-ionized water (149 g, 8.28 mol). The organic layer was separated in a glass separating funnel and added to toluene (125 g, 1.36 mol), then washed twice with a 3.5 wt% solution of sodium chloride (149 g). After stripping off excess solvent, 211 g $C_4F_9CH_2CF_2CH_2CH_2SO_2Cl$ (**ID**) was obtained in 82.8% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86–3.82 (2H, m), 2.83–2.63 (2H, m). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.37 to 81.44 (2F, m), −92.99 to 93.20 (2F, m), −112.88 to 113.12, (2F, m), −124.57 to 124.69 (2F, m), −126.09 to 126.21 (3F, m).

4.18. Synthesis of 3,3,5,5,7,7,8,8,9,9,10,10,10-tridecafluoro-decanesulfonyl chloride (IID)

An autoclave was charged with $C_4F_9(CH_2CF_2)_2CH_2CH_2SCN$ (269 g, 0.62 mol) and acetic acid (130 g, 2.17 mol) under nitrogen and heated to 45–50 °C. Chlorine gas (132 g, 1.86 mol) was fed for 10 h and de-ionized water was fed for 8 h. After feeding, the reaction was left to stir at 45–50 °C for 1 h. A second addition of chlorine gas (25 g, 0.352 mol) was fed over 2.5 h at 45–50 °C and continued left to stir for 1 h. The crude product was heated at 70 °C and washed with de-ionized water (149 g, 8.28 mol). The organic layer was separated in a glass separating funnel and added to toluene (125 g, 1.36 mol), then washed twice with a 3.5 wt% solution of sodium chloride (149 g). After stripping off excess solvent, 307 g $C_4F_9(CH_2CF_2)_2CH_2CH_2SO_2Cl$ (**IID**) was obtained in 85.6% yield. ^{1}H NMR (Benzene-d_6, 400 MHz) δ 3.06–3.00 (2H, m), 2.26 (2H, p, J = 16.1 Hz), 2.09–1.94 (2H, m), 1.78 (2H, p, J = 15.3 Hz). ^{19}F NMR (Benzene-d_6, 376 MHz) δ −81.66 (2F, tt, J_1 = 9.6 Hz, J_2 = 3.4 Hz), −89.50 to 89.79 (2F, m), −96.07 to 96.34 (2F, m), −112.67 to 112.96 (2F, m), −124.69 (2F, m), −126.21 to 126.35 (3F, m).

4.19. Synthesis of 3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-decanesulfonyl chloride (IIID)

An autoclave was charged with a mixture of $C_6F_{13}CH_2CF_2CH_2CH_2SCN$ (291 g, 0.62 mol) and acetic acid (130 g, 2.17 mol) under nitrogen and heated to 45–50 °C. Chlorine gas (132 g, 1.86 mol) was fed for 10 h and de-ionized water was fed for 8 h. After feeding, the reaction was left to stir at 45–50 °C for 1 h. A second addition of chlorine gas (25 g, 0.352 mol) was fed over 110 min at 45–50 °C and left to stir for 1 h. The crude product was heated at 70 °C and washed with de-ionized water (149 g, 8.28 mol). The organic layer was separated in a glass separating funnel and added to toluene (125 g, 1.36 mol), then washed twice with a 3.5 wt% solution of sodium chloride (149 g). After stripping off excess solvent, 286 g $C_6F_{13}CH_2CF_2CH_2CH_2SO_2Cl$ (**IIID**) was obtained 90.4% yield. ^{1}H NMR (Benzene-d_6, 400 MHz) δ 3.09–3.04 (2H, m), 2.08–1.85 (2H, m). ^{19}F NMR (Benzene-d_6, 376 MHz) δ −81.64 (3F, tt, J_1 = 9.8 Hz, J_2 = 2.6 Hz), −95.44 to 95.70 (2F, m), −112.72 to 113.00 (2F, m), −122.12 to 122.39 (2F, m), −123.25 to 123.48 (2F, m), −123.54 to 123.76 (2F, m), −126.61 to 126.83 (2F, m).

4.20. Synthesis of 3,3,4,4-tetrafluoro-4-heptafluoropropyloxy-butane-1-sulfonyl chloride (VD)

An autoclave was charged with $C_3F_7OCF_2CF_2CH_2CH_2SCN$ (231 g, 0.62 mol) and acetic acid (130 g, 2.17 mol) under nitrogen and heated to 50–55 °C. Chlorine gas (132 g, 1.86 mol) was fed for 10 h and de-ionized water was fed for 8 h. After feeding, the reaction was left to stir at 50–55 °C for 2 h. A second addition of chlorine gas (20 g, 0.282 mol) and deionised water (7 g, 0.389 mol) were fed over 2 h at 50–55 °C and continued to stir for 1 h. A third addition of chlorine gas (10 g, 0.141 mol) was fed over 45 min at 45 °C and left to stir for another 2 h. The crude product was heated at 70 °C

and washed with de-ionized water (149 g, 8.28 mol). The organic layer was separated in a glass separating funnel and added to toluene (125 g, 1.36 mol), then washed twice with a 3.5 wt% solution of sodium chloride (149 g). A Dean–Stark trap was used to strip off excess solvent, and 228 g $C_3F_7OCF_2CF_2CH_2CH_2SO_2Cl$ (**VD**) was obtained in 89.9% yield of ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83–3.79 (2H, m), 2.77–2.64 (2H, m). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −81.60 (3F, t, J = 7.3 Hz), −84.71 to 84.84 (2F, m), −87.74 to 87.81 (2F, m), −117.42 (2F, t, J = 17.0 Hz), −130.17 (2F, s).

4.21. Synthesis of 3,3,4,4-tetrafluoro-4-pentafluoroethyloxy-butane-1-sulfonyl chloride (VID)

An autoclave was charged with a mixture of $C_2F_5OCF_2CF_2CH_2CH_2SCN$ (200 g, 0.62 mol) and acetic acid (130 g, 2.17 mol) under nitrogen and heated to 45–50 °C. Chlorine gas (132 g, 1.86 mol) was fed for 10 h and de-ionized water (47 g, 2.60 mol) was fed for 6–7 h. After feeding, the reaction was left to stir at 45–50 °C for 1 h. A second addition of chlorine gas (15 g, 0.211 mol) was fed over 1.5 h at 45–50 °C and continued to stir for 1 h. The crude product was heated at 70 °C and washed with de-ionized water (149 g, 8.28 mol). The organic layer was separated in a glass separating funnel and added to toluene (125 g, 1.36 mol), then washed twice with a 3.5 wt% solution of sodium chloride (149 g). A Dean–Stark trap was used to strip off excess solvent, and 189 g $C_2F_5OCF_2CF_2CH_2CH_2SO_2Cl$ (**VID**) was obtained in 84.0% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98–3.88 (2H, m), 2.96–2.79 (2H, m). ^{19}F NMR ($CDCl_3$, 376 MHz) δ −87.09 (2F, s), −87.82 to 87.97 (2F, m), −88.83 to 88.96 (2F, m), −117.38 (3F, t, J = 16.6 Hz).

4.22. Synthesis of 3,3,5,5,6,6,7,7,8,8,8-Undecafluoro-octane-1-sulfonic acid (IE)

$C_4F_9CH_2CF_2CH_2CH_2SO_2Cl$ (10 g, 0.0244 mol) was added dropwise to a flask charged with warm (70 °C) methanol (10 g, 0.313 mol). The reaction mixture was heated at 70 °C for 24 h. The flask was equipped with a Dean–Stark trap with reflux condenser and heated to 100 °C to evaporate excess solvent. This yielded 9.3 g (97.1%) of $C_4F_9CH_2CF_2CH_2CH_2SO_3H$ (**IE**) that was diluted with 70 °C de-ionized water (21.7 g) to give a 30 wt% active ingredient concentrated solution. ^{1}H NMR (D_2O, 400 MHz) δ 3.04–2.95 (2H, m), 2.87–2.67 (2H, m), 2.46–2.29 (2H, m). ^{19}F NMR (D_2O, 376 MHz) δ −83.18 (3F, tt, J_1 = 9.8 Hz, J_2 = 2.7 Hz), −96.41 to 96.69 (2F, m), −113.84 to 114.15 (2F, m), −125.81 (2F, s), −127.34 to 127.54 (2F, m).

4.23. Synthesis of 3,3,5,5,7,7,8,8,9,9,10,10,10-Tridecafluoro-decane-1-sulfonic acid (IIE)

$C_4F_9(CH_2CF_2)_2CH_2CH_2SO_2Cl$ (20 g, 0.0421 mol) was added dropwise to a flask charged with warm (70 °C) methanol (20 g, 0.625 mol). The reaction mixture was heated at 70 °C for 24 h. The flask was equipped with a Dean–Stark trap with reflux condenser and heated to 100 °C to evaporate excess solvent. This yielded 18.9 g (98.4%) of $C_4F_9(CH_2CF_2)_2CH_2CH_2SO_3H$ (**IIE**) that was diluted with 70 °C de-ionized water (44.1 g) to give a 30 wt% active ingredient concentrated solution. ^{1}H NMR (D_2O, 400 MHz) δ 2.93–2.86 (2H, m), 2.83–2.66 (2H, m), 2.66–2.50 (2H, m), 2.34–2.19 (1H, m), 2.11 (2H, s). ^{19}F NMR (D_2O, 376 MHz) δ −83.07 to 83.16 (3F, m), −91.17 to 91.46 (2F, m), −97.13 to 97.40 (2F, m), 113.66–113.96 (2F, m), −125.85 (2F, m), −127.33 to 127.51 (2F, m).

4.24. Synthesis of 3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-decane-1-sulfonic acid (IIIE)

$C_6F_{13}CH_2CF_2CH_2CH_2SO_2Cl$ (20 g, 0.0392 mol) was added dropwise to a flask charged with warm (70 °C) methanol (10 g, 0.624 mol). The reaction mixture was heated at 70 °C overnight. The flask was equipped with a Dean–Stark trap with reflux condenser and heated to 100 °C to evaporate excess solvent. This yielded 19.3 g (100%) of $C_6F_{13}CH_2CF_2CH_2CH_2SO_3H$ (**IIIE**) that was diluted with 70 °C de-ionized water (45 g) to give a 30 wt% active ingredient concentrated solution. ^{1}H NMR (D_2O, 400 MHz) δ 3.14–3.09 (2H, m), 2.96–2.78 (2H, m), 2.57–2.42 (2H, m). ^{19}F NMR (D_2O, 376 MHz) δ −83.29 (3F, t, J = 10.0), −96.59 to −96.84 (2F, m), −113.66 to −113.96 (2F, m), −123.03 to −123.31 (2F, m), −124.25 to −124.52 (2F, m), −124.72 to −124.91 (2F, m), −127.89 to −128.05 (2F, m).

4.25. Synthesis of 3,3,4,4-tetrafluoro-4-heptafluoropropyloxy-butane-1-sulfonic acid (VE)

$C_3F_7OCF_2CF_2CH_2CH_2SO_2Cl$ (10 g, 0.0242 mol) was added dropwise to a flask charged with warm (70 °C) methanol (10 g, 0.313 mol). The reaction mixture was heated at 70 °C for 24 h. The flask was equipped with a Dean–Stark trap with reflux condenser and heated to 100 °C to evaporate excess solvent. This yielded 9.3 g (97.5%) of $C_3F_7OCF_2CF_2CH_2CH_2SO_3H$ (**VE**) that was diluted with 70 °C de-ionized water (21.7 g, 1.21 mol) to give a 30 wt% active ingredient concentrated solution. ^{1}H NMR (D_2O, 400 MHz) δ 2.99–2.91 (2H, m), 2.49–2.31 (2H, m). ^{19}F NMR (D_2O, 376 MHz) δ −82.74 (3F, t, J = 7.1 Hz), −85.65 to 85.81 (2F, m), −88.31 to 88.43 (2F, m), −118.62 (2F, t, J = 18.9 Hz), −131.23 (2F, s).

4.26. Synthesis of 3,3,4,4-tetrafluoro-4-pentafluoroethyloxy-butane-1-sulfonic acid (VIE)

A 100 mL, three-neck round bottomed flask was charged with methanol (20.0 g, 0.0.624 mol) under nitrogen and heated to 70 °C. $C_2F_5OCF_2CF_2CH_2CH_2SO_2Cl$ (20.0 g, 0.0616 mol) was added dropwise to the reaction mixture and allowed to reflux for 20 h. The methanol was then removed through Dean–Stark distillation and rotary evaporated to yield a brown, viscous, liquid product $C_2F_5OCF_2CF_2CH_2CH_2SO_3H$ (**VIE**) (18.86 g, 100%). The product was then diluted with 70 °C distilled water to form a 30 wt% aqueous solution. ^{1}H NMR (D_2O, 400 MHz) δ 2.93–2.87 (2H, m), 2.42–2.27 (2H, m). ^{19}F NMR (D_2O, 376 MHz) δ −88.55 to −88.58 (3F, m), −88.65 to −88.75 (2F, m), −90.03 to −90.13 (2F, m), −118.76 to −118.88 (2F, t, J = 17.7 Hz).

4.27. Synthesis of 1-octanesulfonic acid, 3,3,5,5,6,6,7,7,8,8,8-undecafluoro–sodium salt (1:1) (IF)

$C_4F_9CH_2CF_2CH_2CH_2I$ (140 g, 0.33 mol) was added to a mixture of ethanol (165 mL) and water (165 mL). Sodium sulfite (83 g, 0.66 mol) was added, followed by copper powder (8 g). The reaction mixture was stirred vigorously under reflux for a week. 500 mL water was added and the mixture was filtered at 75 °C. The filtrate was cooled and $C_4F_9CH_2CF_2CH_2CH_2SO_3Na$ (**IF**) precipitated was collected by filtration as a white solid (112 g, 84%). m.p. 225–227 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.22–3.05 (4H, m), 2.59–2.46 (2H, m). ^{19}F NMR ($CDCl_3$, 376 Hz) δ −81.44 (3F, tt, J_1 = 9.7 Hz, J_2 = 4.1 Hz), −95.39 (2F, tt, J_1 = 30.0 Hz, J_2 = 15.0 Hz), −112.90 to −113.13 (2F, m), −124.98 to −125.00 (2F, m), −126.16 to −126.27 (2F, m). Calcd. for $C_8H_6F_{11}O_3SNa$: %C, 22.49; %H, 1.21. Found: %C, 23.20; %H 1.46.

4.28. Synthesis of 1-butanesulfonic acid, 3,3,4,4-tetrafluoro-4-(1,1,2,2,3,3,3-heptafluoropropoxy)–sodium salt (1:1) (VF)

$C_3F_7OCF_2CF_2CH_2CH_2I$ (220 g, 0.5 mol) was added to a mixture of ethanol (250 mL) and water (250 mL). Sodium sulfite (126 g, 1 mol) was added, followed by copper powder (15 g). The reaction

mixture was stirred vigorously under reflux for a week. 500 mL water was added and the mixture was filtered at 75 °C. The filtrate was cooled and $C_3F_7OCF_2CF_2CH_2CH_2SO_3Na$ (**VF**) precipitated was collected by filtration as a white solid (86 g, 41.4%). m.p. 180.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.19–3.15 (2H, m), 2.69–2.56 (2H, m). ^{19}F NMR ($CDCl_3$, 376 Hz) δ −81.58 (3F, t, J = 7.0 Hz), −84.78 to −84.92 (2F, m), −88.15 (2F, t, J = 13.3 Hz), −117.80 (2F, t, J = 18 Hz), −130.19 (2F, s). Calcd. for $C_7H_4F_{11}O_4SNa$: %C, 19.32; %H, 1.15. Found: %C, 20.20; %H, 0.97.

*4.29. Synthesis of 1-butanesulfonic acid, 1,1,2,2,3,3,4,4-octafluoro-4-(1,1,2,2,2-pentafluoroethoxy)–sodium salt (1:1) (**VIF**)*

$C_2F_5OCF_2CF_2CH_2CH_2I$ (195 g, 0.5 mol) was added to a mixture of ethanol (250 mL) and water (250 mL). Sodium sulfite (126 g, 1 mol) was added, followed by copper powder (15 g). The reaction mixture was stirred vigorously under reflux for a week. 500 mL water was added and the mixture was filtered at 75 °C. The filtrate was cooled and $C_2F_5OCF_2CF_2CH_2CH_2SO_3Na$ (**VIF**) precipitated was collected by filtration as a white solid (112 g, 61.2%). m.p. 135–137 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.20–3.16 (2H, m), 2.70–2.57 (2H, m). ^{19}F NMR ($CDCl_3$, 376 Hz) δ −86.95 (3F, s), −87.97 to 88.07 (2F, m), −88.71 to 88.82 (2F, m), −117.72 (2F, t, J = 18 Hz). Calcd. for $C_6H_4F_9O_4SNa$: %C, 18.86; %H, 1.30. Found: %C, 19.68; %H, 1.10.

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