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Gemini cationic surfactants with flexible perfluorinated-ether chains

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ABSTRACT

This research aims at providing alternatives for long-chain fluorosurfactants, such as perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and their derivatives. Gemini quaternary ammonium fluorosurfactants with perfluorinated-ether chains were synthesized and their surface tensions were measured. The surface tensions at critical micelle concentration (γ_{cmc}) are at the range of 14.7–23.3 mN/m and among them γ_{cmc} of four perfluorinated-chain surfactants are below 16 mN/m.We found that the flexibility of perfluorinated-ether chains, such as $CF_3(OCF_2)_n$-, contributed significantly to enhance the surface activities. We also synthesized gemini cationic surfactants with $C_6F_{13}CH_2CH_2$- groups and their γ_{cmc} are between 15.5 to 20.1 mN/m. Good linkage design, such as -$(CH_2)_n$- (where n is odd), -$CH_2CH_2OCH_2CH_2$- and 1,2-phenylenebis(methylene), helps for lowering surface energy. The current research provides an approach for discovering non-bioaccumulative surfactants.

1. Introduction

Fluorinated surfactants have unique functions severing as irreplaceable ingredients for highly-demanded applications including fire-fighting and oil-proofing [1,2]. However, traditionally, these applications use long-chain per/polyfluoroalkyl substances (PFASs) which are toxic, persistent, bioaccumulative and of long-distance transportation. The oldest and most studied examples are perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and their derivatives, which are banned/restricted by Stockholm Convention [3,4]. Although the alternative strategy using short-chain perfluoroalkyl substances has been developed, normal short-chain fluorosurfactants were unqualified for the application which required extremely high surface activities. Surfactants with elegantly-designed structures are needed to meet the requirement of high performance alongside with low environmental risk.

Gemini surfactants have attracted much attention owing to their fascinating properties of lower critical micelle concentration (CMC) and higher surface activity compared with monomeric surfactants [1,5,6,7]. For example, the surface tension at the critical micelle concentration (γ_{cmc}) of a gemini surfactant 1,2-bis[dimethyl-(3-perfluorooctyl-2-hydroxypropyl)ammonium]ethane bromide is 13.7 mN/m, that is lower than the normal fluorosurfactants [8]. However, this surfactant contains two perfluorooctyl groups which are not environmental friendly. It is generally believed that the compounds with perfluorooctyl groups will decompose in the environment to generate bioaccumulative perfluorooctanoic acid or its derivatives which are harmful to human being's health. In the same research, when using perfluorohexyl groups to replace perfluorooctyl groups, the γ_{cmc} increases to 19.8 mN/m [8]. Shortening of perfluoroalkyl chains is unsuccessful to keep the surface properties. The new surfactant structures with both surface activity and environmental benignity are required. We recently discovered that some substances with perfluorinated-ether chains are less toxic and bioaccumulative than PFOA. For examples, salts of $CF_3(OCF_2)_2COOH$ and $CF_3(OCF_2)_3COOH$ demonstrated almost no accumulationin the liver or serum; whereas a salt of $CF_3(OCF_2)_4COOH$ was accumulated but with weaker potential than PFOA [9]. Thus, the surfactants with perfluorinated-ether chains are considered to desirable alternative candidates. In this article, we report our design of gemini cationic surfactants with perfluorinated-ether chains and the evaluation of their surface properties.

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2. Results and discussion

We synthesized fluorinated gemini cationic surfactants in two steps. The reactions of 3-dimethylaminopropylamine with fluorinated esters, carbonyl fluorides or a sulfonyl chloride gave tertiary amines with fluorinated tails (**1** - **9**) (Scheme 1). The tertiary amines reacted with bromides gave gemini cationic surfactants with perfluorinated-ether chains (**10** - **31**, Scheme 2) and with perfluorohexyl groups (**32** - **39**, Scheme 3). We also synthesized single-chain surfactant **40** and **41** through methylation or butylation of tertiary amine **9** with iodomethane or 1-bromobutane (Scheme 3).

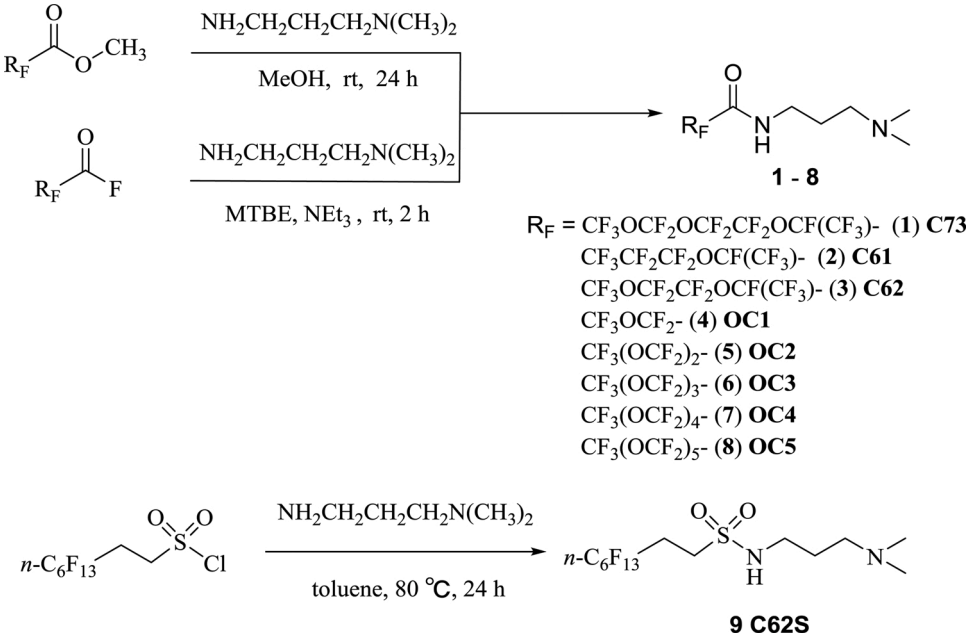
After we obtained the gemini quaternary ammonium surfactants, the surface tensions in gradient concentration were measured. The critical micelle concentrations and the surface tensions at the critical micelle concentration were calculated and depicted in Table 1.

The surface tensions at critical micelle concentration of compouds in Table 1 are at the range of 14.7–23.3 mN/m. The γ_{cmc} of compounds **17 OC5-Bu-OC5**, **21C73-ether-C73**, **28 OC4-*p*-phenyl-OC4**, **29 OC5-*p*-phenyl-OC5** and **34 C62*S*-Pent-C62*S*** are below 16 mN/m. To the best of our knowledge, few gemini cationic surfactants can reach such high surface activities like ours [8,10,11]. The critical micelle concentrations of these five compounds are $7 \sim 8 \times 10^{-4}$ mol/L (about 1 g/L).

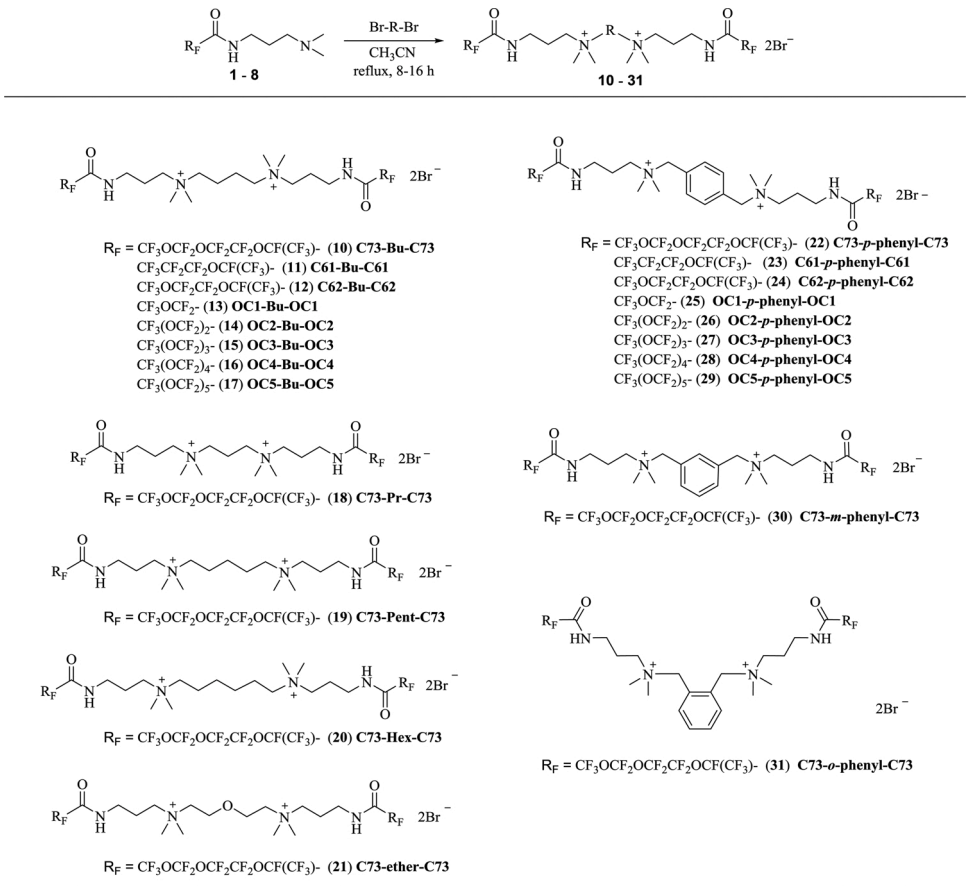
In the series of compound **10 C73-Bu-C73** to **17 OC5-Bu-OC5**, the surface tensions at the critical micelle concentration of compounds **17 OC5-Bu-OC5** are the lowest. The structures of compounds in this series are same except for perfluorinated-ether substituents. The substituent of compound **17 OC5-Bu-OC5** is $CF_3(OCF_2)_5$ group, that of compound **16 OC4-Bu-OC4** is $CF_3(OCF_2)_4$ group, and that of compound **15 OC3-Bu-OC3** is $CF_3(OCF_2)_3$ group. Compounds **33 C62*S*-Bu-C62*S***, a similar compound with $C_6F_{13}CH_2CH_2$ group as the substituent is of a higher surface tension at the critical micelle concentration (18.2 mN/m) than compound **17 OC5-Bu-OC5** (15.7 mN/m), compound **16 OC4-Bu-OC4** (16.2 mN/m) and compound **15 OC3-Bu-OC3** (17.0 mN/m). In general, the great surface activities of fluorosurfactants highly relate to the extremely weak attractive intermolecular forces due to the low polarizability of fluorine [1,12]. A longer perfluorinated carbon chain results a higher surface activity. Compared with compound **33 C62*S*-Bu-C62*S***, compounds **15 OC3-Bu-OC3** and **16 OC4-Bu-OC4** are in close chain lengths, but with lower fluorine content due to the insertion of oxygen atoms. The flexibility of oxygen-linkage in compound **15 OC3-Bu-OC3** and **16 OC4-Bu-OC4** may allow wider coverage on the surface, and as a result lower the surface tension. The flexibility of perfluorinated-ether chains seems to be a predominant factor to increase surface activities other than the length or the fluorine content of perfluorinated substituents. With this assumption, it is easily understood that the best surface activity was found for compound **17 OC5-Bu-OC5**. For compound **10 C73-Bu-C73**, with $CF_3OCF_2OCF_2CF_2OCF(CF_3)$ group, even similar in length and fluorine content, is less flexible and shows a higher surface tension than that of compound **15 OC3-Bu-OC3** to **17 OC5-Bu-OC5**.

In the series of compound **10 C73-Bu-C73**, **18 C73-Pr-C73** to **21 C73-ether-C73**, we examined the effect of the alkyl linkage. We observed that the surface tensions at CMC of compound **18 C73-Pr-C73** (16.5 mN/m), **19 C73-Pent-C73** (17.4 mN/m) and **21 C73-ether-C73** (15.0 mN/m) were significantly lower than those of compound **10 C73-Bu-C73** (18.6 mN/m) and **20 C73-Hex-C73** (19.7 mN/m). $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2CH_2$ and $CH_2CH_2OCH_2CH_2$ are better linkages than $CH_2CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2CH_2CH_2$. We name the phenomenon as the"odd number effect". The odd number effect was also found for the series of compound **32 C62*S*-Pr-C62*S*** to **36 C62*S*-ether-C62*S***. The surface tensions at CMC of **32 C62*S*-Pr-C62*S*** (16.6 mN/m), **34 C62*S*-Pent-C62*S*** (15.5 mN/m), **36 C62*S*-ether-C62*S*** (16.0 mN/m) are significantly lower than those of **33 C62*S*-Bu-C62*S*** (18.2 mN/m), **35 C62*S*-Hex-C62*S*** (18.9 mN/m). The alkyl chains prefer zigzag conformation. The odd-number carbon chains are helpful for the orientation of two hydrophobic fluorinated groups towards outside the water surface and thus reduce the surface tensions.

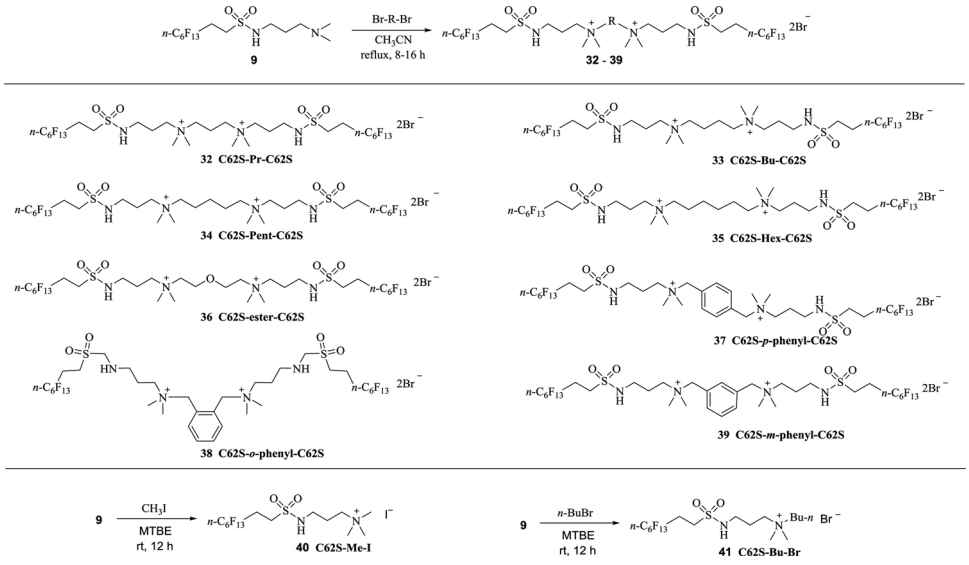
We also found an interesting *ortho*-effect when we used bis(methylene)benzene groups as the linkages. For *n*-C_6F_{13}-substituted compounds, the surface activity of *ortho*-substituted compound (**38 C62*S*-*o*-phenyl-C62*S***, 16.2 mN/m) is better than *meta*- (**39 C62*S*-*m*-phenyl-C62*S***, 19.2 mN/m) and *para*- (**37 C62*S*-*p*-phenyl-C62*S***, 20.1 mN/m) analogues. The orientation becomes an important factor while perfluorohexyl is rigid. We propose that the orientation is very important structure design when the hydrophobic groups in the gemini surfactantsare rigid. However, the surface activities of **30 C73-*m*-phenyl-C73** (*meta*, 17.6 mN/m) and **31 C73-*o*-phenyl-C73** (*ortho*, 17.1 mN/m) is close. The highly flexible **27 OC3-*p*-phenyl-OC3** (16.1 mN/m), **28 OC4-*p*-phenyl-OC4** (15.2 mN/m), and **29 OC5-*p*-phenyl-OC5** (14.7 mN/m), even *para*-substituted, exhibit excellent surface activities. These facts



Scheme 1. Synthesis of tertiary amines with fluorinated tails.



Scheme 2. Synthesis of gemini cationic surfactants with perfluorinated-ether chains.



Scheme 3. Synthesis of cationic surfactants with perfluorohexyl group.

mean that the *ortho*-effect becomes less important if the hydrophobic chains within gemini surfactants are flexible. The surface tensions (15.5–18.9 mN/m) at CMC of gemini quaternary ammonium surfactants **32 C62S-Pr-C62S** to **36 C62S-ether-C62S** with $C_6F_{13}CH_2CH_2$- groups are close to or higher than single-chain analogue **41 C62S-Bu-Br** (15.9 mN/m). The effect of counter ion was found when we compared the γ_{cmc} of bromide **41 C62S-Bu-Br** with that of iodide **40 C62S-Me-I** (22.4 mN/m).

The surface energy for single-chain carbon-based moieties are in the following orders: $CF_3 < CF_2 < CH_3 < CH_2$ [1,13]. If the compounds contains more moieties with low surface energies, the compounds are more surface active. Perfluoroalkyl surfactants possess greater surface activities over hydrocarbon analogue. The silicone surfactants achieve low surface energy not only because of the low surface energy of methyl groups but also because of the unique flexibility of the siloxane backbone [1,14]. Although compound **29 OC5-*p*-phenyl-OC5** with

Table 1
The γ_{cmc}, CMC, A_{min}, and purity of fluorinated gemini quaternary ammonium surfactants.

Compound		γ_{cmc} (mN/m)	CMC ($\times10^{-4}$mol/L)	A_{min} (nm^2)	Purity[a]
10	**C73-Bu-C73**	18.6	7.8	–	78 %
11	**C61-Bu-C61**	21.6	9.4	–	70 %
12	**C62-Bu-C62**	19.9	16	–	89 %
13	**OC1-Bu-OC1**	23.3	35	–	77 %
14	**OC2-Bu-OC2**	22.1	28	–	94 %
15	**OC3-Bu-OC3**	17.0	9.8	–	88 %
16	**OC4-Bu-OC4**	16.2	8.5	–	88 %
17	**OC5-Bu-OC5**	15.7	7.6	–	77 %
18	**C73-Pr-C73**	16.5	8.4	–	71 %
19	**C73-Pent-C73**	17.4	8.5	–	96 %
20	**C73-Hex-C73**	19.7	6.0	–	93 %
21	**C73-ether-C73**	15.0	7.7	4.4	pure
27	**OC3-*p*-phenyl-OC3**	16.1	10	2.2	pure
28	**OC4-*p*-phenyl-OC4**	15.2	7.3	3.6	pure
29	**OC5-*p*-phenyl-OC5**	14.7	7.7	2.8	pure
30	**C73-*m*-phenyl-C73**	17.6	8.9	9.7	pure
31	**C73-*o*-phenyl-C73**	17.1	9.7	8.3	pure
32	**C62S-Pr-C62S**	16.6	5.8	4.3	pure
33	**C62S-Bu-C62S**	18.2	7.7	5.5	pure
34	**C62S-Pent-C62S**	15.5	7.9	3.6	pure
35	**C62S-Hex-C62S**	18.9	4.9	3.2	pure
36	**C62S-ether-C62S**	16.0	15	4.9	pure
37	**C62S-*p*-phenyl-C62S**	20.1	4.9	3.7	pure
38	**C62S-*o*-phenyl-C62S**	16.2	3.9	4.2	pure
39	**C62S-*m*-phenyl-C62S**	19.2	4.8	6.0	pure
40	**C62S-Me-I**	22.4	16	2.1	pure
41	**C62S-Bu-Br**	15.9	13	2.6	pure

[a] The purities of compounds were determined by NMR analysis.

$CF_3(OCF_2)_5$ groups and compound **37 C62S-*p*-phenyl-C62S** with $CF_3(CF_2)_5$ groups have the same number of CF_3 and CF_2 groups, the surface tension at CMC of compound **29 OC5-*p*-phenyl-OC5** (14.7 mN/m) is much lower than that of **37 C62S-*p*-phenyl-C62S** (20.1 mN/m). Compound **27 OC3-*p*-phenyl-OC3** (16.1 mN/m) with $CF_3(OCF_2)_3$ groups and **28 OC4-*p*-phenyl-OC4** (15.2 mN/m) with $CF_3(OCF_2)_4$ groups even with less number of CF_2 groups are also much better than **37 C62S-*p*-phenyl-C62S**. Silmilar as the silicone surfactants, the flexibility of perfluorinated-ether chains on compound **29 OC5-*p*--phenyl-OC5** are one of the essential reasons for increasing surface activities. Oxygen insertion into perfluoroalkyl chain is an effective way to lowering surface energy.

A_{min} corresponds to the area per surfactant molecule at the air-water interface at the critical micelle concentration [2]. We calculated A_{min} by using the Gibbs equation

$$\Gamma_{max} = -\frac{1}{2.303 \times nRT} \times \frac{d\gamma}{d\log c}$$

and the equation

$$A_{min} = \frac{10^{14}}{N_A \Gamma_{max}}$$

The "*n*" was equal to 3 for gemini cationic surfactants, and the "n" was taken as 2 for quanternary ammonium surfactants **40** and **41**. A_{min} were calculated and depicted in Table 1 for pure surfactants that we synthesized. The A_{min} of the gemini surfactants are in the range of 2.2 to 9.7 nm^2 bigger than the ones for single chain surfactant **40** and **41**. The observation consists with the fact that gemini surfactants are bigger than single chain surfactants. The greater molecular volume of perfluoroalkyl moieties and the larger cross section of fluorocarbon chains over hydrocarbon counterparts make the A_{min} bigger and the packing density per unit area lower.

Some of PFASs are toxic, persistent and bioaccumulative. The bioaccumulation are the essential property which attracts great concern. The concern is originated from the fact that these imperceptible bioaccumlative substances will be superimposed over time and may make the cells in the organism undergo irreversible changes leading to cancer or other deseases eventually [15]. Hence, bioaccumulation deserves more attention than toxicity. Hunting for alternatives with no or low bioaccumulation, therefore, becomes an important strategy to reduce the risk of PFASs. In the mice exposure experiment, we found that some perfluoroether-based carboxylate were without or with low bioaccumulation. For examples, $CF_3(OCF_2)_2CO_2K$ and $CF_3(OCF_2)_3CO_2K$ demonstrated almost no accumulation in the liver or serum; whereas $CF_3(OCF_2)_4CO_2K$ was accumulated but with much weaker potential than PFOA [9]. The further design of surfactants with those less bioaccumulative perfluorinated-ether chains may provide a serial of fluorinated surfactants with lower risk, although some references showed the compounds with perfluoroether chains were still toxic to zebrafish [16] and were still hard to decompose in simulative degragation experiments [17]. In compare of some environmentally friendly short chain perfluorinated alkyl compounds [18], perfluorinated-ether compounds shows more variables and better surface properites. Research on the development of surfactants based on perfluorinated-ether chains should be looked as one of effective approaches to solve PFOS/PFOA problems.

3. Conclusions

Gemini cationic surfactants with perfluorinated-ether chains were developed. The surface activities were evaluated and compared with analogues with perfluorohexyl groups. All the surfactants can reduce efficiently the surface tension of water. Five of them (**17 OC5-Bu-OC5**, **21 C73-ether-C73**, **28 OC4-*p*-phenyl-OC4**, **29 OC5-*p*-phenyl-OC5** and **34 C62S-Pent-C62S**) achieve the γ_{cmc} below than 16 mN/m. The flexibility of perfluorinated-ether chains account significantly for enhancement of surface activities. The good linkages such as -$(CH_2)_n$- (where n is odd), -$CH_2CH_2OCH_2CH_2$- and 1,2-phenylenebis(methylene) are also important for increasing the surface activities. Considering some of perfluorinated ethers functionalities have been proved to be more environmental friendly than PFOA, the current research display a promising future of alternatives for bioaccumulative surfactants.

4. Experimental

4.1. General information

Fluorinated starting materials were provided by Sanming Hexafluo Chemicals Co., LTD. (see SI), and all other reagents were of AR grade quality and used without further purification. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Chemical shifts for ^{19}F NMR are reported in ppm downfield from fluorotrichloromethane ($CFCl_3$). ^{13}C NMR was broad-band decoupled from hydrogen nuclei. Coupling constants are reported as hertz (Hz). Signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The resonances corresponding the N-H protons are not included in the analysis – possibly due to exchange broadening. HRMS (ESI) data were tested on a Water Micromass GCT Premier. Surface tensions were obtained with Dataphysics DCAT 21 surface tension meter.

4.2. Typical experimental procedures

Procedure A:

To a 100 mL round-bottom flask containing a magnetic stirring bar was added 3-dimethylaminopropylamine (20 mmol, 2.04 g, 2 eq.), *tert*-butyl methyl ether (10 mL), and triethylamine (30 mmol, 3.03 g, 1.5 eq.). Stir the reaction mixture evenly. Then compound $CF_3OCF_2OCF_2CF_2OCF(CF_3)COF$ (10 mmol, 3.98 g, 1.0 eq.) was dropped in and the mixture was stirred at room temperature for 2 h. After the reaction,

the mixture was added with water (100 mL), and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration, the organic extract was concentrated by rotary evaporation under vacuum. The final compound product was obtained as a light-yellow liquid (**1**, 4.65 g, 94 %).

Procedure B:

To a 50 mL two-necked round-bottom flask containing a magnetic stirring bar was added 3-dimethylaminopropylamine(20 mmol, 2.04 g, 1 eq.), methanol (10 mL), and triethylamine (30 mmol, 3.03 g, 1.5 eq.). $CF_3OCF_2COOCH_3$ (20 mmol, 3.88 g, 1.0 eq.) was added to dropwise by constant pressure funnel. The mixture was stirred at room temperature for 20 h. After the reaction, the mixture was added with water (100 mL), and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration, the organic extract was concentrated by rotary evaporation under vacuum. The final compound product was obtained as a light-yellow liquid (**4**, 4.44 g, 84 %).

Procedure C:

To a 50 mL three-necked round-bottom flask containing a magnetic stirring bar was added 3-dimethylaminopropylamine (24 mmol, 2.44 g, 1.2 eq.) and toluene (12 mL). The three-necked flask was installed with a condenser and a constant-pressure funnel. Then, the mixture was heated to 45 °C. $C_6F_{13}CH_2CH_2SO_2Cl$ (20 mmol, 8.92 g, 1 eq.) was added dropwise via the constant-pressure funnel. The solution was allowed to warm to 75 °C and stirred for 24 h. After that, the solution was added with warm aqueous solution of 4% sodium chloride (200 mL), and then the aqueous phase was extracted with DCM (3 × 40 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration, the organic extract was concentrated by rotary evaporation under vacuum. (Note: a large amount of foam turned out during evaporation and the addition of a small amount of ethanol alleviated the generation of the foam) The crude product was yellow solid. Recrystallization using ethanol as solvent gave the final product as a white solid (**9**, 6.96 g, 68 %).

Procedure D:

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added **1** (4 mmol, 1998 mg, 2 eq.), $BrCH_2CH_2CH_2CH_2Br$ (2 mmol, 432 mg, 1eq.), and CH_3CN (6 mL). The mixture was stirred at 80 ℃ for 12 h. After that, the mixture was concentrated by rotary evaporation under vacuum. The crude solid product was recrystallized with acetone and ether and gave the final product as a white solid (**10**, 2222 mg, 92 %).

Procedure E:

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added compound **4** (4 mmol, 1057 mg, 2 eq.), $BrCH_2CH_2CH_2CH_2Br$ (2 mmol, 432 mg, 1eq.), and CH_3CN (4 mL). The mixture was stirred at 80 ℃ for 10 h. The mixture was concentrated by rotary evaporation under vacuum. The residue was dissolved in a small amount of methanol or acetone. The addition of ether or DCM to the solution gave a turbid liquid layer which was separated and evaporated under vacuum. The purification process was repeated for three times. The final product was obtained as a light-yellow liquid (**13**, 1280 mg, 86 %).

Procedure F:

Into a 25 mL three-necked round-bottom flask were added **9** (2 mmol, 1025 mg, 1.0 equiv.), and *t*-butylmethylether (5 mL) under a nitrogen atmosphere.The iodomethane (3 mmol, 426 mg, 1.5 equiv.) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed by evoparation under vacuum.The crude solid product was recrystallized with acetone and petroleum ether (acetone / petroleum ether = 1:3 v/v). The final product was obtained as a white solid (**40**, 1125 mg, 86 %).

4.3. Data for compounds

2-(2-(difluoro(trifluoromethoxy)methoxy)-1,1,2,2-tetrafluoroethoxy)-*N*-(3-(dimethylamino)propyl)-2,3,3,3-tetrafluoropropanamide (**1**):

This compound was synthesized using procedure A and obtained as a light-yellow liquid (4.65 g, 94 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.36 – 3.24 (m, 2 H), 2.31 (t, J =7 Hz, 2 H), 2.18 (s, 6 H), 1.74 – 1.64 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.3 – -55.4 (m, 2 F), -58.9 (t, J = 11 Hz, 3 F), -84.2 (s, 3 F), -86.8 (dd, J = 146, 18 Hz, 1 F), -90.2 (dd, J = 146, 8 Hz, 1 F), -91.6–-91.9 (m, 2 F),-134.0 (dd, J = 188 Hz, 1 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.5 (d, J =26 Hz), 58.0, 45.3, 39.6, 27.2, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}F_{13}N_2O_4$ $[M+H]^+$: 497.0741, found: 497.0732. IR (film) $\nu_{/cm}^{-1}$: 3347, 2955, 2831, 2791, 1714, 1532, 1470, 1309, 1219, 1106, 1010, 989, 963, 916, 869, 794, 765, 720, 647.

N-(3-(dimethylamino)propyl)-2,3,3,3-tetrafluoro-2-(perfluoropropoxy)propanamide (**2**):

This compound was synthesized using procedure A and obtained as a light-yellow liquid(3.81 g, 92 %). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 9.48 (s, 1 H), 3.51 – 3.40 (m, 2 H), 2.41 (t, J =6 Hz, 2 H), 2.20 (s, 6 H), 1.74 (m, 2 H).^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -81.6 (ddq, J = 149, 19, 7 Hz, 1 F), -82.2 (t, J =7 Hz, 3 F), -83.4 (d, J =2 Hz, 3 F), -85.6 (dm, J =149 Hz, 1 F), -130.6 (s, 2 F), -133.2 (dd, J = 20, 7 Hz, 1 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.3 (d, J =26 Hz), 58.1, 45.4, 39.6, 27.3, carbons corresponding to the $CF_3CF_2CF_2OCF(CF_3)$-group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{11}H_{13}F_{11}N_2O_2$ $[M-H]^-$: 413.0729, found: 413.0730. IR (film) $\nu_{/cm}^{-1}$: 3341, 2955, 2831, 1716, 1533, 1470, 1343, 1232, 1163, 991, 809, 720, 629, 535, 456.

N-(3-(dimethylamino)propyl)-2,3,3,3-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy)propanamide (**3**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid (7.75 g, 90 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.32 – 3.23 (m, 2 H), 2.32 – 2.23 (m, 2 H), 2.15 (s, 6 H), 1.70 – 1.61 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD) δ -57.1 (t, J = 9 Hz, 3 F), -84.2 (d, J =2 Hz, 3 F), -86.6 (dd, J = 147, 18 Hz, 1 F), -90.3 (dd, J = 147, 8 Hz, 1 F),-91.9 – -92.1 (m, 2 F), -134.1 (dd, J = 18, 8 Hz, 1 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.5 (d, J =27 Hz), 58.1, 45.4, 39.7, 27.3, carbons corresponding to the $CF_3OCF_2CF_2OCF(CF_3)$-group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{11}H_{13}F_{11}N_2O_3$ $[M+H]^+$: 431.0823, found: 431.0825. IR (film) $\nu_{/cm}^{-1}$: 3346, 2654, 1978.17, 1711, 1537, 1469, 1222, 1075, 1041, 988, 902, 794, 764, 717, 683, 529.

N-(3-(dimethylamino)propyl)-2,2-difluoro-2-(trifluoromethoxy) acetamide (**4**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid (5.28 g, 84 %).^{1}H NMR (400 MHz, CD_3OD): δ 3.20 (t, J =7 Hz, 2 H), 2.24 (t, J =7 Hz, 2 H), 2.12 (s, 6 H), 1.67 – 1.57 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -56.8 (t, J = 9 Hz, 3 F), -81.7 (q, J = 9 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 158.9 (t, J =33 Hz), 120.7 (q, J =264 Hz), 115.0 (t, J =282 Hz), 58.0, 45.3, 39.4, 27.2. HRMS-ESI (*m/z*): calcd for $C_8H_{13}F_5N_2O_2$ $[M-H]^-$: 263.0824, Found: 263.0825. IR (film) ν/cm^{-1}: 3312, 2830, 1716, 1548, 1465, 1348, 1239, 1161, 1059, 1038, 989, 797, 668.

2-(difluoro(trifluoromethoxy)methoxy)-*N*-(3-(dimethylamino)propyl)-2,2-difluoroacetamide (**5**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid in (4.54 g, 86 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.14 (t, J =7 Hz, 2 H), 2.18 (t, J =7 Hz, 2 H), 2.05 (s, 6 H), 1.61 – 1.51 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.0 – -55.2 (m, 2 F), -58.6 (t, J = 9 Hz, 3 F), -81.5 (t, J =10 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 158.9 (t, J =33 Hz), 119.9 (q, J =264 Hz), 119.2 (t, J =269 Hz), 115.2 (t, J =283 Hz),58.0, 45.3, 39.5, 27.2.HRMS-ESI (*m/z*): calcd for $C_9H_{13}F_7N_2O_3$ $[M-H]^-$: 329.0742; found: 329.0743. IR (film) ν/cm^{-1}: 3316, 2953, 2789, 1716, 1544, 1375, 1301, 1002, 989, 862, 765, 682.

2-((difluoro(trifluoromethoxy)methoxy)difluoromethoxy)-*N*-(3-(dimethylamino)propyl)-2,2-difluoroacetamide (**6**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid (7.13 g, 90 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.19 (t, J =7 Hz, 2 H), 2.24 (t, J =7 Hz, 2 H), 2.11 (s, 6 H), 1.66 – 1.58 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.5 –-54.7 (m, 2 F), -56.8 – -57.0 (m,

2 F), -58.7 (t, $J = 9$ Hz, 3 F), -81.6 (t, $J = 11$ Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 158.8(t, J =33 Hz), 119.8 (q, J =265 Hz), 119.3 (t, J =270 Hz), 118.4 (t, J =270 Hz), 115.3 (t, J =284 Hz), 58.1, 45.3, 39.5, 27.3 carbons corresponding to the $CF_3OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI(*m/z*): calcd for $C_{10}H_{13}F_9N_2O_4$ [M—H] $^-$: 395.0659; found: 395.0659. IR (film) v/cm^{-1}: 3690, 3319, 2790, 1716, 1544, 1375, 1235, 1073, 860, 795, 764, 688.

N-(3-(dimethylamino)propyl)-2,2,4,4,6,6,8,8,10,10,10-undecafluoro-3,5,7,9-tetraoxadecanamide (**7**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid (7.95 g, 86 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.23 (t, J =7 Hz, 2 H), 2.29 (t, J =7 Hz, 2 H), 2.15 (s, 6 H), 1.70 – 1.61 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.5 – -54.7 (m, 2 F), -56.3 – -56.5 (m, 2 F), -56.9– -57.0 (m, 2 F), -58.7– -58.8 (m, 3 F), -81.6 (t, $J = 11$ Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 158.8 (t, J =33 Hz), 119.9 (q, J =265 Hz), 119.5 (t, J =270 Hz), 118.6 (t, J =269 Hz), 118.5 (t, J =270 Hz), 115.3 (t, J =284 Hz), 58.3, 45.4, 39.8, 27.2. HRMS-ESI (*m/z*): calcd for $C_{11}H_{13}F_{11}N_2O_5$ [M−H] $^-$: 461.0576; found: 461.0577.IR (film) ν/cm^{-1}: 3649, 3327, 2870, 2790, 1717, 1544, 1465, 1235, 1065, 997, 944, 846, 796, 689.

N-(3-(dimethylamino)propyl)-2,2,4,4,6,6,8,8,10,10,12,12,12-tridecafluoro-3,5,7,9,11-pentaoxadodecanamide (**8**):

This compound was synthesized using procedure B and obtained as a light-yellow liquid (9.61 g, 89 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.16 (t, J =7 Hz, 2 H), 2.23 (t, J =7 Hz, 2 H), 2.09 (s, 6 H), 1.64 – 1.53 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.6 – -54.7 (m, 2 F), -56.4 – -56.6 (m, 4 F), -57.0 – -57.2 (m, 2 F), -58.9 (t, $J = 9$ Hz, 3 F), -81.6 (t, $J = 11$ Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 158.9 (t, J =33 Hz), 58.2, 45.3, 39.6, 27.2 carbons corresponding to the $CF_3OCF_2OCF_2OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}F_{13}N_2O_6$ [M+H]$^+$: 529.0639; found: 529.0641. IR (film) ν/cm^{-1}: 3317, 2955, 2870, 2791, 1717, 1465, 1054, 1004, 862, 796, 765, 687.

N-(3-(dimethylamino)propyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-sulfonamide (**9**) [19]:

This compound was synthesized using procedure C and obtained as a white solid (6.96 g, 68 %).m.p.: 81.6–82.4℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 3.31– 3.27 (m, 2 H), 3.13 (t, J =6 Hz, 2 H), 2.71 – 2.53 (m, 2 H), 2.34 (t, J =6 Hz, 2 H), 2.16 (s, 6 H), 1.69–1.63 (m, 2 H). ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ -81.5 (tt, $J = 10$, 2 Hz, 3 F), -113.8 – -114.0 (m, 2 F), -122.3 – -122.4 (m, 2 F), -123.1 – -123.4 (m, 2 F), -123.5 – -123.7 (m, 2 F), -126.5 – -126.7 (m, 2 F).

N^1,N^4-bis(1,1,1,3,3,5,5,6,6,8-decafluoro-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-yl)-N^1,N^1,N^4,N^4-tetramethylbutane-1,4-diaminium bromide (**10**):

This compound was synthesized using procedure D. The crude solid product was recrystallized with methanol and DCM, givng the final product as a white solid (2222 mg, 92 %). m.p.: 143.8–144.5 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.61 – 3.36 (m, 12 H), 3.17 (s, 12 H), 2.18 – 2.07 (m, 4 H), 1.94 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.2 – -55.4 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -84.0 (s, 6 F), -86.6 (dd, $J = 146$, 18 Hz, 2 F), -90.0 (dd, $J = 146$, 8 Hz, 2 F), -91.5 – -91.7 (m, 4 F), -133.9(dd, $J = 18$, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 64.6, 63.3, 51.6, 38.2, 23.4, 20.7, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identifieddue to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{28}H_{34}Br_2F_{26}N_4O_8$ [M—H] $^-$: 1205.0255; found: 1205.0248.IR (film) ν^{-1}_{cm}: 3418, 3049, 2960, 2055, 1712, 1632, 1538, 1485, 1196, 1026, 964, 870, 792, 721, 636.

N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(3-(2,3,3,3-tetrafluoro-2-(perfluoropropoxy)propanamido)propyl)butane-1,4-diaminium bromide (**11**):

This compound was synthesized using procedure D and obtained as a white solid (1838 mg, 88 %). m.p. 172.2–174.8℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.57 – 3.41 (m, 12 H), 3.17 (s, 12 H), 2.18 – 2.08 (m, 4 H), 1.95−1.90 (m, 4 H). ^{19}F NMR (376 MHz, $(CD_3)_2CO$): -81.7 (ddq, $J = 149$, 19, 7 Hz, 2 F), -82.9 (t, J =7 Hz, 6 F), -83.9 (s, 6 F), -86.1 (dm, J =150 Hz, 2 F), -131.1 (s, 4 F), -134.0 (dd, $J = 19$, 7 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): 159.8 (d, J =27 Hz), 64.6, 63.2, 51.6, 32.8, 23.4, 20.7 carbons corresponding to the $CF_3CF_2CF_2OCF(CF_3)$- group cannot be identifieddue to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{26}H_{34}Br_2F_{22}N_4O_4$ [M—H] $^-$: 1041.0523; found: 1041.0509. IR (film) ν/cm^{-1}: 3419, 3049, 1711, 1541, 1342, 1396, 1165, 1072, 990, 906, 809, 748, 629, 540.

N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(3-(2,3,3,3-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy)propanamido)propyl)butane-1,4-diaminium bromide (**12**):

This compound was synthesized using procedure D and obtained as a white solid (1958 mg, 91 %). m.p.: 267.1–269.0℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.55 (m, 4 H), 3.52 – 3.41 (m, 8 H), 3.20 (s, 12 H), 2.21 – 2.09 (m, 4 H), 2.02 – 1.90 (m, 4 H). ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ -56.9 (t, $J = 9$ Hz, 6 F), -83.8 (s, 6 F), -86.2 (dd, $J = 147$, 18 Hz, 2 F), -90.0 (dd, $J = 147$, 8 Hz, 2 F), -91.6 – -91.8 (m, 4 F), -133.9 (dd, $J = 18$, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 64.6, 63.2, 51.6, 38.2, 23.4, 20.7, carbons corresponding to the $CF_3OCF_2CF_2OCF(CF_3)$- group cannot be identifieddue to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{26}H_{34}Br_2F_{22}N_4O_6$ [M – Br]$^+$: 995.1305; found: 995.1293.IR (film) ν/cm^{-1}: 3418, 3042, 2963, 2057, 1713, 1538, 1485, 1224, 1068, 985, 903, 795, 720, 616.

N^1,N^4-bis(3-(2,2-difluoro-2-(trifluoromethoxy)acetamido)propyl)-N^1,N^1,N^4,N^4-tetramethylbutane-1,4-diaminium bromide (**13**):

This compound was synthesized using procedure E and obtained as a light-yellow liquid (1280 mg, 86 %). ^{1}H NMR (400 MHz, CD_3OD):δ 3.58 – 3.49 (m, 4 H), 3.49 – 3.36 (m, 8 H), 3.17 (s, 12 H), 2.18 – 2.05 (m, 4 H), 1.94 (m, 4 H).^{19}F NMR (376 MHz, CD_3OD): δ -55.6 (t, $J = 9$ Hz, 6 F), -80.5 (q, $J = 9$ Hz, 4 F).HRMS-ESI (*m/z*): calcd for $C_{20}H_{34}Br_2F_{10}N_4O_4$ [M – Br]$^+$: 663.1598; found: 663.1595. IR (film) v/cm^{-1}: 3419, 3041, 2360, 1783, 1693, 1035, 956, 794, 541. 418.

N^1,N^4-bis(3-(2-(difluoro(trifluoromethoxy)methoxy)-2,2-difluoroacetamido)propyl)-N^1,N^1,N^4,N^4-tetramethylbutane-1,4-diaminium bromide (**14**):

This compound was synthesized using procedure E and obtained as a light-yellow liquid (1507 mg, 86 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.64 – 3.55 (m, 4 H), 3.54 – 3.46 (m, 8 H), 3.24 (s, 12 H), 2.25 – 2.13 (m, 4 H), 2.05 – 1.85(m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.9 – -55.0 (m, 4 F), -58.5 (t, $J = 9$ Hz, 6 F), -81.3 (t, $J = 11$ Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.2 (t, J =33 Hz), 119.8 (q, J =263 Hz), 119.2 (t, J =270 Hz), 115.0 (t, J =284 Hz), 64.4, 63.2, 51.7, 38.1, 23.4, 20.7. HRMS-ESI (*m/z*): calcd for $C_{22}H_{34}Br_2F_{14}N_4O_6$ [M –Br]$^+$: 795.1433; found: 795.1426. IR (film) ν/cm^{-1}: 3418, 3065, 2066, 1550, 1236, 1141, 963, 896, 797, 683.

N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(1,1,1,3,3,5,5,7,7-nonafluoro-8-oxo-2,4,6-trioxa-9-azadodecan-12-yl)butane-1,4-diaminium bromide (**15**):

This compound was synthesized using procedure E and obtained as a light-yellow liquid (1501 mg, 90 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.60 – 3.51 (m, 4 H), 3.51 – 3.42 (m, 8 H), 3.20 (s, 12 H), 2.22 – 2.08 (m, 4 H), 1.97 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4 – -54.6 (m, 4 F), -56.7 – -56.9 (m, 4 F), -58.6 (t, $J = 9$ Hz, 6 F), -81.3 (t, $J = 11$ Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.2 (t, J =33 Hz), 119.8 (q, J =265 Hz), 119.3 (t, J =270 Hz), 118.4 (t, J =270 Hz), 115.3 (t, J =284 Hz), 64.5, 63.2, 51.6, 38.1, 23.5, 20.7. HRMS-ESI (*m/z*): calcd for $C_{24}H_{34}Br_2F_{18}N_4O_8$ [M – Br]$^+$: 927.1267; found: 927.1258. IR (film) ν/cm^{-1}: 3426, 3071, 2964, 2069, 1715, 1552, 1485, 1231, 1076, 985, 917, 854, 792, 684.

N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(1,1,1,3,3,5,5,7,7,9,9-undecafluoro-10-oxo-2,4,6,8-tetraoxa-11-azatetradecan-14-yl)butane-1,4-diaminium bromide (**16**):

This compound was synthesized using procedure E and obtained as a light-yellow liquid (2007 mg, 88 %). ^{1}H NMR (400 MHz, CD_3OD): δ 3.58 – 3.49 (m, 4 H), 3.49 – 3.42 (m, 8 H), 3.18 (s, 12 H), 2.17 – 2.08(m, 4 H), 1.95 – 1.85 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4– -54.5 (m, 4 F), -56.2– -56.4 (m, 4 F), -56.8 – -56.9 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F),

-81.3 (t, $J = 11$ Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD) δ 159.2 (t, J =33 Hz), 64.5, 63.2, 51.6, 38.1, 23.5, 20.7, carbons corresponding to the $CF_3OCF_2OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{26}H_{34}Br_2F_{22}N_4O_{10}$ [M – Br]$^+$: 1059.1102; found: 1059.1084. IR (film) ν/ cm^{-1}: 2849, 1714, 1557, 1488, 1255, 1219, 1111, 1064, 931, 781.

N^1,*N*^{1},*N*^{4},*N*^{4}-tetramethyl-*N*^{1},*N*^{4}-bis(1,1,1,3,3,5,5,7,7,9,9,11,11-tridecafluoro-12-oxo-2,4,6,8,10-pentaoxa-13-azahexadecan-16-yl)butane-1,4-diaminium bromide (**17**):

This compound was synthesized using procedure E and obtained as a light-yellow liquid (2239 mg, 88 %).^{1}H NMR (400 MHz, CD_3OD): δ 3.59 – 3.51 (m, 4 H), 3.46 (m, 8 H), 3.20 (s, 12 H), 2.19 – 2.11 (m, 4 H), 2.03 – 1.87 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4 – -54.6 (m, 4 F), -56.2 – -56.5 (m, 8 F), -56.8 – -57.0 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -81.3 (t, $J = 11$ Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.2 (t, J =33 Hz), 64.5, 63.2, 51.7, 38.1, 23.5, 20.7 carbons corresponding to the $CF_3OCF_2OCF_2OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{28}H_{34}Br_2F_{26}N_4O_{12}$ [M – Br]$^+$: 1191.0936; found: 1191.0924. IR (film) ν/cm^{-1}: 3418, 3076, 2958, 1714, 1633, 1487, 1227, 1054, 1003, 958, 683.

N^1,*N*^{3}-bis(1,1,1,3,3,5,5,6,6,8-decafluoro-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-yl)-*N*^{1},*N*^{1},*N*^{3},*N*^{3}-tetramethylpropane-1,3-diaminium bromide (**18**):

This compound was synthesized using procedure D and obtained as a white solid (1910 mg, 88 %).m.p.: 134.6–136.1℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.59 – 3.39 (m, 12 H), 3.21 (s, 12 H), 2.47 – 2.34 (m, 2 H), 2.19 – 2.05 (m, 4 H).^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.6 –-58.7 (m, 6 F), -84.0 (s,6 F), -86.5 – -86.8 (m, 2 F), -89.8 – -90.3 (m, 2 F), -91.6 – -91.8 (m, 4 F), -133.9 – -134.0 (m, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 63.9, 61.7, 51.8, 38.2, 23.4, 18.4 carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{27}H_{32}Br_2F_{26}N_4O_8$ [M—H] $^-$: 1191.0099; found: 1191.0095. IR (film) ν/ cm^{-1}: 3399, 3048, 2965, 2050, 1708, 1632, 1538, 1485, 1445, 1395, 1220, 1107, 1025, 956, 869, 794, 767, 719.

N^1,*N*^{5}-bis(1,1,1,3,3,5,5,6,6,8-decafluoro-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-yl)-*N*^{1}, *N*^{1}, *N*^{5}, *N*^{5}-tetramethylpentane-1,5-diaminium bromide (**19**):

This compound was synthesized using procedure D. The crude solid product was recrystallized with methanol and ether, giving the final product as a white solid (2175 mg, 89 %).m.p.: 165.7–166.8℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.43 (m, 12 H), 3.13 (s, 12 H), 2.14 – 2.03 (m, 4 H), 1.91 – 1.87 (m, 4 H), 1.49 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -84.0 (d, J =1 Hz, 6 F), -86.6 (dd, $J = 146$, 18 Hz, 2 F), -90.1 (dd, $J = 146$, 8 Hz, 2 F), -91.5 – -91.7 (m, 4 F), -133.9(dd, $J = 188$ Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 65.2, 63.0, 51.6, 38.2, 24.0, 23.4, 23.1, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{29}H_{36}Br_2F_{26}N_4O_8$ [M—H] $^-$: 1219.0412; found: 1219.0403. IR (film) ν/ cm^{-1}: 3521, 3342, 3221, 3065, 2972, 2945, 2868, 1708, 1633, 1556, 1497, 1449, 1319, 1212, 1108, 1014, 977, 964, 956, 906, 889, 869, 719, 701, 608.

N^1,*N*^{6}-bis(1,1,1,3,3,5,5,6,6,8-decafluoro-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-yl)-*N*^{1},*N*^{1},*N*^{6},*N*^{6}-tetramethylhexane-1,6-diaminium bromide (**20**):

This compound was synthesized using procedure D and the crude solid product was recrystallized with methanol and ether. The final product was obtained as a white solid (2349 mg, 95 %).m.p.: 188.6–189.4℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.49 – 3.36 (m, 12 H), 3.13 (s, 12 H), 2.12 – 2.02 (m, 4 H), 1.89−1.79 (m, 4 H), 1.58−1.45 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -84.0 (s, 6 F), -86.6 (dd, $J = 146$, 18 Hz, 2 F), -90.0 (dd, $J = 146$, 8 Hz, 2 F), -91.5 – -91.7 (m, 4 F), -133.9 (dd, $J = 188$ Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 65.5, 62.8, 51.5, 38.2, 26.6, 23.5, 23.2, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{30}H_{38}Br_2F_{26}N_4O_8$ [M – Br]$^+$: 1155.1452; found: 1155.1447.IR (film) v/cm^{-1}: 3418, 2956, 1713, 1633, 1539, 1308, 1107, 1026, 954, 869, 792.

N,*N*'-(oxybis(ethane-2,1-diyl))bis(1,1,1,3,3,5,5,6,6,8-decafluoro-*N*,*N*-dimethyl-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-aminium) bromide (**21**):

This compound was synthesized using procedure D. The final product was obtained as a white solid (2326 mg, 95 %).m.p.: 169.5–171.8 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 4.11–4.00 (m, 4 H), 3.79–3.71 (m, 4 H), 3.49 – 3.31 (m, 8 H), 3.19 (s, 12 H), 2.12 – 1.98 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -83.9 (s, 6 F), -86.8 (dd, $J = 146$, 19 Hz, 2 F), -89.8 (dd, $J = 146$, 8 Hz, 2 F), -91.5 – -91.7 (m, 4 F), -133.8 (m, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ159.9 (d, J =27 Hz), 65.7, 65.1, 63.8, 52.3, 38.2, 23.6, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{28}H_{34}Br_2F_{26}N_4O_9$ [M—H] $^-$: 1221.0205; found: 1221.0205. IR (film) v/cm^{-1}: 1706, 1653, 1558, 1540, 1208, 1104, 956, 869, 717, 637, 418.

N,*N*'-(1,4-phenylenebis(methylene))bis(1,1,1,3,3,5,5,6,6,8-decafluoro-*N*,*N*-dimethyl-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-aminium) bromide (**22**):

This compound was synthesized using procedure D and obtained as a white solid (2287 mg, 91 %). m.p.: 160.8–161.6 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4 H), 4.67 (s, 4 H), 3.52 – 3.40 (m, 8 H), 3.14 (s, 12 H), 2.23 – 2.14 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, $J = 9$ Hz, 6 F), -84.0 (d, J =1 Hz, 6 F), -86.6 (dd, $J = 146$, 18 Hz, 2 F), -90.0 (dd, $J = 146$, 8 Hz, 2 F), -91.5 – -91.7 (m, 4 F), -133.9 (dd, $J = 18$, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 135.1, 131.4, 68.6, 63.2, 50.7, 38.2, 23.6 carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{32}H_{34}Br_2F_{26}N_4O_8$ [M—H]$^+$: 1175.1139, found: 1175.1139. IR (film) ν^{-1}_{cm}: 3050, 3492, 2877, 1708, 1616, 1556, 1481, 1454, 1319, 1111, 1012, 964, 871, 834, 795, 758, 721, 703, 641, 540, 458.

N,*N*'-(1,4-phenylenebis(methylene))bis(*N*,*N*-dimethyl-3-(2,3,3,3-tetrafluoro-2-(perfluoropropoxy)propanamido)propan-1-aminium) bromide (**23**):

This compound was synthesized using procedure D and obtained as a white solid (2010 mg, 92 %). m.p.: 158.6–160.4 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 7.78 (s, 4 H), 4.69 (s, 4 H), 3.50 – 3.42 (m, 8 H), 3.16 (s, 12 H), 2.26 – 2.16(m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -81.7 (ddq, $J = 149$, 19, 7 Hz, 2 F), -82.9 (t, J =7 Hz, 6 F), -83.9 (s, 6 F), -86.1 (dm, J =149 Hz, 2 F), -131.1 (s, 4 F), -134.0 (dd, $J = 19$, 6 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 135.1, 131.4, 68.6, 63.2, 50.8, 38.2, 23.6, carbons corresponding to the $CF_3CF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{30}H_{34}Br_2F_{22}N_4O_4$ [M – Br]$^+$: 1011.1407, found: 1011.1393. IR (film) ν^{-1}_{cm}: 3417, 3029, 1713, 1538, 1484, 1341, 1232, 1072, 991, 876, 748, 631, 536.

N,*N*'-(1,4-phenylenebis(methylene))bis(*N*,*N*-dimethyl-3-(2,3,3,3-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethoxy)propanamido)propan-1-aminium) (**24**):

This compound was synthesized using procedure D and obtained as a white solid (2024 mg, 90 %). m.p.: 159.4–160.3 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4 H), 4.68 (s, 4 H), 3.50 – 3.40 (m, 8 H), 3.15 (s, 12 H), 2.25 – 2.14 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -57.0 (t, $J = 9$ Hz, 6 F), -83.9 (d, J =2 Hz, 6 F), -86.3 (dd, $J = 147$, 18 Hz, 2 F), -90.1 (dd, $J = 147$, 8 Hz, 2 F), -91.7 – -91.9 (m, 4 F), -134.0 (dd, $J = 18$, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =26 Hz), 135.1, 131.4, 68.6, 63.2, 50.8, 38.2, 23.6, carbons corresponding to the $CF_3OCF_2CF_2OCF(CF_3)$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{30}H_{34}Br_2F_{22}N_4O_6$ [M—H] $^-$: 1121.0421, found: 1121.0424. IR (film) ν^{-1}_{cm}: 3395, 3028, 2848, 1706, 1645, 1540, 1224, 1026, 903, 796, 720, 642.

N,*N*'-(1,4-phenylenebis(methylene))bis(3-(2,2-difluoro-2-

(trifluoromethoxy)acetamido)-*N*,*N*-dimethylpropan-1-aminium) bromide (**25**):

This compound was synthesized using procedure D and obtained as a white solid (1426 mg, 90 %). m.p.: 226.1–227.2℃^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4 H), 4.69 (s, 4 H), 3.50 – 3.40 (m, 8 H), 3.15 (s, 12 H), 2.26 – 2.14 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -56.7 (t, J = 9 Hz, 6 F), -81.6 (q, J = 9 Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.4 (t, J =33 Hz), 135.1, 131.5, 120.7 (q, J =264 Hz), 114.9 (t, J =283 Hz), 68.5, 63.2, 50.8, 38.0, 23.7. HRMS-ESI (*m/z*): calcd for $C_{24}H_{34}Br_2F_{10}N_4O_4$. [M−H] $^-$: 789.0714, found: 789.0719. IR (film) ν/cm^{-1}: 3417, 3065, 2068, 1715, 1556, 1484, 1343, 1239, 1111, 876, 638, 526.

N,*N*'-(1,4-phenylenebis(methylene))bis(3-(2-(difluoro(trifluoromethoxy)methoxy)-2,2-difluoroacetamido)-*N*,*N*-dimethylpropan-1-aminium) bromide (**26**):

This compound was synthesized using procedure D and obtained as a yellow viscous liquid (1664 mg, 90 %).^{1}H NMR (400 MHz, CD_3OD): δ 7.79 (s, 4 H), 4.71 (s, 4 H), 3.51 – 3.42 (m, 8 H), 3.17 (s, 12 H), 2.25 – 2.18 (m, 4 H). ^{19}F NMR (376 MHz, CD3OD): δ -54.9 – -55.1 (m, 4 F), -58.5 (t, J = 9 Hz, 6 F), -81.3 (t, J =11 Hz, 4 F). ^{13}C NMR (100 MHz, CD3OD): δ 159.1 (d, J =121.4 Hz), 135.1, 131.5, 68.4, 63.2 50.8, 38.0, 23.7, carbons corresponding to the $CF_3OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{26}H_{34}Br_2F_{14}N_4O_6$. [M – Br]$^+$: 843.1433; found: 843.1426. IR (film) v/cm^{-1}: 3418, 3064, 2071, 1714, 1557, 1486, 1234, 1095, 962, 796, 680.

N,*N*'-(1,4-phenylenebis(methylene))bis(1,1,1,3,3,5,5,7,7-nonafluoro-*N*,*N*-dimethyl-8-oxo-2,4,6-trioxa-9-azadodecan-12-aminium) bromide (**27**):

This compound was synthesized using procedure D and obtained as a white solid (1923 mg, 91 %). m.p.: 210.1–212.6 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4 H), 4.68 (s, 4 H), 3.49 – 3.40 (m, 8 H), 3.15 (s, 12 H), 2.24 – 2.15 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4 – -54.6 (m, 4 F), -56.7 – -56.9 (m, 4 F), -58.6 (t, J = 9 Hz, 6 F), -81.3 (t, J = 11 Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.4 (d, J=33 Hz), 135.1, 131.5, 68.4, 63.2, 50.7, 38.0, 23.7, carbons corresponding to the $CF_3OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{28}H_{34}Br_2F_{18}N_4O_8$ [M –Br]$^+$:975.1267; found: 975.1257.IR (film) ν/cm^{-1}: 3427, 3056, 2073, 1713, 1557, 1481, 1223, 1003, 960, 834, 689, 457.

N,*N*'-(1,4-phenylenebis(methylene))bis(1,1,1,3,3,5,5,7,7,9,9-undecafluoro-*N*,*N*-dimethyl-10-oxo-2,4,6,8-tetraoxa-11-azatetradecan-14-aminium) bromide (**28**):

This compound was synthesized using procedure D and obtained as a white solid (2187 mg, 92 %). m.p.: 210.2–211.4 ℃.^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4 H), 4.68 (s, 4 H), 3.49–3.39 (m, 8 H), 3.15 (s, 12 H), 2.25 – 2.15 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4 – -54.5 (m, 4 F), -56.2 – -56.4 (m, 4 F), -56.8 – -56.9 (m, 4 F), -58.6 (t, J = 9 Hz, 6 F), -81.3 (t, J = 11 Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.2 (t, J =33 Hz), 135.1, 131.5, 68.4, 63.2, 50.8, 38.0, 23.7, carbons corresponding to the $CF_3OCF_2OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{30}H_{34}Br_2F_{22}N_4O_{10}$ [M—H] $^-$: 1185.0218, found: 1185.0222. IR (film) ν/cm^{-1}: 3486, 3069, 2361, 1702, 1633, 1566,1454, 1231,1064, 997,940,834, 641, 458.

N,*N*'-(1,4-phenylenebis(methylene))bis(1,1,1,3,3,5,5,7,7,9,9,11,11-tridecafluoro-*N*,*N*-dimethyl-12-oxo-2,4,6,8,10-pentaoxa-13-azahexadecan-16-aminium) bromide (**29**):

This compound was synthesized using procedure D and obtained as a white solid (2337 mg, 93 %). m.p.: 220.4–221.4 ℃.^{1}H NMR (400 MHz, CD_3OD): δ 7.78 (s, 4 H), 4.70 (s, 4 H), 3.50 – 3.42 (m, 8 H), 3.17 (s, 12 H), 2.28 – 2.18 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -54.4 – -54.6 (m, 4 F), -56.2 – -56.4 (m, 8 F), -56.8 – -57.0 (m, 4 F), -58.7 (t, J = 9 Hz, 6 F), -81.3 (t, J = 11 Hz, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.2 (t, J =33 Hz), 135.1, 131.5, 68.5, 63.2, 50.8, 38.0, 23.7, carbons corresponding to the $CF_3OCF_2OCF_2OCF_2OCF_2OCF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{32}H_{34}Br_2F_{26}N_4O_{12}$ [M—H] $^-$: 1317.0052; found: 1317.0056. IR (film) ν/cm^{-1}: 3418, 3073, 1713, 1636, 1550, 1484, 1224, 1053, 687.

N,*N*'-(1,3-phenylenebis(methylene))bis(1,1,1,3,3,5,5,6,6,8-decafluoro-*N*,*N*-dimethyl-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-aminium) bromide (**30**):

This compound was synthesized using procedure D and obtained as a white solid in (2337 mg, 93 %). m.p.: 218.0–219.2 ℃.^{1}H NMR (400 MHz, CD_3OD): δ 8.04 (s, 1 H), 7.83 (t, J =8 Hz, 2 H), 7.72 (t, J =8 Hz, 1 H), 4.76 (s, 4 H), 3.54 –3.40 (m, 8 H), 3.18 (s, 6 H), 3.17 (s, 6 H), 2.27 – 2.17 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, J = 9 Hz, 6 F), -83.9 (s, 6 F), -86.7 (dd, J = 146, 18 Hz, 2 F), -89.9 (ddd, J = 146, 8, 2 Hz, 2 F), -91.5–-91.7 (m, 4 F), -133.7 (dd, J = 18, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 138.9, 136.6, 131.4, 130.0, 68.6, 63.2, 50.7, 38.2, 23.7.HRMS-ESI (*m/z*): calcd for $C_{32}H_{34}Br_2F_{26}N_4O_8$ [M – Br]$^+$: 1175.1139, found: 1175.1122. IR (film) $\nu^{-1}_{/cm}$: 3396, 3208, 3021, 2051, 1711, 1630, 1537, 1483, 1387, 1220, 1108, 1026, 956, 920, 869, 794, 718, 637.

N,*N*'-(1,2-phenylenebis(methylene))bis(1,1,1,3,3,5,5,6,6,8-decafluoro-*N*,*N*-dimethyl-9-oxo-8-(trifluoromethyl)-2,4,7-trioxa-10-azatridecan-13-aminium) bromide (**31**):

This compound was synthesized using procedure D and obtained as a white solid (2337 mg, 93 %). m.p.: 106.8–108.1 ℃.^{1}H NMR (400 MHz, CD_3OD): δ 7.86−7.83 (m, 2 H), 7.80 – 7.75 (m, 2 H), 5.02 (s, 4 H), 3.74 – 3.56 (m, 4 H), 3.53 – 3.40 (m, 4 H), 3.16 (s, 6 H), 3.12 (s, 6 H), 2.22 – 2.09 (m, 4 H).^{19}F NMR (376 MHz, CD_3OD): δ -55.1 – -55.3 (m, 4 F), -58.7 (t, J = 9 Hz, 6 F), -83.9 (s, 6 F), -86.8 (dd, J = 146, 18 Hz, 2 F), -89.9 (ddd, J = 146, 8 Hz, 2 F), -91.5–-91.7 (m, 4 F), -133.8 (dd, J = 18, 8 Hz, 2 F). ^{13}C NMR (100 MHz, CD_3OD): δ 159.9 (d, J =27 Hz), 136.9, 132.8, 130.5, 66.1, 63.3, 50.3, 50.1, 38.2, 23.7, carbons corresponding to the $CF_3OCF_2OCF_2CF_2OCF(CF_3)$- group cannot be identifieddue to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{32}H_{34}Br_2F_{26}N_4O_8$ [M—H] $^-$: 1253.0255, found: 1253.0255. IR (film) $\nu^{-1}_{/cm}$: 3443, 3041, 1714, 1539, 1487, 1311, 1223, 1106, 654, 868, 788, 651.

N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis(3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propyl)propane-1,3-diaminium bromide (**32**):

This compound was synthesized using procedure D. The crude solid product was recrystallized with ethanol, giving the final product as a white solid (1202 mg, 98 %).m.p.: 272.6–273.2℃, ^{1}H NMR (400 MHz, CD_3OD): δ 3.59 – 3.47 (m, 8 H), 3.45 – 3.38 (m, 4 H), 3.27– 3.23 (m, 16 H), 2.77 – 2.60 (m, 4 H), 2.44 – 2.32 (m, 2 H), 2.15 – 2.05 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (t, J =10 Hz, 6 F), -114.7 – -115.0 (m, 4 F), -122.9 – -123.1 (m, 4 F), -123.9–-124.1 (m, 4 F), -124.2 – -124.4 (m, 4 F), -127.4 – -127.6 (m, 4 F). ^{13}C NMR (100 MHz, CD_3OD) δ 62.9, 61.2, 52.4, 44.0, 40.7, 27.2 (t, J =22 Hz), 24.9, 18.5, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{29}H_{40}Br_2F_{26}N_4O_4S_2$ [M – Br]$^+$:1145.1254; found: 1145.1251. IR (film) $\nu^{-1}_{/cm}$: 3419, 2924, 1638, 1305, 1233, 1145, 1092, 964, 913, 515.

N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propyl)butane-1,4-diaminiumbromide (**33**):

This compound was synthesized using procedure D and obtained as a white solid (2283 mg, 92 %). m.p.: 259.8–260.9℃, ^{1}H NMR (400 MHz, CD_3OD): δ 3.53 – 3.40 (m, 12 H), 3.26 (t, J =6 Hz, 4 H), 3.17 (s, 12 H), 2.79 – 2.62 (m, 4 H), 2.13 – 2.04 (m, 4 H), 1.97–1.88 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (m, 6 F), -114.7 – -114.9 (m, 4 F), -122.8 – -123.0 (m, 4 F), -123.8 – -124.0 (m, 4 F), -124.2 – -124.3 (m, 4 F), -127.3–-127.4 (m, 4 F).^{13}C NMR (100 MHz, CD_3OD): δ 64.0, 62.7, 52.0, 44.0, 40.8, 27.2 (t, J =23 Hz), 24.8, 20.7, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (*m/z*): calcd for $C_{30}H_{42}Br_2F_{26}N_4O_4S_2$ [M—H] $^-$: 1237.0526; found: 1237.0512. IR (film) $\nu^{-1}_{/cm}$:3418, 3103, 2859, 1632, 1487, 1305, 1207, 1144, 1093, 964, 848, 747, 708, 652, 518.

N^1,N^1,N^5,N^5-tetramethyl-N^1,N^5-bis(3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propyl)pentane-1,5-diaminium bromide (**34**):

This compound was synthesized using procedure D and obtained as a white solid (2359 mg, 94 %).m.p.: 261.8–262.5 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.50 – 3.39 (m, 12 H), 3.25 (t, J =6 Hz, 4 H), 3.15 (s, 12 H), 2.77 – 2.60 (m, 4 H), 2.10 – 2.00 (m, 4 H), 1.99 – 1.87 (m, 4 H), 1.58 – 1.46 (m, 2 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (t, J =10 Hz, 6 F), -114.7 – -114.9 (m, 4 F), -122.9 – -123.0 (m, 4 F), -123.7 – -124.1 (m, 4 F), -124.2 – -124.3 (m, 4 F), -127.3 – -124.5 (m, 4 F).^{13}C NMR (100 MHz, CD_3OD):δ 64.5, 62.3, 51.0, 44.0, 40.8, 27.2 (t, J =22 Hz), 25.0, 23.8, 23.0, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{31}H_{44}Br_2F_{26}N_4O_4S_2$ [M—H] $^-$:1251.0683; found: 1251.0699. IR (film) $\nu^{-1}_{/cm}$: 3418, 3104, 2920, 2850, 2064, 1632, 1486, 1445, 1305, 1144, 1092, 963, 847, 776, 708, 652, 517.

N^1,*N*^{1},*N*^{6},*N*^{6}-tetramethyl-*N*^{1},*N*^{6}-bis(3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propyl)hexane-1,6-diaminium bromide (**35**):

This compound was synthesized using procedure D and obtained as a white solid (2385 mg, 94 %).m.p.: 270.6–271.1 ℃. ^{1}H NMR (400 MHz, CD_3OD): δ 3.52 – 3.37 (m, 12 H), 3.25 (t, J =6 Hz, 4 H), 3.15 (s, 12 H), 2.78 – 2.60(m, 4 H), 2.11 – 2.00 (m, 4 H), 1.94 – 1.82 (m, 4 H), 1.58 – 1.48 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (t, J =10 Hz, 6 F), -114.7 – -114.9 (m, 4 F), -122.8–-123.1 (m, 4 F), -123.8–-124.1 (m, 4 F), -124.1–-124.4 (m, 4 F), -127.3 – -127.5 (m, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 65.1, 62.2, 51.9, 44.0, 40.8, 27.2 (t, J =22 Hz),26.5, 24.9, 23.0, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{32}H_{46}Br_2F_{26}N_4O_4S_2$ [M – Br]$^+$: 1187.1723; found: 1187.1713.IR (film) $\nu^{-1}_{/cm}$: 3417, 2952, 2866, 2057, 1639, 1487, 1446, 1327, 1145, 1093.

N,*N*'-(oxybis(ethane-2,1-diyl))bis(*N*,*N*-dimethyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium) bromide (**36**):

This compound was synthesized using procedure D and obtained as a white solid (2287 mg, 91 %).m.p.: 268.3–269.5℃. ^{1}H NMR (400 MHz, CD_3OD): δ 4.09 – 4.02 (m, 4 H), 3.79 – 3.72 (m, 4 H), 3.64 – 3.56 (m, 4 H), 3.46 – 3.38 (m, 4 H), 3.28 (t, J =6 Hz, 4 H), 3.22 (s, 12 H), 2.79 – 2.60 (m, 4 H), 2.14 – 2.01 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (t, J =10 Hz, 6 F), -114.7 – -114.9 (m, 4 F), -122.8 – -123.1 (m, 4 F),-123.8 – -124.1 (m, 4 F), -124.1 – -124.4 (m, 4 F), -127.3 – -127.5 (m, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 65.8, 65.6, 64.1, 52.3, 44.1, 41.0, 27.2 (t, J =23 Hz), 24.9 carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{30}H_{42}Br_2F_{26}N_4O_5S_2$ [M—H] $^-$: 1253.0475; found: 1253.0469. IR (film) $\nu^{-1}_{/cm}$: 3452, 3067, 2867, 1481, 1444, 1366, 1308, 1123, 1074, 1020, 912, 849, 778, 709, 603, 564, 519.

N,*N*'-(1,4-phenylenebis(methylene))bis(*N*,*N*-dimethyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium) bromide (**37**):

This compound was synthesized using procedure D and obtained as a white solid (2423 mg, 94 %). m.p.: 264.9–265.2℃. ^{1}H NMR (400 MHz, D_6-DMSO): δ 7.69 (s, 4 H), 7.61 (t, J =6.0 Hz, 2 H), 4.63 (s, 4 H), 3.42 – 3.34(m, 8 H), 3.09 – 3.05 (m, 4 H), 3.01 (s, 12 H), 2.73 – 2.57 (m, 4 H), 2.06 – 1.98 (m, 4 H). ^{19}F NMR (376 MHz, D_6-DMSO): δ -82.4 – -82.5 (m, 6 F), -114.7 – -114.9 (m, 4 F), -122.9 – -123.1 (m, 4 F), -123.8 – -124.1 (m, 4 F), -124.2 – -124.4 (m, 4 F), -127.3 – -127.5 (m, 4 F). ^{13}C NMR (100 MHz, D_6-DMSO) δ 133.4, 130.0, 65.7, 61.1, 49.4, 42.1, 25.4(t, J =22 Hz), 23.1, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{34}H_{42}Br_2F_{26}N_4O_4S_2$ [M – Br]$^+$: 1207.1410; found: 1207.1400. IR (film) $\nu^{-1}_{/cm}$: 3278, 3050, 1488, 1308, 1144, 1075, 998, 778, 711, 746, 695, 560, 521, 497.

N,*N*'-(1,2-phenylenebis(methylene))bis(*N*,*N*-dimethyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium) bromide (**38**):

This compound was synthesized using procedure D. The crude solid product was recrystallized with methanol and ethyl ether. The final product was obtained as a white solid (2320 mg, 90 %).

m.p.: 237.8–239.8 ℃,^{1}H NMR (400 MHz, CD3OD): δ 7.89 – 7.82 (m, 2 H), 7.80 – 7.74 (m, 2 H), 4.95 (s, 4 H), 3.65 – 3.57 (m, 4 H), 3.43 – 3.38 (m, 4 H), 3.27 (t, J =6.0 Hz, 4 H), 3.13 (s, 12 H), 2.79– 2.60 (m, 4 H), 2.17– 2.05 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.4 – -82.5 (m, 6 F), -114.7 – -114.9 (m, 4 F), -122.8 – -123.1 (m, 4 F), -123.8 – -124.1 (m, 4 F), -124.2 – -124.5 (m, 4 F), -127.3 – -127.5 (m, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 136.9, 132.8, 130.5, 66.5, 63.5, 50.4, 44.3, 40.8, 27.2 (t, J =22 Hz), 24.9, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{34}H_{42}Br_2F_{26}N_4O_4S_2$ [M -Br]$^+$:1207.1410, found: 1207.1405.IR (film) v/cm^{-1}: 3426, 3105, 2850, 2032, 1630, 1482, 1305, 1143, 1092, 963, 779, 738, 652, 517.

N,*N*'-(1,3-phenylenebis(methylene))bis(*N*,*N*-dimethyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium) bromide (**39**):

This compound was synthesized using procedure D. The crude solid product was recrystallized with acetone and ether. The final product was obtained as a white solid (2345 mg, 91 %). m.p.: 247.8–248.4℃, ^{1}H NMR (400 MHz, CD_3OD): δ 7.92 (s, 1 H), 7.82 (d,J =8 Hz, 2 H), 7.72 (t, J =8 Hz, 1 H), 4.73 (s, 4 H), 3.54 – 3.38 (m, 8 H), 3.28 (t, J =6 Hz, 4 H), 3.16 (s, 12 H), 2.78 – 2.62 (m, 4 H), 2.25 – 2.14 (m, 4 H). ^{19}F NMR (376 MHz, CD_3OD): δ -82.5 (t, J =10 Hz, 6 F), -114.6 – -114.9 (m, 4 F), -122.6– -123.1 (m, 4 F), -123.8 – -124.1 (m, 4 F), -124.1– -124.4 (m, 4 F), -127.2 – -127.5(m, 4 F). ^{13}C NMR (100 MHz, CD_3OD): δ 138.5, 136.7, 131.4, 130.1, 68.1, 62.8, 51.1, 44.0, 40.8, 27.2 (t, J =22 Hz), 25.0, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS-ESI (m/z): calcd for $C_{34}H_{42}Br_2F_{26}N_4O_4S_2$ [M – Br]$^+$: 1207.1410; found: 1207.1400. IR (film) $\nu^{-1}_{/cm}$: 3414, 3108, 2850, 1633, 1448, 1304, 1194, 1144, 1092, 962, 747, 655, 518.

N,*N*,*N*-trimethyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium iodide (**40**):

This compound was synthesized using procedure F and obtained as a white solid (1125 mg, 86 %). m.p.: 264.4–265.2℃.^{1}H NMR (400 MHz, CD_3OD) δ 3.53 – 3.47 (m, 2 H), 3.44 – 3.39 (m, 2 H), 3.26 (t, J =8 Hz, 2 H), 3.20 (s, 9 H), 2.78 – 2.61 (m, 2 H), 2.08 (m, 2 H).^{19}F NMR (376 MHz, CD_3OD) δ -82.5 (tt, J = 10, 2 Hz, 3 F), -114.7 – -115.0 (m, 2 F), -122.8 – -123.1 (m, 2 F), -123.8 – -124.1 (m, 2 F), -124.2 – -124.5 (m, 2 F), -127.2 – -127.5 (m, 2 F). ^{13}C NMR (100 MHz, CD_3OD) δ 65.5, 53.9, 44.1, 40.8, 27.2 (t, J =23 Hz), 25.2, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS – ESI (m/z): Calculated for $C_{14}H_{20}IF_{13}N_2O_2S$ [M—I]$^+$:527.1032. Found: 527.1025. R (film) $\nu^{-1}_{/cm}$: 3605, 3434, 3105, 3013, 2881, 1628, 1482, 1444, 1368, 1234, 1145, 1091, 1029, 965, 887, 781, 747, 712, 651, 560, 522, 459 cm^{-1}.

N,*N*-dimethyl-*N*-butyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonamido)propan-1-aminium bromide (**41**):

This compound was synthesized using procedure F and obtained as a white solid (1245 mg, 89 %). m.p.: 184.9–185.6℃.^{1}H NMR (400 MHz, CD_3OD) δ 3.50 – 3.29 (m, 6 H), 3.24 (t, J =6 Hz, 2 H), 3.13 (s, 6 H),2.74–2.62 (m, 2 H), 2.09 – 1.98 (m, 2 H), 1.85 – 1.72 (m, 2 H), 1.50 – 1.39 (m, 2 H), 1.04 (t, J =8 Hz, 3 H).^{19}F NMR (376 MHz, CD_3OD) δ -82.5 (t, J =7 Hz, 3 F), -114.7 – -114.9 (m, 2 F), -122.8 – -123.1 (m, 2 F), -123.8 – -124.1 (m, 2 F), -124.2 – -124.5 (m, 2 F), -127.2 – -127.5 (m, 2 F).^{13}C NMR (100 MHz, CD_3OD)δ 65.4, 62.8, 51.6 (t, J =4 Hz), 44.1, 40.9, 27.2 (t, J =22 Hz), 25.5, 24.8, 20.7, 13.9, carbons corresponding to the $CF_3CF_2CF_2CF_2CF_2CF_2$- group cannot be identified due to C–F coupling. HRMS – ESI (m/z): Calculated for $C_{17}H_{26}BrF_{13}N_2O_2S$ [M—H]$^-$:647.0618. Found:647.0620. R (film) $\nu^{-1}_{/cm}$:3046, 2849, 1481, 1333, 1144, 1094, 1035, 989, 808, 778, 739, 696, 652, 558, 519, 470.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2020.109632.

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