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# Synthesis and Characterization of a Series of Biofriendly Fluoroether Betaines

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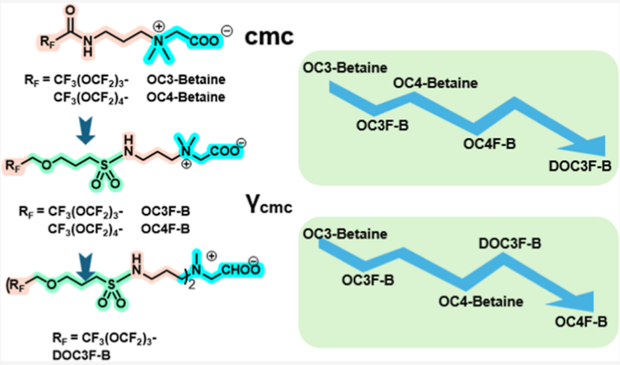

**ABSTRACT:** Fluoroether approach has been extensively employed as an alternative to conventional fluorinated surfactants; however, it faces challenges such as inadequate performance of short fluoroether chains and environmental contamination from long fluoroether chains. This study aims to address the conflict between environmental compatibility and the performance of fluoroether surfactants. The design of the surfactants is centered around the OC chain ($CF_3(OCF_2)_n-$), utilizing reduced fluorine content to achieve superior surface activity. A series of surfactant molecules featuring elongated hydrophobic chains and dual-chain structures have been synthesized and characterized. All of the molecules have good surface activity at low concentrations. Among them, $CF_3(OCF_2)_4CH_2O(CH_2)_3SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COO^-$ (OC4F-B), which employs a strategy of extending the hydrophobic chain by insertion of $-CH_2O(CH_2)_3-$, shows the best performance. This surfactant can achieve a surface tension of 20 mN/m at a concentration of 0.005 wt %, which is 20 times lower than that required for $CF_3(OCF_2)_4CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$ (OC4-betaine) to attain the same surface tension. In contrast, $(CF_3(OCF_2)_3CH_2O(CH_2)_3SO_2NHCH_2CH_2)_2N^+(CH_3)CH_2COO^-$ (DOC3F-B), utilizing both dual-chain and extended carbon chain strategies, exhibits a critical micelle concentration that is diminished by 2 orders of magnitude relative to OC3-betaine, reaching to 0.047 g/L. Merely adjusting the length of the fluorocarbon chain is insufficient to reconcile the conflict between the performance and environmental impact of fluorinated surfactants. This study introduces an innovative approach by incorporating hydrocarbon hydrophobic chains and adopting a dual-chain design, thereby addressing this challenge effectively.

## ■ INTRODUCTION

Fluorinated surfactants are truly the super surfactants among the surfactant families because they can decrease the surface tension of water below the limit of those hydrocarbon counterparts. Meanwhile, fluorinated surfactants are extremely stable to acids, alkalis, oxidants, and reductants, even at high temperature, because of the low polarizability of the fluorine atom and the strong C−F bond. This unique property ensures their indispensable role in many fields like firefighting foams, inks, electronic printing, and biological and medical technologies.[1]

The extreme stability and toxicity of fluorinated surfactants, however, have become insurmountable obstacles on the way to their widespread application. Some traditional surfactants such as PFOS, PFOA, and PFHxS have been completely banned in 2009, 2019, and 2023, respectively, because of their significant adverse impacts to the environment and living organisms.[2] Recently, the legacy of fluor surfactants, classified as one kind of perfluoroalkyl and polyfluoroalkyl substances (PFAS), has been receiving increasing attention. In 2023, the European Chemicals Agency (ECHA) published proposed restrictions on more than 10,000 types of PFAS. As of 26 September 2023, the proposal had garnered more than 5600 comments, and committees are finalizing the further evaluation of the entire restriction proposal.[3] Considering that fluorinated surfactants are irreplaceable in some fields, finding potential alternatives with high surface activity while being environmentally friendly shows great significance.

Recently, alternatives to traditional fluorinated surfactants can mainly be divided into two categories: short-chain fluorinated surfactants and fluoroether surfactants, which are also guiding the research of developing novel fluorinated surfactants.[4−7] In the first series, chains with no more than 6 fluorocarbons are applied to design surfactant molecules. Specific examples include 6:2 fluorotelomer sulfonic acid (6:2

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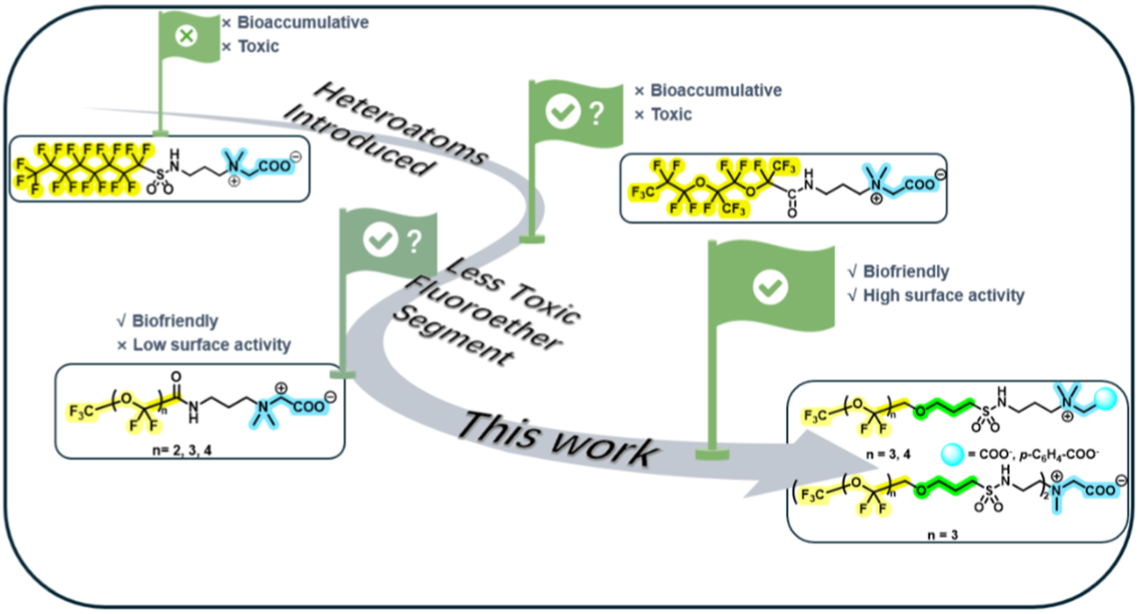
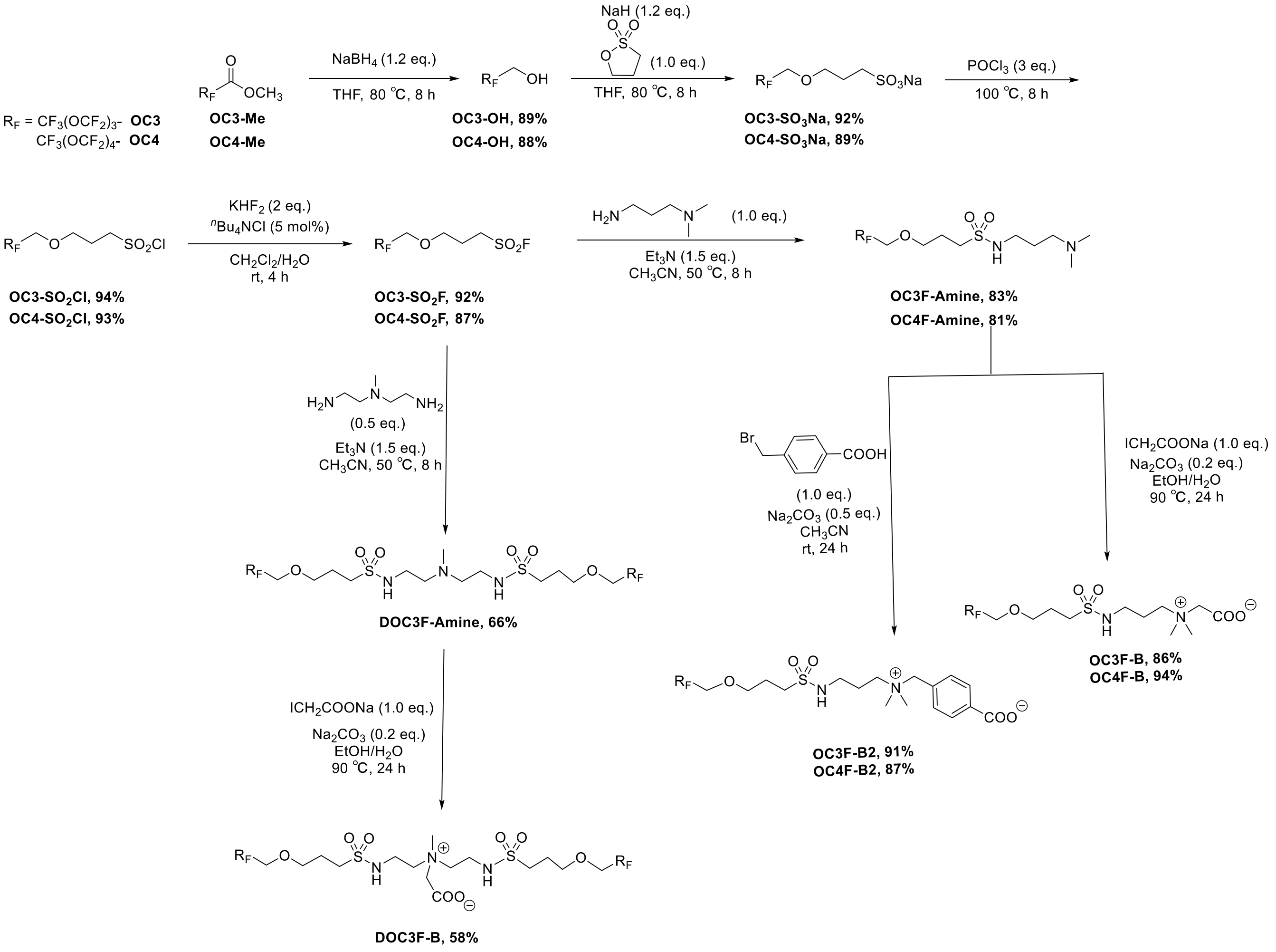
Scheme 1. Development of Fluoroether Surfactants



Scheme 2. Synthetic Route for Betaines



FTS), which is recently used as an alternative to PFOS in the chromium plating industry;[8] Y-type short-chain fluorinated surfactant developed by Liu et al.;[9] nonionic gemini surfactants with short fluorocarbon chains synthesized by Wang et al.;[10] novel fluorinated surfactants with perfluorinated branched ether chains developed by Guo et al.,[11] and so on. And in the second series, heteroatoms are incorporated into the fluorocarbon chain to introduce potential degradation sites in fluoroether surfactants, such as sulfonate,[12,13] phosphate,[14] phosphocholine,[15] betaine,[16−18] amine oxide,[19] carboxylate,[20] and gemini cationic surfactants.[21] Furthermore, extending the hydrophobic chain and inserting oxygen atoms can positively impact the performance of surfactants. For example, we can observe that when the total number of fluorinated carbons is 5, the molecules with extended hydrophobic chains and more inserted oxygen atoms like OC5, C61, and C62[22] exhibit lower surface tension and critical micelle concentration (cmc) compared to the unextended C6 chain without oxygen insertion.[16]

Selecting a fluoroether chain without verifying its ecofriendliness, however, can pose significant risks. For instance, in our previous study,[16] we utilized a fluoroether segment designated as $CF_3CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)-$(C92)[22] to synthesize C92-betaine,[22] which demonstrated exceptional surface activity and achieved a minimum surface tension of 15.5 mN/m. Nonetheless, HFPO-TA,[22] which is the precursor and degradation product of C92-betaine,[22] has shown to be bioaccumulative and toxic in the toxicity studies.[5,23,24] Making a hasty choice, as a result, may be caught in a vicious circle of "lock-in" effect.[25] OC fluoroether chain with structural formula $CF_3(OCF_2)_n-$ has been used to design surfactants in our previous study.[16] The biotoxicity of their carboxylates has been studied by Dai et al.,[26−29] revealing low toxicity when $n = 2$, 3, and 4. However, the surface activities of betaines synthesized from these segments are unsatisfactory. In contrast, when $n = 5$, the surfactant exhibits high biological toxicity in spite of its superior performance. There is an urgent requirement for a systematic approach to address the conflict between the performance and the environmental impact of fluorinated surfactants.

In this study, we focus on the second strategy and employ OC3 and OC4 segments to design novel fluoroether betaines (Scheme 1). To enhance the performance of these surfactants, we introduced several structural modifications. First, we aim to improve the surface activity by attaching hydrophobic segments ($-CH_2O(CH_2)_3-$) to the original fluorinated chain. Second, we design a dual-chain structure to enhance the surface activity. Finally, we incorporate two different hydrophilic groups to investigate their influence on the surface activity of the betaines. After the target molecules are synthesized, their surface tension will be measured and compared with previous studies. Through this work, we hope to provide insights into the future design of alternatives to conventional fluorinated surfactants.

## ■ EXPERIMENTAL SECTION

**Reagents and Materials.** OC3-Me and OC4-Me were obtained from Sanming Hexafluo Chemicals Company. Sodium hydride (60% dispersion in mineral oil) and 1,3-propane sultone (99%) were purchased from Aladdin. Phosphorus oxychloride was purchased from J&K Scientific. All chemicals and reagents were obtained commercially and used without further purification.

**Surfactant Synthesis.** The synthesis of the family of fluorinated surfactants followed the process outlined in Scheme 2. Detailed synthetic information is provided in the following text and in the Supporting Information.

**Structural Characterization.** $^1H$ NMR and $^{19}F$ NMR spectra were recorded on an Agilent (400 and 376 MHz) spectrometer, and TMS was used as the internal standard in the $^1H$ NMR test. $^{13}C$ NMR spectra were recorded on a Bruke AM300 (100 MHz) spectrometer. The detailed spectra of each compound are provided in the Supporting Information.

**Surface Tension Measurements.** Cmc values were determined using a Krüss K100C (Krüss Company, Germany) tensiometer equipped with a Wilhelmy plate (the length and thickness was 19.9 and 0.2 mm, respectively). Surfactant solutions at different concentrations were prepared in 50 mL volumetric flasks using deionized water and allowed to stand overnight to ensure complete dissolution and mixing. Surface tension measurements were conducted at concentrations of 0.1, 0.01, and 0.001 wt %.

## ■ RESULTS

**Synthesis Experiment Part.** Our target molecules were synthesized from methyl ester via a six-step reaction sequence (Scheme 2). Following reduction with sodium borohydride, the corresponding alcohol (OC3-OH) was obtained. In the subsequent step, the alcohol was deprotonated in the presence of sodium hydride and underwent a ring−opening reaction with 1,3-propane sultone. To ensure complete deprotonation and an efficient reaction, an equimolar amount of reagent, an excess of base, and mechanical mixing were employed. After an 8 h reaction, direct filtration yielded sodium sulfonate (OC3-$SO_3Na$) with a maximum yield of 92%. Subsequently, 3 equiv of phosphorus oxychloride was employed to synthesize the corresponding sulfonyl chloride (OC3-$SO_2Cl$). Following the methodologies reported by Sharpless and Barbasiewicz,[30,31] tetrabutylammonium chloride was utilized to catalyze chlorine-fluorine exchange reaction, resulting in the isolation of the pure product (OC3-$SO_2F$) with a final yield of 92%.

Following the reaction of sulfonyl fluoride with 3-(dimethylamino)propylamine, the betaine precursor (OC3F-amine) was successfully synthesized in a yield of 83%. Subsequently, the tertiary amine underwent a nucleophilic substitution reaction with sodium iodoacetate, resulting in the final product (OC3F-B) with an approximate yield of 86%. OC4F-B and OC4F-B2 are synthesized via a comparable synthetic route.

However, when attempting the reaction between sulfonyl fluoride and *N*-methyl-2,2′-diaminodiethylamine using equimolar amounts, the reaction did not proceed to completion. Specifically, reacting with 0.5 equiv of *N*-methyl-2,2′-diaminodiethylamine at 80 °C in acetonitrile for 12 h resulted in a final NMR conversion rate of only 66% for sulfonyl fluoride. Consequently, we investigated the effects of the reaction temperature, reaction time, base concentration, and other relevant factors to optimize the reaction conditions. When the molar ratio of sulfonyl fluoride to *N*-methyl-2,2′-diaminodiethylamine was adjusted to 4:1, only the target product DOC3F-amine was obtained. Subsequently, silica column chromatography with an eluent (DCM/MeOH = 15:1) was employed to separate the product from the raw materials. Finally, after the amine was obtained, a nucleophilic reaction was performed to synthesize the final product (DOC3F-B).

**Surface Tension Measurement.** Following the successful synthesis of all five surfactants, their surface tensions at specified concentrations were measured. The surface tension values for each surfactant at various concentrations are listed in Table 1. As the hydrophobic chain length increases, the surface tension of the molecules decreases significantly. Among them, OC3F-B and OC3F-B2 with a longer hydrophobic chain decrease the surface tension by approximately 12 mN/m compared to OC3-betaine at 0.1 wt %; OC4F-B and OC4F-B2 can also decrease the surface tension by about 3 mN/m

**Table 1. Surface Tension of Different Surfactants at Different Concentrations**

| compound | surface tension (mN/m) | | | $T$ (°C) |
|---|---|---|---|---|
| | 0.1 wt % | 0.01 wt % | 0.001 wt % | |
| OC3F-B | 18.8 | 27.9 | 42.8 | 25 |
| OC3F-B2 | 19.8 | 28.4 | 49.9 | 25 |
| DOC3F-B | | 20.9 | 35.7 | 25 |
| OC4F-B | 16.1 | 16.8 | 30.0 | 25 |
| OC4F-B2 | 16.9 | 17.9 | 30.3 | 25 |
| OC3-betaine[a] | 30.6 | 45.4 | 57.2 | 22 |
| OC4-betaine[b] | 19.1 | 40.1[b] | | 24 |

[a] Data of OC3-betaine and OC4-betaine come from ref 16. [b] Data of OC4-betaine in 0.01 wt % come from the results of curve fitting.

relative to surfactants with the same fluorinated chain length, achieving a surface tension as low as 16 mN/m. As the concentration decreased, the surface tension of the surfactant solution also increased. While the OC4F-B and OC4F-B2 exhibited relatively better performance, maintaining surface tensions below 18 mN/m even at low concentrations (0.01 wt %).

It is worth noting that the betaine with two hydrophobic chains (DOC3F-B) shows a significant decline in solubility, becoming insoluble at 0.1 wt %. However, its surface tension at a low concentration can remain low. At 0.01 wt %, DOC3F-B can still achieve a surface tension of 20.9 mN/m, demonstrating the effectiveness of the dual-chain design.

To further investigate the relationship between the structure and surface activity, cmc, surface excess concentrations ($\Gamma_{max}$), and limiting molecular area ($A_{min}$) were calculated from the Gibbs equation based on the curve diagram of surface tension ($\gamma$) and concentration ($\log C$) we measured. These parameters describe the behavior of fluorinated surfactants at the air–water interface.

According to the Gibbs equation, $\Gamma_{max}$ and $A_{min}$ can be determined using the following formula

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

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

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature, and $\gamma$ and $C$ are the surface tension and concentration of the aqueous solution of surfactants, respectively. $N_A$ is Avogadro's constant ($6.022 \times 10^{23}$ mol$^{-1}$). The results are summarized in Table 2, and the relationship between the surface tension and concentration is illustrated in Figure 1.

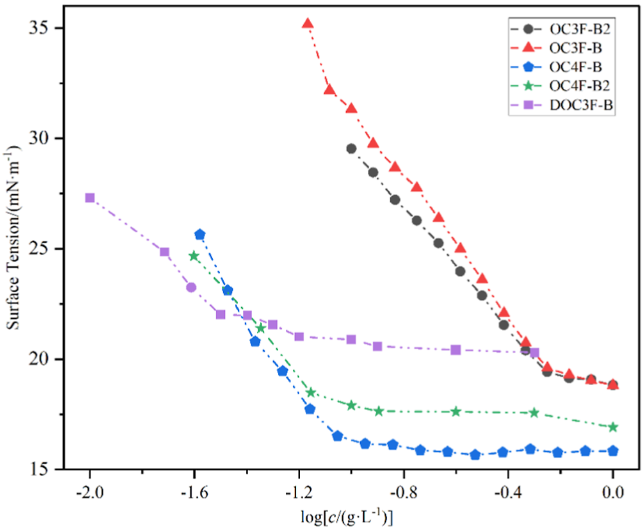


**Figure 1.** $\gamma$-log $c$ curves for fluorinated surfactants.

cmc is a key parameter for evaluating the performance of a surfactant. As presented in Table 2, OC3F-B and OC3F-B2 exhibited markedly reduced carbon-crystal values after the extension of their carbon chains. The impact of increasing chain length was particularly pronounced in OC4F-B and OC4F-B2, with cmc values decreasing to 0.087 and 0.075 g/L, respectively. The introduction of the new hydrophilic group, benzoate anions, results in a slight increase in $\gamma_{cmc}$ but simultaneously leads to a decrease in cmc. $A_{min}$ is commonly used to describe the average area occupied by each molecule when the molecules are closely packed at the interface. Based on the data we calculated, it is evident that an increase in the number of hydrophobic segments leads to a significant enhancement in the molecular limiting area. The $A_{min}$ value for OC3F-B is 0.59 nm$^2$. OC4F-B exhibits a comparable $A_{min}$ to that of OC3F-B. In contrast, the novel dual-chain structure of DOC3F-B significantly increases the $A_{min}$ to 0.86 nm$^2$. The introduction of the benzoate anion as a new hydrophilic group, however, results in slight increase in $A_{min}$. $\Gamma_{max}$ quantifies the tendency of surfactant molecules to move toward the phase interface. From the results in Table 2, it is evident that the usage of more fluoroether chains can remarkably decrease the $\Gamma_{max}$. Notably, the $\Gamma_{max}$ of DOC3F-B reach as low as $1.9 \times 10^{-10}$ mol/cm$^2$. In contrast, the introduction of a new hydrophilic group appears to have a minimal impact on $\Gamma_{max}$.

**Foam Performance and Thermal Stability.** To further explore the practical application potential of the synthesized surfactants, we conducted foam performance analysis on several synthesized betaines. To ensure the test concentration closely mimics actual usage conditions, we evaluated the foam performance of all compounds at a concentration of 0.01 wt % over a period from the end of foaming to the foam's half-life. From the test results, we quantified the foaming ability of the

**Table 2. Comparison of Surface Activities of Synthesized Surfactants**

| compound | $\gamma_{cmc}$ (mN/m) | cmc | | $A_{min}$ (nm$^2$) | $\Gamma_{max}$ ($\times 10^{-10}$ mol/cm$^2$) | $T$ (°C) |
|---|---|---|---|---|---|---|
| | | ($\times 10^{-4}$ mol/L) | (g/L) | | | |
| OC3F-B | 19.2 | 10.2 | 0.57 | 0.59 | 2.8 | 22 |
| OC3F-B2 | 19.5 | 8.8 | 0.56 | 0.69 | 2.4 | 22 |
| DOC3F-B | 21.0 | 0.48 | 0.047 | 0.86 | 1.9 | 25 |
| OC4F-B | 16.1 | 1.4 | 0.087 | 0.55 | 3.0 | 25 |
| OC4F-B2 | 18.0 | 1.1 | 0.075 | 0.80 | 2.0 | 25 |

Table 3. Foam Performance Parameters of Several Fluor Surfactants in Aqueous Solutions[a]

| surfactant | $V_{max}$ (mL) | $t_{FVS50\%}$ (s) | $t_{FLS75\%}$ (s) | $F$ ($\times 10^6$ mL·s) | $\alpha$ | $\overline{MBA}_{initial}$ ($\times 10^4$ $\mu m^2$) | $\overline{MBA}_{FVS50\%}$ ($\times 10^6$ $\mu m^2$) |
|---|---|---|---|---|---|---|---|
| OC3F-B | 179 | 10,110 | 30 | 1.8 | 3.6 | 6.1 | 3.0 |
| DOC3F-B | 49 | | | | 1.0 | | |
| OC4F-B | 203 | >10,800 | 91 | >2.2 | 4.1 | 4.3 | 0.8 |

[a] $V_0$ = 50 mL, foaming time 30 s.

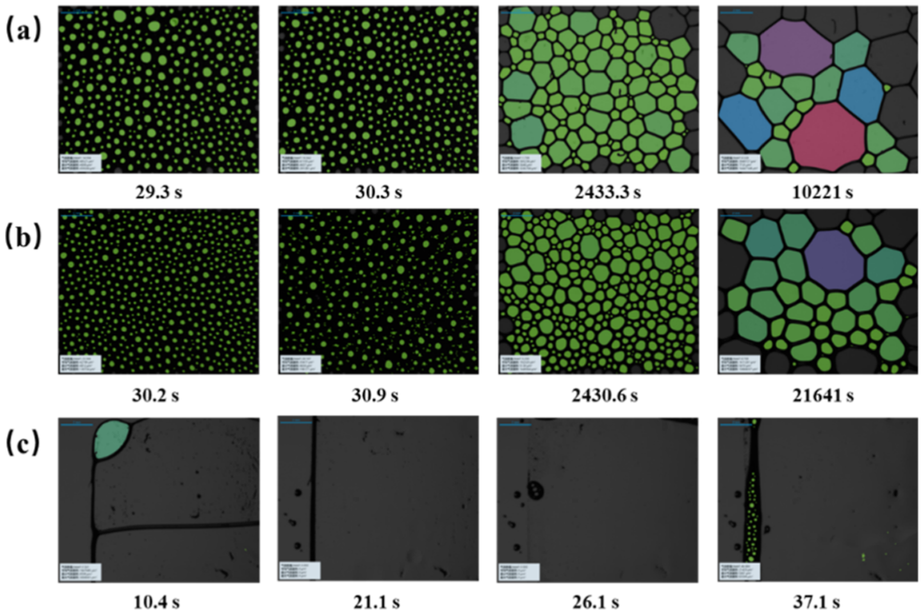


Figure 2. Microscope pictures of the foam approximately between the maximum bubble height and the half-life period. (a) 0.01 wt % OC3F-B. (b) 0.01 wt % OC4F-B. (c) 0.01 wt % DOC3F-B.

compounds by the maximum foam volume ($V_{max}$) and expansion $\alpha$, which is calculated by formula $\alpha = \frac{V_{max}}{V_0}$, where $V_0$ is the initial volume of surfactant solution and $V_{max}$ is the maximum foam volume; evaluated the surfactants' ability to stabilize the foam by the foam half-life ($t_{FVS50\%}$), which is defined as the time at which foam volume stability decreases to 50% of its maximum value; and assessed the molecule's ability to retain water by the 25% drainage time ($t_{FLS75\%}$), which is the time required from the beginning of foam formation to the precipitation of 25% liquid in volume from the foam, which is also an indicator of foam stability. Finally, we calculated the foam integration value $F$ by formula $F = V_{max} \times t_{FVS50\%}$ to qualitatively compare the foam performance of the surface-active agents. The results of the tests are shown in Table 3.

From the data presented in Table 3, it is evident that OC4F-B exhibits the most excellent foaming capability, generating liquid foam with a volume of 4.1 times that of its initial state. In contrast, OC3F-B, at a concentration of 0.01 wt.%, demonstrates a lower surface activity than OC4F-B, as indicated by its $\alpha$ value of 3.6, which marginally compromises its foaming performance.

Notably, DOC3F-B, despite having a surface tension of 20.9 mN/m at the same concentration, fails to produce dense bubbles during the foaming process, resulting in a foaming multiple of merely 1. This observation underscores that the foaming characteristics of surfactants are influenced not onlyy by surface tension but also significantly by the molecular structure of the compound. The dual-chain structure of DOC3F-B may impede the surfactant molecules from packing tightly at the water–air interface, thereby creating large air channels that cause the formed bubbles to burst easily, ultimately preventing foam generation. Conversely, the linear chain structure of OC3F-B and OC4F-B facilitates closer packing of the molecules, leading to a more durable foam. With a similar structural foundation, OC4F-B's higher surface activity enables it to retain water for an extended period, boasting a 25% liquid evolution time ($t_{FLS75\%}$) of 91 s—3-fold that of OC3F-B—and a foam half-life that exceeds 3 h of testing time, significantly surpassing OC3F-B's 10,110 s. Furthermore, the final foam synthesis value calculation results affirm OC4F-B's superior foaming performance. However, whether considering OC3F-B or OC4F-B, both exhibit superior foaming properties at lower concentrations compared to some previously reported surfactants that could serve as foam stabilizing agents.[12]

Figure 2 presents a foam shape map during the foam test process, providing a more intuitive understanding of the variations in foam properties among the different surfactants. Both OC3F-B and OC4F-B generate dense small bubbles (depicted as green dots in the figure) during the bubbling stage. As time progresses, these small bubbles coalesce to form larger bubbles (represented by large green dots and nongreen areas), which eventually rupture. At the foam half-life of OC3F-B (10,221 s), the system predominantly consists of large-area bubbles. Data from Table 3 reveal that the average bubble area $\overline{MBA}_{FVS50\%}$ at this stage has reached $3.0 \times 10^6$ $\mu m^2$. Conversely, by the end of the test, OC4F-B (21,641 s) exhibited an average bubble area of only $0.8 \times 10^6$ $\mu m^2$. The bubbling process of DOC3F-B reveals a near absence of dense bubble formation, and its distinctive foaming performance and surface activity suggest potential application prospects in the field of low-surface-tension defoaming agents.

To evaluate the thermal stability of the synthesized fluoroether betaines, differential scanning calorimetry (DSC) analysis was performed on OC4F-B, which is the most promising candidate among the five synthesized compounds. As shown in the DSC thermogram (Figure 3), no distinct endothermic or exothermic peaks were observed within the temperature range of 30−200 °C, indicating the absence of glass transition or phase transitions under these conditions. This behavior suggests that the molecular structure of OC4F-B remains intact and stable up to 200 °C, which is a critical attribute for practical applications requiring resistance to thermal degradation.

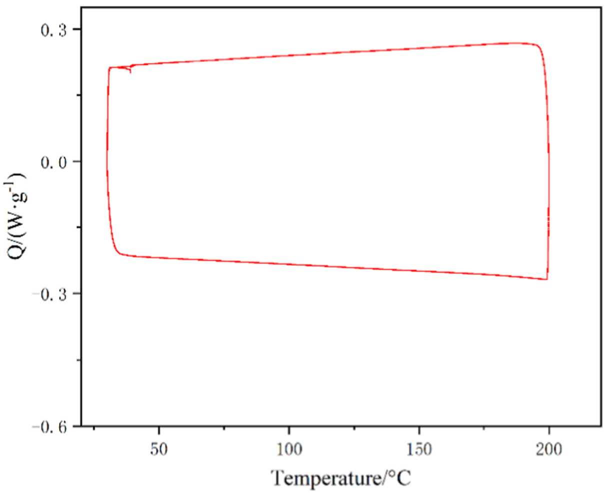


**Figure 3.** DSC test results for OC4F-B.

## DISCUSSION

The carboxylic acids derived from the OC segments ($(CF_3(OCF_2)_n-)$) employed in this study were evaluated for their biological toxicity by Dai,[26−28,31] Conley,[32] and Jackson[33] et al. in recent years. PFO3OA with three repeated $OCF_2$ units demonstrates low biotoxicity and exhibits environmentally friendly characteristics. The biotoxicity and bioaccumulative properties of PFO4DA containing four consecutive $OCF_2$ groups increase relative to shorter-chain analogues but remains lower than that of the traditional fluorinated surfactant PFOA in the mouse hepatotoxicity experiment.[26,31] When $n = 5$, the biotoxicity of PFO5DoDA is comparable to that of PFOA and is even higher in some organisms.[27,31] However, from the perspective of surface activity, the performance of surfactants improves significantly with an increase in the number of fluorocarbon atoms. For instance, in Wang's 2022 study,[11] the cmc of OC5-betaine decreased by over 100 times compared to OC3-betaine and the surface tension at cmc decreased by nearly 6 mN/m. Consequently, there exists an inherent conflict between the surfactant activity and environmental friendliness. Achieving a balance between these two aspects constitutes the primary focus of this research.

The results indicate that the strategy of extending the hydrophobic carbon chain by attaching an adjacent hydro-

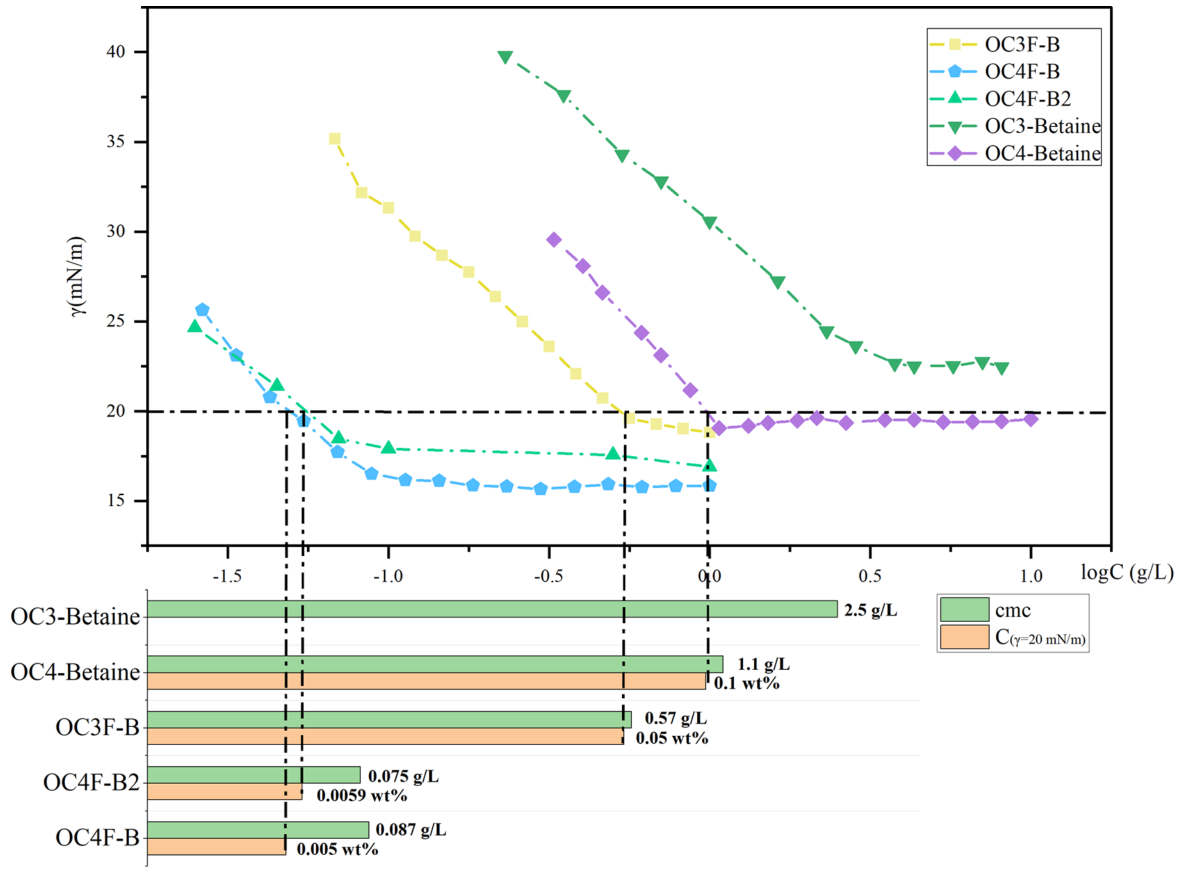


**Figure 4.** Comparison of cmc and concentrations at surface tension of 20 mN/m of several betaines in this research and ref 16.

phobic hydrocarbon segment to the perfluorinated chain yielded favorable outcomes. Compared with OC3-betaine, the cmc of the chain-extended OC3F-B decreased significantly by a factor of 5 to 0.57 g/L. Concurrently, the surface tension at the cmc reduced by 3 to 19.2 mN/m, indicating substantial improvements in surface activity. For the DOC3F-B molecule, which employs both carbon chain extension and double-chain strategies, the cmc decreased by 2 orders of magnitude compared to OC3-betaine, reaching as low as 0.047 g/L. For the OC4 segment, which originally outperformed OC3, the carbon chain extension strategy further enhanced its performance. Under single-chain conditions, OC4F-B achieved a cmc comparable to that of DOC3F-B, decreasing by a factor of 12 relative to OC4-betaine and reaching an extremely low value of 0.087 g/L. The surface tension at the cmc was further reduced to 16.1 mN/m, comparable to that of OC5-betaine. Furthermore, at an actual usage concentration of 0.01 wt %, the surface tension of OC4F-B is approximately 20 mN/m lower than that of OC4-betaine, demonstrating a significant improvement in performance. Thereby, OC4F-B has achieved an optimal balance between environmental friendliness and high surface activity.

In practical surfactant applications, surface tension data at low concentrations are particularly significant, especially at 0.01 wt %. Experimental results demonstrate that OC4F-B/B2 and DOC3F-B exhibit exceptional surface activity at this concentration. Specifically, DOC3F-B achieves a surface tension of 20.9 mN/m, while OC4F-B reduces water's surface tension to 16.8 mN/m, which is notably lower than the 45.4 mN/m observed for OC3-betaine. Although OC3F-B exhibits a surface tension of 27.9 mN/m at this concentration, it still represents a reduction of nearly 20 mN/m compared to its preoptimized structure. Additionally, we investigated the corresponding concentrations required for different molecules to achieve a surface tension of 20 mN/m to evaluate their practical application value. As shown in Figure 4, OC3F-B requires only 0.05 wt % to reach this surface tension after carbon chain extension, whereas OC3-betaine cannot achieve this effect at this concentration, and OC4-betaine requires 0.1 wt %. In contrast, DOC3F-B further reduces the concentration requirement to 0.01 wt %, while the most efficient OC4F-B achieves the same surface tension at just 0.005 wt %, a 10-fold improvement over OC3F-B, demonstrating strong practical application potential.

The successful design can be attributed primarily to the enhanced hydrophobic properties, which result from the introduction of an extended hydrocarbon segment and the modification of dual hydrophobic chains. This modification leads to a more pronounced hydrophobic effect and, consequently, improved surface activity. The attribution of the introduction of an extended hydrocarbon segment can be interpreted more deeply by reviewing our previous research. The cmc of the molecule 6:2FTSNa[23] with an extended nonfluorinated chain decreased by 2 times compared to the original structure, and the surface tension decreased to 11.3 mN/m. The benefits of the dual-chain design are mutually corroborated by our recent research. The dual-chain compound D361-B demonstrated significant performance improvements compared to C361-B.[18] A drawback of the dual-chain strategy is the decreased solubility of surfactant molecules, which is attributed to enhanced hydrophobic properties. Consequently, achieving a balance between the solubility and surface activity is crucial.

In this study, we synthesized an additional series (B2 series) incorporating a different hydrophilic group. The cmc of OC3F-B2 decreased by 10% relative to that of OC3F-B, while the surface tension at cmc increased by 0.3 mN/m. For OC4F-B2, the cmc was reduced by 30% compared to OC4F-B, yet the surface tension at the cmc rose by 2 mN/m. Analysis of the experimental data indicates that the introduction of a new hydrophilic group did not significantly enhance surface activity. Although these modifications led to a slight reduction in the cmc, they were accompanied by an increase in the surface tension. Therefore, it appears that the most direct and effective approach to improving surface activity may lie in modifying the hydrophobic end.

## ■ CONCLUSIONS

We successfully synthesized a series of fluorinated surfactants featuring extended hydrophobic chains via a six-step sequence, achieving a relatively high yield. These novel molecules were systematically compared with previously reported analogous compounds. The results demonstrated that the new surfactants exhibit superior surface activity at low concentrations and significantly reduce the cmc, which has positive implications for practical applications. While increasing the number of fluorocarbons is the most direct and effective approach to enhancing molecular surface activity, it also invariably results in a corresponding increase in molecular toxicity. This study provides a feasible strategy for the design of novel fluorinated surfactants by elongating the fluorinated hydrophobic chains with nonfluorinated moieties or augmenting the number of hydrophobic chains to modify short-chain surfactants. However, the six-step reaction route is still too long for practical industrial application, necessitating further exploration of more efficient synthetic pathways. Additionally, comprehensive investigations into the biotic toxicity and bioaccumulation potential of these synthesized molecules are requisite to ensure their safe utilization and prevent adverse environmental impacts.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.5c00254.

Description of the experimental procedure to synthesis fluoroether surfactants along with $^1$H NMR, $^{19}$F NMR, and $^{13}$C NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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