Development of a Completely New PFOS Alternative with Lower Surface Tension for Minimizing the Environmental Burden

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Improving the technical performance of related industrial products is an efficient strategy to reducing the application quantities and environmental burden for toxic chemicals. A novel polyfluoroalkyl surfactant potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate(F404) was synthesized by a commercializable route. It had a surface tension(γ) of 18.2 mN/m at the critical micelle concentration(CMC, 1.04 g/L), significantly lower than that of perfluorooctane sulfonate(PFOS, *ca*. 33.0 mN/m, 0.72 g/L), and exhibited remarkable suppression of chromium-fog at a dose half that of PFOS. The half maximal inhibitory concentration(IC_{50}) values in HepG2 cells and the lethal concentration of 50%(LC_{50}) in zebrafish embryos after 72 hpf indicated a lower toxicity for F404 in comparison to PFOS. In a UV/sulphite system, 89.3% of F404 were decomposed after 3 h, representing a defluorination efficiency of 43%. The cleavage of the ether C—O bond during the decomposition would be expected to form a short chain $\cdot C_4F_9$ as the position of the ether C—O in the F404 fluorocarbon chains is C4—O5. The ether unit is introduced in the perfluoroalkyl chain to improve water solubility, biocompatibility and degradation, thereby minimizing the environmental burden.

Keywords Perfluorooctane sulfonate(PFOS); Surface tension; Chromium-fog inhibitor; Perfluoropolyether

1 Introduction

Per- and polyfluoroalkyl substances(PFASs) have the unique properties of high surface activity and chemical stability, and are called "super surfactants". They are widely used in various industries and products ranging from non-stick coatings, carpets, paper, paints, fire-fighting foams, electroplating processes, imaging materials, etc.[1−4]. The fluorinated surfactants offer the highest surface activity among all types of surfactants and are much more efficient than the hydrocarbon surfactants and siloxane surfactants[5−7]. With the wide industrial production and use, there are a lot of environmental and health concerns around PFAS caused by their bioaccumulation potential, persistence, global distribution and toxicity[8]. Perfluorooctane sulfonate(PFOS), its salts and perfluorooctane sulfonyl fluoride(PFOSF), were listed into the Annex B by Stockholm Convention on Persistent Organic Pollutants(POPs) in 2009 to restrict the production and use[9]. In the electrolytic chromium plating process, chromic acid could be released with the rising gases to form chromic acid fog and seriously influence the health of workers in the factories and nearby residents. PFOS, with low surface tension and extremely high stability, is usually utilized as an ideal chromium-fog inhibitor in the electroplating plant[10]. Although it has been listed into POPs and required to phase out internationally, PFOS usage is exempted in some specialized fields, such as fire-fighting foams and electroplating industry because of the lack of suitable substitutes. However, considering the potential hazard of PFOS and its derivatives, it is the most critical issue to develop appropriate PFOS alternatives for fluorine chemical industry and related industries.

Since 3M Company phased out the products based on C6, C8 and C10 chemistry in 2000, there has been a trend among global producers to replace long-chain PFAS and their precursors[11]. Alternative strategies for PFOS include shortening the length of the fluoroalkyl chain, such as perfluorobutane sulfonic acid(PFBS), introducing heteroatoms into the fluoroalkyl chain, such as perfluoroalkyl ether potassium sulfonate(F-53) and chlorinated polyfluorinated ether sulfonate(F-53B), and replacing part of the C—F bonds in the fluoroalkyl chain with C—H bonds, such as 6:2 fluorotelomer sulfonic acid(6:2 FTSA)[12−15]. However, the similar structure of the alternatives with the legacy PFAS led to the same concerns about their impact on the environment and ecosystem health[16]. For instance, a chlorinated polyfluorinated ether sulfonate(F-53B) has been widely applied as a mist suppressant by the chrome plating industry in China for decades, nevertheless the investigation on its toxicity, persistence and presence in the environment is controversial[17−20]. It might be expected that the alternatives are less hazardous to the environment and humans[16]. However, decreased application performance could also mean

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that larger quantities would be needed to obtain similar performance to the replaced PFAS. This would then still result in widespread pollution, even with low bioaccumulation and toxicity alternatives, such as short-chain PFAS[8,21−23]. Indeed, a crucial aspect of the research in development of perfluorinated alternatives is finding compounds that display superior surface tension in order to reduce the amount used in real applications, and thus decrease the release potential and environmental burden.

As far back as in 1970s, perfluoropolyether(PFPE) surfactants, which easily form microemulsions with water and the corresponding oils, have been of great interest to surface chemistry researchers[24−26]. PFPE surfactants have better flexibility, biocompatibility, water solubility, and lower Kraft points than perfluoroalkyl surfactants[7]. For instance, the surface tension value for a novel fluorinated surfactant perfluoropolyether amide propyl betaine is about 16.87 mN/m at the critical micelle concentration(CMC) of 0.07 mmol/L, and the surface tension value for its sodium salt is about 22.6 mN/m at the CMC of 1.28 mmol/L, both lower than that of sodium perfluorooctanoate(24.7 mN/m, 3.12 mmol/L)[7,27]. One or several alkylether linkages in the fluoroalkyl chain could be expected to reduce bioaccumulation potential compared to full-carbon-chain predecessor without other atoms PFAS, although the effect on toxicity remains unclear[13,28,29]. Meanwhile, it has been proved that the etheric bond introduces a weak point in the perfluoroalkyl chain, facilitating its degradation by hydrated electron[30].

In this study, a completely new polyfluoroalkyl surfactant potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate(hereinafter referred to as F404) was synthesized by a commercializable route. The synthesized product was characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{19}F NMR and high-resolution accurate mass orbitrap mass spectrometer(HRMS). To compare the technical performance with PFOS, the surface tensions were measured and the CMC values were calculated. Furthermore, the application potential for F404 as PFOS alternative was evaluated by the chromium-fog inhibition ratios in the electrolytic chromium plating process as an example. The acute toxicity and environmental persistence of the novel PFPE surfactant were also studied.

2 Experimental

2.1 Synthesis of F404

The acetyl chloride reacted with tetrahydrofuran using zinc powder as a catalyst to give an 87% yield of 4-chlorobutyl acetate. Then 4-chlorobutyl acetate was treated with aqueous sodium sulfite to give 1-hydroxy-4-butanesulfonic acid, which

was immediately treated with 1-bromobutane and an alkali to give a 75% yield of sodium 4-butoxy-1-butylsulfonate(SBBS) (Fig.1). Phosphorus oxychloride was used as the chlorinating reagent, and a 65% yield of 4-butoxy-1-butylsulfonyl chloride (BBSC) was achieved. The BBSC was fluorinated using potassium fluoride as the fluorinating reagent and triethanolamine as a catalyst to give an 85% yield of 4-butoxy-1-butylsulfonyl fluoride(BBSF). Perfluoro-4-butoxy-1-butylsulfonyl fluoride was synthesized through the electrolysis of BBSF with anhydrous hydrogen fluoride at a specified current(2 A) and voltage(5 V). In the presence of an alkali and calcium oxide, perfluoro-4-butoxy-1-butylsulfonyl fluoride was converted into F404 with a yield of 80%. This route involved relatively simple procedures and a common starting material, making it suitable for industrial production. F404 has obtained the Chemical Abstracts Service(CAS) registration number provided by American Chemical Society: 2407909-49-1. The equation(Figs.S1—S11) of each step and the characterization of the products are shown in the Electronic Supplementary Material of this paper.
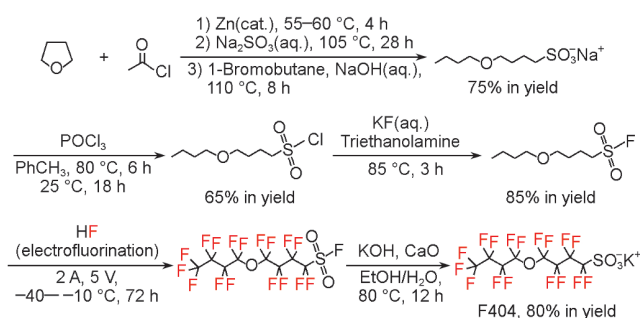

Fig.1 Synthetic reaction route of F404

2.2 Instrumental Analysis

F404 was identified by the QExactive Orbitrap HRMS(Thermo Scientific, CA), operated in a negative electrospray ionization (ESI) mode in full scan(m/z 200—700) at a resolution of 140000. Quantitative analysis of F404 and PFOS in all samples was accomplished using a high performance liquid chromatograph (HPLC, Ultimate 3000 HPLC, Thermo Fisher, CA, USA) equipped with an electrospray ionization tandem mass spectrometer(ESI-MS/MS, Triple Quad 4500, Applied Biosystems/MDS SCIEX, USA) operated in a negative mode. An ion-chromatograph system(IC, Climax C153, CQS, Germany) consisting with an IC anion exchange column (2.6×150 mm, 10 μm, sykam GmbH, Germany), and a conductivity detector with a suppressor device was used to measure the F$^-$ concentration. The detailed parameters of the instrument analysis(Table S1) and quality assurance are shown in the Electronic Supplementary Material of this paper.

2.3 Surface Tension Measurement

The surface tensions of PFOS and F404 were tested using the platinum plate method by a BZY-101 automatic surface tensiometer(Shanghai Fangrui Instrument Co., Ltd., China). A series of PFOS and F404 concentrations(0.1—6 g/L) was dissolved in 80—90 °C ultrapure water until no dissolved solids were observed. Later the solutions were equilibrated at room temperature for 5 h and measured at (25±0.1) °C. Each sample was prepared and measured in triplicate. The value of surface tension for ultrapure water of (25±0.1) °C was (71.8±0.27) mN/m, with the relative standard deviation(RSD) of 0.37%[31]. The concentration of PFOS or F404 in each solution was analyzed using an HPLC-ESI-MS/MS.

2.4 Analysis of Chromium-fog Inhibition in Electroplating

The electroplating process was performed according to the operating manual[32]. A sample electroplating device was used(Fig.S12, see the Electronic Supplementary Material of this paper). Briefly, the electroplating solution was prepared as follows. First, 200 g of CrO_3 was dissolved in the pure water, added 1.08 mL of H_2SO_4, and made to 1 L volume. Before electroplating the chromic acid solution was heated to 60 °C. A copper sheet and a lead block were connected to the anode and cathode of the rectifier(Shaoxing Heli Rectifier Factory, China) with the electricity of 10 A, respectively. No additive and additive of chromium-fog depressants groups were performed in the same process, including 0(no additive), 0.04 g/L PFOS, 0.08 g/L PFOS, 0.04 g/L F404, and 0.08 g/L F404. The chrome fog samples were collected in 1.5 L/min flow with 10 mL of 2% HNO_3 absorption liquid at 0—1(Sample 1, S1), 2—3(S2), 4—5 (S3), 6—7(S4) and 8—9 min(S5) of the electroplating process. The samples were sealed immediately and analyzed as soon as they were collected. All the experiments were repeated five times within one month and repeated once after one month to investigate the stability of chromium-fog inhibition. The concentration of Cr^{6+} was determined by an inductively coupled plasma mass spectrometer(ICP-MS, iCAP RQ, Thermo Fisher, CA, USA) after the dilution with 2% HNO_3. The detailed parameters of the quantitative analysis of Cr^{6+} are shown in the Electronic Supplementary Material of this paper.

2.5 Acute Toxicity and Degradability Test

The acute toxicity was tested for HepG2 and zebrafish embryos by exposing to F404 and PFOS, respectively. The half maximal inhibitory concentration(IC_{50}) of cell survival in HepG2 cells and the lethal concentration of 50%(LC_{50}) in zebrafish embryos were calculated. The degradability of F404 and PFOS in water was performed by UV-activated sulphite system using quartz tubes(Fig.S13, see the Electronic Supplementary Material of this paper) according to the previous study[20]. The details were shown in the Electronic Supplementary Material of this paper.

3 Results and Discussion

3.1 Identification of F404

Under the catalysis of zinc powder, commercial tetrahydrofuran and acetyl chloride were used to react with sodium sulfite and further with *n*-butane bromide to obtain sodium 4-butoxybutane-1-sulfonate. $POCl_3$ was used to obtain the corresponding sulfonyl chloride. The precursor compound 4-butoxybutane-1-sulfonyl fluoride was obtained by the reaction with KF. Finally, HF was used as the fluorine source to obtain the product by electrolytic fluorination, which is purified into salt to obtain the perfluorinated product(Fig.1). Results from NMR showed chemical shifts of CF_2 at δ –82.6, –84.3 and –84.5. Some chemical shifts were biased towards low-field positions at δ –115.9, –112.1, –126.5 and –127.7 because of the electron-withdrawing ability caused by sulfonate(Figs.S14 and S15, see the Electronic Supplementary Material of this paper). On the other hand, due to the mutual coupling between C—F and F—F bonds, the chemical shifts of their carbon spectra were densely distributed between δ 121 and 105. The results from FTIR show that the characteristic absorption peaks of several special groups were as follows: the CF_3—CF_2 bond at 736 cm^{-1}, the C—F bond at 1132 cm^{-1}, and the extension peak of the C—O—C bond at 1201 cm^{-1}. The main characteristic peaks of sulfonic acid groups: absorption peaks at 1342, 1244, 1064 and 665 cm^{-1} are more obvious(Figs.S16 and S17, see the Electronic Supplementary Material of this paper). The major fragmentation ions, $[M-K]^-$(m/z 514.92426, mass error –0.62 ppm), $[C_4F_9O]^-$(m/z 234.98035, –0.81 ppm), $[C_3F_7]^-$ (m/z 168.98819, –3.73 ppm), $[C_4F_7SO_4]^-$(m/z 276.94052, –2.1 ppm), $[SO_3]^-$(m/z 79.95588, –12 ppm), and $[FSO_3]^-$(m/z 98.95431, –9.2 ppm) were observed in an HRMS MS2 full scan mode in the F404 standard solution(Fig.S18, see the Electronic Supplementary Material of this paper).

3.2 Surface Tension

Surface tension measurements of PFOS and F404 were carried out at room temperature(*ca*. 25 °C). Surface tension values decreased with an increasing concentration as expected [Fig.2(A)]. Surface tensions of F404 solutions reached constant
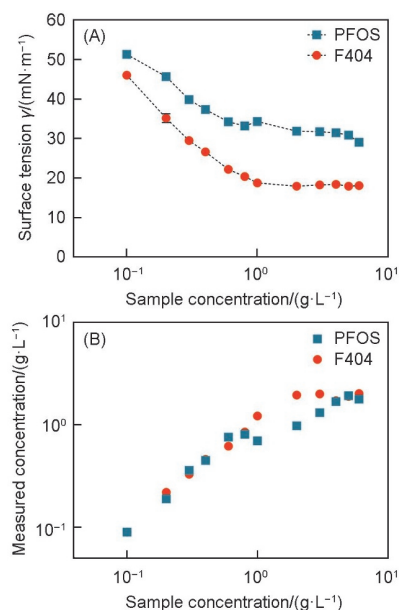
Fig.2 Surface tension(γ)-concentration(c) curve of PFOS and F404 in aqueous media at 25 °C(A) and measured concentration of PFOS and F404 in each solution for surface tension(B)

equilibrium values at the range of 17.9—18.4 mN/m at concentrations >1.0 g/L in the ultrapure water, whereas surface tensions of PFOS decreased at an inflection point of 33.2 mN/m at a concentration of 0.8 g/L and continued to slowly decrease. The surface tension values for PFOS($C_8F_{17}SO_3K$) in this study were lower than those reported by Shinoda et al.[3] but consistent with those by Costanza and coworkers[33]. These observations clearly show F404 has superior surface activity properties compared to PFOS. The critical micellar concentrations(CMC) is a basic parameter for nearly every application of surfactants, which can be obtained at the breakpoint in the γ versus lgc plots[34]. As shown in Fig.S19 (see the Electronic Supplementary Material of this paper), it is observed that F404 exhibits a relatively higher CMC value of 1.04 g/L and a lower γ_{cmc} of ca. 18.2 mN/m in comparison to 0.72 g/L and ca. 33.0 mN/m for PFOS.

The actual concentrations of PFOS and F404 in each solution for surface tension measurements were analysed to verify the solubility[Fig.2(B)]. At concentrations <1.0 g/L, the measured concentrations of PFOS and F404 in each solution for surface tension tests were the same, which were consistent with the sample concentration. It was confirmed that the differences in surface tension between PFOS and F404 were from the physicochemical properties at the same concentrations in the ultrapure water. At the concentration of 1—3 g/L, the measured concentrations of F404 were greater than those of PFOS, while at the concentrations of 4—6 g/L they were approximately equal but lower than their theoretical concentrations. Separate phase liquid thin film was observed

on the surface of the solution at a concentration of 0.8 g/L for PFOS or 2 g/L for F404. When the theoretical concentrations increased to >1 g/L for PFOS or >4 g/L for F404, visible lamella floating was observed on the surface of the solution. The interference of lamella floating was responsible for the deviation between measured and sample concentrations of the solution at concentrations greater than CMC values.

3.3 Chromium-fog Inhibition Ability in Electroplating

Following the promising results of lower surface tension, the chromium-fog inhibition ability of F404 during electrolytic chromium process was tested at the lab scale. The concentrations of chromium-fog(measured by Cr^{6+}) decreased sharply from 33.4 μg/L to 0.013 and 0.008 μg/L in the PFOS and F404 treatments, respectively, at a dose of 0.08 g/L, representing the inhibition ratios of 99.96% and 99.98%, respectively[Fig.3(A)]. Noteworthily, when halving the concentrations of the additive to 0.04 g/L, chromium-fog was still drastically suppressed with an inhibition ratio of 99.73% by F404, whereas the foam covered only a quarter of the liquid level with the chromium-fog inhibition ratios of 81.05% by PFOS(Video S1 0.04 g/L F404 and Video S2 0.04 g/L PFOS, see the Electronic Supplementary Material of this paper). Fine and
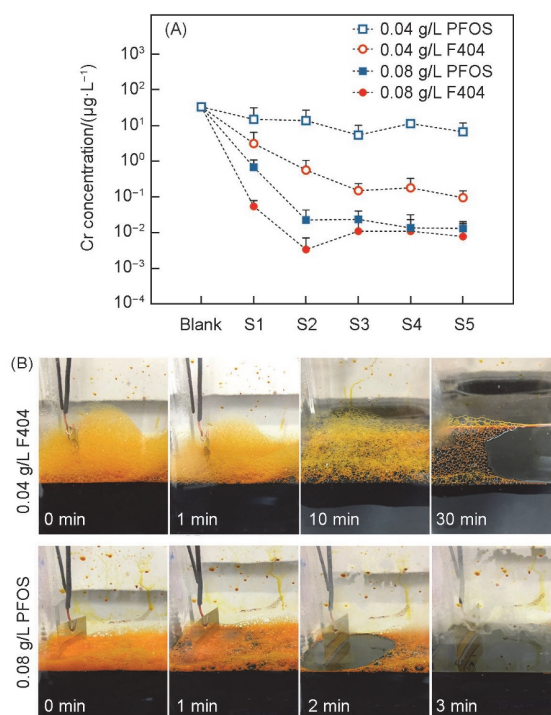

Fig.3 Concentration of Cr^{6+} in absorption liquid collected during the analysis of chromium-fog inhibition in lab-scale electroplating(A) and typical images of foam caused by F404 and PFOS after electroplating for 0—30 min(B)

thick foam was observed for F404 with 4.0—5.5 and 2.5—4.0 cm for 0.08 and 0.04 g/L additive after 10 min in electroplating, respectively, and significantly thicker than that using 0.08 g/L PFOS(Fig.S20, see the Electronic Supplementary Material of this paper). After the electroplating was terminated, it was surprising to discover that the foam did not completely disappear within 10 min in the F404 group, but continuously reducing the chromium fog in the atmosphere[Fig.3(B)]. The chromium-fog inhibition by F404 was stable when repeating it after one month. All these observations show that F404, exhibiting lower surface tension, is a more efficient chromium-fog inhibitor at a lower additive amount.

3.4 F404 Exhibiting Lower Toxicity than PFOS in Both Cells and Zebrafish Embryos

Both PFOS and F404 exhibited toxic effects on HepG2 cells within the exposure dose range. PFOS exhibited lethal effect when the exposure dose increased to 200 μmol/L, while the same dose for F404 did not induce a significant lethal effect on the cells(Fig.S21, see the Electronic Supplementary Material of this paper). The calculated IC_{50} values for PFOS and F404 were (245±7.80) and (402±21.9) μmol/L, respectively(Table 1). In previous studies, after HepG2 cells were treated with 200—300 μmol/L PFOS, the cell viability was 40%—60%, which was consisted with the data in the study[35,36]. The lower IC_{50} value indicated a lower toxicity of F404 when comparing with PFOS. And 5 μmol/L PFOS induced a significant lethal effect on zebrafish embryos at 72 hpf, with increased effects for 10 and 50 μmol/L PFOS-exposed individuals. The hatching rates of embryos were also suppressed in these groups in a dose-dependent manner. In contrast, F404 showed no effect on the hatching rate of embryos within the exposure dose range, and only 10 and 50 μmol/L F404 showed significant lethal effects after 72 hpf. The calculated LC_{50} values of PFOS and F404 were (3.91±1.18) and (8.91±0.28) μmol/L, respectively(Table 1). In previous studies, the 96 h LC_{50} values of F-53B on zebrafish embryos were 13.8—15.5 mg/L, which was lower than those of PFOS with the values of 17—71 mg/L, indicating that F-53B seems to be more toxic than PFOS[17,19]. However, the obtained mortality and hatching rate data in zebrafish embryos exposed to F404 both showed a lower toxicity for F404 in comparison to PFOS (Fig.S22, see the Electronic Supplementary Material of this paper).

Table 1 Calculated IC_{50} in HepG2 cell and LC_{50} in zebrafish embryos after 72 hpf for PFOS and F404

Compound	HepG2, IC_{50}/(μmol·L⁻¹)	Zebrafish embryos, LC_{50}/(μmol·L⁻¹)
PFOS	245±7.80	3.91±1.18
F404	402±21.9	8.91±0.28

3.5 Degradation Feasibility of F404 and PFOS by UV/Sulphite System

Fig.4 shows the irradiation-time dependence of the photoreaction for F404 and PFOS under a UV/sulphite system. The concentrations of F404 and PFOS decreased, and the concentrations of F⁻ increased with increasing irradiation. After 1.5 h of irradiation, 99.9% of the initial PFOS concentration of 40 μmol/L was decomposed. Complete removal of PFOS was achieved within 3 h, and the corresponding defluorination efficiency was 93%. A slower decomposition rate was observed for F404, as 68.8% and 89.3% of F404 were decomposed after 1.5 and 3 h, corresponding to defluorination efficiencies of 42% and 43%, respectively. With the increasing irradiation after 3 h, there was no continuous decrease in F404 or increase in F⁻ levels. The observed PFOS decomposition in the present system with 20 mmol/L Na_2SO_3(pH=10) was consistent with the previous study[37] that 97.3% of PFOS decomposed after 4 h reaction in the vacuum ultraviolet(VUV)/sulphite systems, whereas the corresponding defluorination efficiencies were higher than those with 68.5%. The differences of PFOS defluorination between the present and previous study[28] could be due to the different wavelengths and intensities of the illuminants. However, different molecular structures of PFOS and F404 could play a more important role in their different decompositions. A slower degradation was observed for F-53($C_8F_{17}SO_4K$) than for PFOS, as the former has a similar structure to F404 with an ether group and the same length of the perfluoroalkyl chain[20]. The presence of the ether group can markedly change the lowest unoccupied molecular orbital(LUMO)[20]. However, defluorination efficiencies of F404 were much lower than those of F-53(ca. 70%), while they both showed ca. 90% decomposition[20]. The difference of defluorination efficiencies was attributed to the chain length of oxygen-segregated fluoroalkyl moieties since the ether oxygen atoms could increase the bond dissociation energy of the C—F bonds on the adjacent —CF_2— moieties[28].
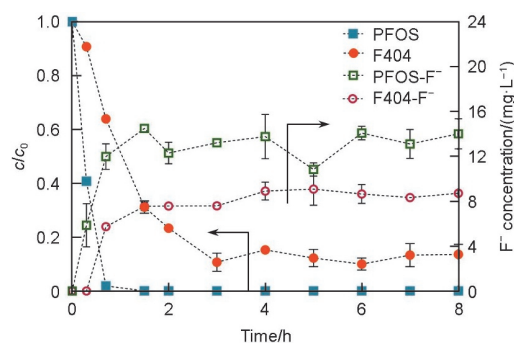

Fig.4 Time profiles of parent compound decay(c/c_0) and defluorination(F⁻ concentration) for PFOS and F404 in UV/sulphite system

According to the density functional theory, the C—F bond dissociation energies(BDEs) for both primary and secondary C—F bonds are lower for PFAS with longer fluoroalkyl chains[38]. The central —CF_2— in the fluoroalkyl chains has the highest affinity to the extra electron, such as hydrated electrons(e_{aq}^-), resulting in the first defluorination at the middle —CF_2— group[38,39]. However, the low C—F bond at the α-position of PFCAs was not found in linear perfluoroalkyl ether carboxylic acids(PFECAs) with an ether oxygen at the β-position. Interestingly, when the chain length of oxygen-segregated fluoroalkyl moieties was longer[$n=2$ or 3 in RF—O—$(CF_2)_n$—COO—], the C—F bond at the α-position becomes lower again[28]. Considering previous theoretical studies[28,38], it could be conjectured that weaker C—F bonds at the α-position were observed in F404[—O—$(CF_2)_4$—SO_3^-] than in F-53[—O—$(CF_2)_2$—SO_3^-], increasing the probability of H/F exchange and decreasing the overall defluorination efficiencies.

With the lowest dissociation energy of C3—O4 bond, the hexafluoropropylene oxide dimer acid(HFPO-DA) molecule was speculated to first split at the ether group to form $C_3F_7\cdot$ and $\cdot C_3F_4O_3^-$ fragments[30]. The phenomenon was supported by the density functional theory, the strength of the two C—O bonds on the ether linkage was asymmetric, as lower BDE was found for the C—O bond farther away from the terminal group than the other one[28]. Based on the above conjecture, for F404 and F-53, the cleavage of the ether C—O bond will form $\cdot C_4F_9$ and $C_6F_{13}\cdot$, which will undergo H/F elimination and hydrolysis to yield $C_3F_7COO^-$ and $C_5F_{11}COO^-$, respectively[30,40,41]. The corresponding shorter chain PFCAs will enter the next reaction cycle and form $C_{n-1}F_{2n-1}$—CH_2—COO^-, which has high recalcitrance[28]. Thereby, with a longer fluorocarbon chain, $C_5F_{11}COO^-$ degraded from F-53 would release more F^- cleaving from the middle —CF_2— group than $C_3F_7COO^-$ from F404.

4 Environmental Implications

The C—F keys in PFASs are considered to be "double-edged sword". The special chemical inertness, hydrophobic hydrophobicity and surface activity determine the performance advantages of its products. While the high energy bond also led to the high chemical and physical stability, bioaccumulation of PFASs. If PFOS and other PFASs were replaced with C—F bond free chemicals, related product performance would be significantly reduced and would not even work in some applications. Also, for developing countries like China, "one size fits all" controls on PFASs in order to reduce environmental risks once is not practical. Total restriction on the production of PFASs would significantly increase their raw material costs or even lead to

supply cuts. Therefore, the development of PFOS alternatives should be step by step, improving technical performance of related industrial products is an efficient strategy to reducing the application quantities and environmental burden for PFASs.

The perfluorinated substitute that we synthesized had a lower surface tension value and better chrome mist suppression effect and was less cytotoxic than currently available PFAS. F404 was found to have the same effect as PFOS, but at half the concentration, it is therefore more environmentally friendly than PFOS. In the further research, one of the most important things is to prepare the product at the kilogram scale in green ways. The ingredients, intermediates, products, and by-products should be analyzed and characterized to control the reaction process. In industrial production, the input ratio of ingredients, reaction parameters and yield should be further adjusted and optimized. In addition, the environment impact on the surrounding environment also needs to be continuously followed up after the quantity production.

5 Conclusions

In our study, a completely new polyfluoroalkyl surfactant F404 was synthesized and characterized. Compared to PFOS, a lower surface tension was observed for F404, making it more efficient in chromium-fog inhibition even at a lower additive amount. Although a slower degradation was observed for F404 than for PFOS, it is expected that the cleavage of the ether C—O bond in F404 will form short chain $C_4F_9\cdot$ as the position of the ether C—O in the F404 fluorocarbon chains is at C4—O5. Additionally, F404 exhibited a lower toxicity compared to PFOS in both cell assays and zebrafish embryos. Based on these promising results, F404 appears to be a high-performance PFOS alternative, which is less hazardous to the environment and organisms with lower doses in industrial applications.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Kissa E., *Fluorinated Surfactants and Repellents, Seconded*, Marcel Dekker, New York, **2001**

[2] Lehmler H.-J., *Chemosphere*, **2005**, *58*(11), 1471

[3] Shinoda K., Hato M., Hayashi T., *The Journal of Physical Chemistry*, **1972**, *76*(6), 909

[4] Wang Z., DeWitt J. C., Higgins C. P., Cousins I. T., *Environmental Science & Technology*, **2017**, *51*(5), 2508

[5] Shi L., Li N., Yan H., Gao Y. A., Zheng L., *Langmuir*, **2011**, *27*(5), 1618

[6] Cameron J. A., *Australian Dental Journal*, **1986**, *31*(5), 364

[7] Shen J., Bai Y., Tai X., Wang W., Wang G., *ACS Sustainable Chemistry & Engineering*, **2018**, *6*(5), 6183

[8] Lindstrom A. B., Strynar M. J., Libelo E. L., *Environmental Science & Technology*, **2011**, *45*(19), 7954

[9] Listing of Perfluorooctane Sulfonic Acid, *Its Salts and Perfluorooctane Sulfonyl Fluoride, Stockholm Convention on Persistent Organic Pollutants (POPs), Program U. N. E., Ed. UNEP-POPS-COP. 4-SC-4-17*, Geneva, Switzerland, **2009**

[10] Guan J., *Forestry Machinery*, **1988**, (6), 57

[11] Ritter S. K., *Chemical & Engineering News*, **2010**, *88*(5), 12

[12] Wang Z., Cousins I. T., Scheringer M., Hungerbühler K., *Environment International*, **2013**, *60*, 242

[13] Munoz G., Liu J., Vo Duy S., Sauvé S., *Trends in Environmental Analytical Chemistry*, **2019**, *23*, e00066

[14] Lin Y., Ruan T., Jiang G., *Chinese Science Bulletin*, **2017**, *62*(24), 2724

[15] Lu Y., Liang Y., Zhou Z., Wang Y., Jiang G., *Environmental Science & Technology*, **2019**, *53*(24), 14091

[16] Wang Z., Cousins I. T., Scheringer M., Hungerbuehler K., *Environment International*, **2015**, *75*, 172

[17] Wang S., Huang J., Yang Y., Hui Y., Ge Y., Larssen T., Yu G., Deng S., Wang B., Harman C., *Environmental Science & Technology*, **2013**, *47*(18), 10163

[18] Shi Y., Vestergren R., Zhou Z., Song X., Xu L., Liang Y., Cai Y., *Environmental Science & Technology*, **2015**, *49*(24), 14156

[19] Shi G., Cui Q., Pan Y., Sheng N., Sun S., Guo Y., Dai J., *Aquatic Toxicology*, **2017**, *185*, 67

[20] Bao Y., Huang J., Cagnetta G., Yu G., *Water Research*, **2019**, *163*, 114907

[21] Ateia M., Maroli A., Tharayil N., Karanfil T., *Chemosphere*, **2019**, *220*, 866

[22] Zhou Z., Liang Y., Shi Y., Xu L., Cai Y., *Environmental Science & Technology*, **2013**, *47*(16), 9249

[23] Ahrens L., Shoeib M., Harner T., Lee S. C., Guo R., Reiner E. J., *Environmental Science & Technology*, **2011**, *45*(19), 8098

[24] Caporiccio G., Burzio F., Carniselli G., Biancardi V., *Journal of Colloid and Interface Science*, **1984**, *98*(1), 202

[25] Monduzzi M., Knackstedt M. A., Ninham B. W., *The Journal of Physical Chemistry*, **1995**, *99*(50), 17772

[26] Shanghai Guangming Electroplating Plant, Shanghai Institute of Organic Chemistry at Chinese Academy of Science, Jiangsu Taizhou Electrochemical Plant, *Mater. Prot.(in Chinese)*, **1976**, *3*(3), 27

[27] Yin Q., Xue W., Bai Y., Wang W., Ma X., Du Z., Wang G., *Journal of Industrial and Engineering Chemistry*, **2016**, *42*, 63

[28] Bentel M. J., Yu Y., Xu L., Kwon H., Li Z., Wong B. M., Men Y., Liu J., *Environmental Science & Technology*, **2020**, *54*(4), 2489

[29] Brandsma S. H., Koekkoek J. C., van Velzen M. J. M., de Boer J., *Chemosphere*, **2019**, *220*, 493

[30] Bao Y., Deng S., Jiang X., Qu Y., He Y., Liu L., Chai Q., Mumtaz M., Huang J., Cagnetta G., Yu G., *Environmental Science & Technology*, **2018**, *52*(20), 11728

[31] Maham Y., Mather A. E., *Fluid Phase Equilibria*, **2001**, *182*(1), 325

[32] Li D., *Formulation and Production of Electroplating Solution*, Chemical Industry Press, Beijing, **2018**

[33] Costanza J., Arshadi M., Abriola L. M., Pennell K. D., *Environmental Science & Technology Letters*, **2019**, *6*(8), 487

[34] Gente G., La Mesa C., Muzzalupo R., Ranieri G. A., *Langmuir*, **2000**, *16*(21), 7914

[35] Hu X.-Z., Hu D.-C., *Archives of Toxicology*, **2009**, *83*(9), 851

[36] Yao X.-F., Cao J., Xu L.-M., Sun X.-C., Kang J., Yang G., Jiang L.-P., Geng C.-Y., Gao C.-Z., Zhong L.-F., Ma Y.-F., *Food and Chemical Toxicology*, **2014**, *67*, 96

[37] Gu Y., Liu T., Wang H., Han H., Dong W., *Science of the Total Environment*, **2017**, *607*, 541

[38] Bentel M. J., Yu Y., Xu L., Li Z., Wong B. M., Men Y., Liu J., *Environmental Science & Technology*, **2019**, *53*(7), 3718

[39] Paul A., Wannere C. S., Schaefer H. F., *The Journal of Physical Chemistry A*, **2004**, *108*(43), 9428

[40] Gu Y., Dong W., Luo C., Liu T., *Environmental Science & Technology*, **2016**, *50*(19), 10554

[41] Nohara K., Toma M., Kutsuna S., Takeuchi K., Ibusuki T., *Environmental Science & Technology*, **2001**, *35*(1), 114