Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

A Class of Efficient Short-Chain Fluorinated Catanionic Surfactants

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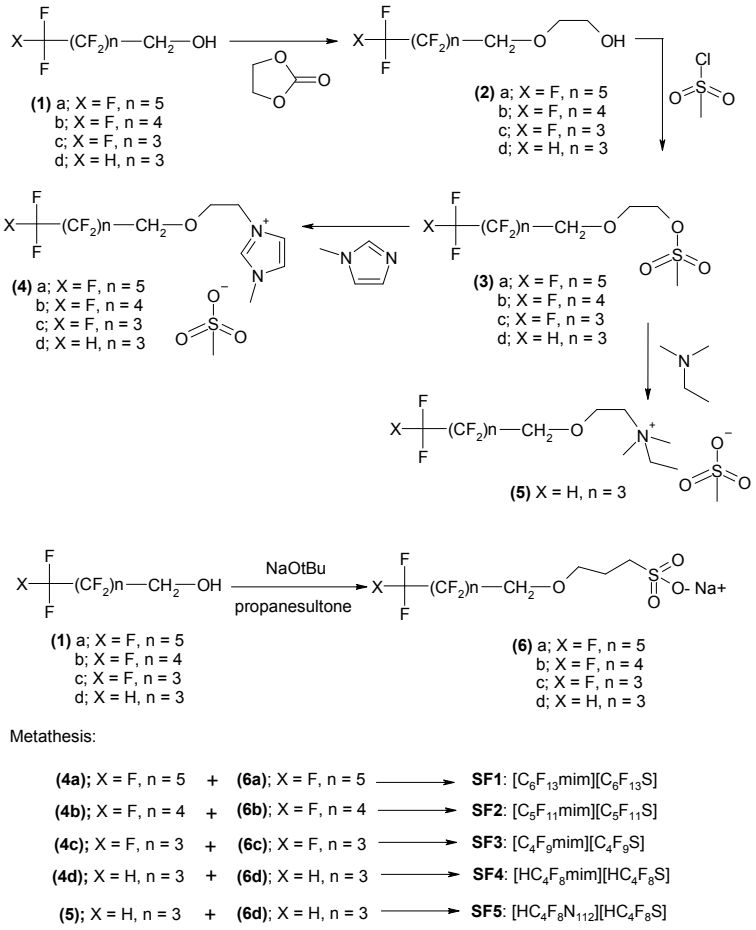
Materials and methods

Ethylene carbonate (CAS 96-49-1, Aldrich, 98%), tetraethylammonium iodide (CAS 68-05-3, Aldrich, 98%), 1H,1H-nonafluoropentan-1-ol (CAS 355-28-2, Apollo Scientific, 97%), 1H,1H-nonafluorohexan-1-ol (CAS 423-46-1, Apollo Scientific, 98%), 1H,1H-nonafluoroheptan-1-ol (CAS 375-82-6, Apollo Scientific, 97%), 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (CAS 355-80-6 , Apollo Scientific, 98%), trimethylamine (CAS 121-44-8, Sigma Aldrich, 99%), methanesulfonyl chloride (CAS 124-63-0, Aldrich, 98%), 1-methylimidazole (CAS 616-47-7, Aldrich, 99%), N,N-dimethylethylamine (CAS 598-56-1, Aldrich, 99%), sodium tert-butoxide (CAS 865-48-5, Aldrich, 97%), and 1,3-propanesultone (CAS 1120-71-4 , Aldrich, 98%) were used without further purification. Tetrahydrofuran was dried over sodium wire prior to use.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer. ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an m/z range of 50 to 1500. Samples were injected as dilute solutions in acetonitrile. All DSC scans (for melting point measurements) were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS). For each sample, three scans were run with scan rates of 5 ^{o}C min^{-1}.

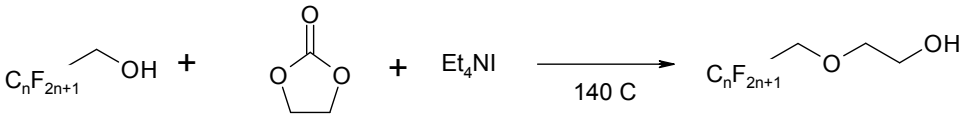
General procedures for the synthesis of fluorosurfactants (SF1-5)

All surfactants were synthesised according to the synthetic scheme given below:



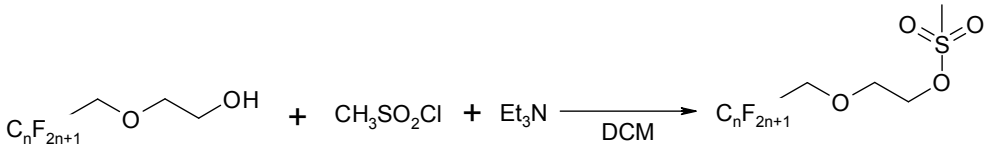
Scheme 1 ESI: Synthetic scheme for fluorosurfactants

Step 1:



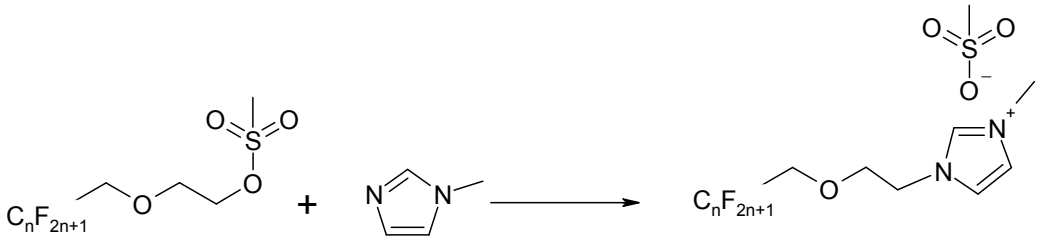
A Schlenk tube connected to a bubbler was charged with a fluorinated alcohol (1 eq.), ethylene carbonate (2 eq.) and a catalytic amount of tetraethylammonium iodide (2 mol% with respect to alcohol). The reaction mixture was stirred and heated at 140 °C for 48 h. The resulting product was poured into water and extracted into ether. The ether extract was washed twice with water and dried over anhyd. $MgSO_4$. Then, ether was removed from the extract on rotary evaporator. The crude product was distilled under high vacuum to yield the required product as the major fraction.

Step 2:



In a round bottom flask fluorinated 'oxy-alcohol' (1 eq.) and Et_3N (1.1 eq.) were added to dry dichloromethane and cooled in ice. To this solution methanesulfonyl chloride (1 eq.) was added drop-wise. The reaction mixture was allowed to warm to room temperature and stirred overnight, then poured into water and shaken in a separating funnel. DCM layer was washed with 2N HCl and dried over anhyd. $MgSO_4$. Removal of the solvent under high vacuum gave the desired product in a good yield.

Step 3:



Fluorinated sulfonate ester (1 eq.) and 1-methylimidazole (1 eq.) in DCM were heated in a screw-cap tube at 50 °C for 24h. Removal of the solvent under high vacuum yielded the desired product **(4)** in near quantitative yield.

A similar procedure was adapted for the reaction involving dimethylethylamine to yield the corresponding tetraalkylammonium methanesulfonate (**5**).

General procedure for the synthesis of sodium salts of fluorinated sulfonates

The appropriate fluorinated alcohol (1 eq.) was added at 0 °C in a suspension of sodium tert-butoxide (1.1 eq.) in dry THF. Mixture was allowed to stir for 30 min., and then a solution of 1,3-propanesultone in dry THF was added dropwise. The reaction mixture was allowed to warm up to r.t. and finally heated at 55 °C overnight. After removal of the solvent, the crude residue was purified by flash column chromatography (Hexane:AcOEt = 1:1) to obtain pure (**6**).

General procedure for cation-anion metathesis

The appropriate salt (**4** or **5**, 4 mmol) and the corresponding sodium salt of fluorinated sulfonate (**6**, 4 mmol) were homogenised with deionised water (0.3 ml) and then extracted into organic solvent. The obtained extract was dried with anhyd. $MgSO_4$. Removal of the solvent under high vacuum yielded the desired catanionic surfactants (**SF1-5**) in high yields. See Table 1 for analytical data.

Table 1 ESI: ^{1}H and ^{19}F NMR, ESMS, and melting temperature or glass transition data for the synthesised fluorosurfactants.

Surfactant	NMR data (400 MHz)	ESMS	Melting point/glass transition
SF1 $[C_6F_{13}mim][\ C_6F_{13}S]$	^{1}H(dmso-d_6): 9.12(s, 1H, Im-H), 7.72(2xs, 2H, Im-H), 4.41(t, 2H, OCH_2), 4.25(t, 2H, OCH_2), 4.10(t, 2H, OCH_2), 3.97(t, 2H, CH_2), 3.85(s, 3H, N-CH_3), 3.63(t, 2H, CH_2), 2.43(t, 2H,CH_2), 1.81(q, 2H,CH_2). ^{19}F(dmso-d_6): -80.5(m, 2xCF_3), 119.0(t, CF_2), 119.2(t, CF_2), 122.3(m, 2xCF_2), 122.8(m, 2xCF_2), 123.1(m, 2xCF_2), 126.0(m, 2xCF_2).	Cation: calc. 459.0742 Observed, 459.0633 Anion: Calc. 470.9936 Observed, 470.9934	MP: - 21^{o}C
SF2 $[C_5F_{11}mim][\ C_5F_{11}S]$	^{1}H(*dmso*-d_6): 9.18(s, 1H, Im-H), 7.78(2xs, 2H, Im-H), 4.49(t, 2H, OCH_2), 4.32(t, 2H, OCH_2), 4.17(t, 2H, OCH_2), 4.05(t, 2H, CH_2), 3.93(s, 3H, N-CH_3), 3.71(t, 2H, CH_2), 2.50(t, 2H,CH_2), 1.89(q, 2H,CH_2). ^{19}F(dmso-d_6): -80.3(m, 2xCF_3), 118.9(t, CF_2), 119.1(t, CF_2), 122.9(m, 2xCF_2), 123.2(m, 2xCF_2), 125.9(m, 2xCF_2).	Cation: calc. 409.0536 Observed, 409.0720 Anion: Calc. 420.9968 Observed, 420.9978	GT: - 3 ^{o}C
SF3 $[C_4F_9mim][\ C_4F_9S]$	^{1}H(dmso-d_6): 9.11(s, 1H, Im-H), 7.73(s, 1H, Im-H), 7.71(s, 1H, Im-H), 4.42(t, 2H, OCH_2), 4.25(t, 2H, OCH_2), 3.99(t, 2H, OCH_2), 3.98(m, 2H, CH_2), 3.86(s, 3H, N-CH_3), 3.64(t, 2H, CH_2), 2.43(t, 2H,CH_2), 1.81(t, 2H,CH_2). ^{19}F(dmso-d_6): -80.6(m, 2xCF_3), 119.2(t, CF_2), 119.4(t, CF_2), 123.9(m, CF_2), 124.0(m, CF_2), 126.2(m, 2xCF_2)	Cation: calc.359.0806 Observed, 359.0771 Anion: Calc.371.0020 Observed, 371.0013	MP: 40^{o}C
SF4 $[HC_4F_8mim][HC_4F_8S]$	^{1}H NMR (300 MHz, CDCl3) δ: 9.90 (s, 1H), 7.37 (s, 1H), 7.19 (s, 1H), 6.29 – 5.83 (m, 2H), 4.61 (t, J = 4.5 Hz, 2H), 4.14 – 3.83 (m, 9H), 3.75 (t, J = 6.3 Hz, 2H), 2.98 – 2.81 (m, 2H), 2.14 (m, 2H), 2.04 (s, 3H). ^{19}F NMR (282 MHz, CDCl3) δ: -120.39, -120.35, -125.84 (t, J = 7.4 Hz), -126.25 (t, J = 7.8 Hz), -130.41 – -130.66 (m), -130.83 – -131.10 (m), -137.72 (s), -137.88 (s).	Cation: calc. 341.0900 Observed, 341.0872 Anion: Calc.353.0094 Observed, 353.0096	GT: - 7 ^{o}C
SF5 $[HC_4F_8N_{112}][HC_4F_8S]$	^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.07 (m, 2H, C**H**F_2), 4.18 (t, 2H, OCH_2), 4.07 (t, 2H, OCH_2), 3.92 (t, 2H, OCH_2), 3.89(t, 2H), 3.73(t, 2H), 3.60(q, 2H, C**H_2**Me), 3.26(s, 6H, NMe_2), 2.86(t, 2H), 2.09(m, 2H), 1.41(t, 3H, CH_2C**H_3**). ^{19}F NMR ($CDCl_3$) δ: -119.8(CF_2), -119.9(CF_2), -125.3 (CF_2), -125.8 (CF_2), -130.0 (m, CF_2), -130.5(m, CF_2), 137.2 (m, CF_2), 137.4(m, CF_2).	Cation: calc. 332.1386 Observed, 332.1223 Anion: Calc. 353.0094 Observed, 353.0091	GT: - 8 ^{o}C

Determination of critical micelle constant (CMC) by interfacial tension and by ^{19}F NMR spectroscopy:

Measurement of interfacial tension (IFT)

Interfacial tension of aqueous surfactant solutions was measured using a Drop Shape Analysis Tensiometer Kruss DSA1 v 1.80 working in the pendant drop mode at a constant temperature of (23±0.5) °C. The needle diameter was chosen as a function of the maximisation of the scale of measurement. Brightness (contrast) was adjusted in order to minimise noise in the image acquisition and digitisation. IFT is derived from the fit of the pendant drop profile, and care was taken to ensure that the apparatus was calibrated with several solvents of known IFT in the range of interest. The drops were left to equilibrate close to the rupture point and at least three consistent measurements per solution were recorded.

^{19}F NMR spectroscopic analysis of the aggregation phenomena:

The same aqueous surfactant solutions prepared for the surface tension measurement were used for obtaining ^{19}F NMR spectra with an external standard ($LiNTf_2$) and a deuterium lock (D_2O) contained in sealed capillary tube. All NMR spectra were phase corrected manually, designating the chemical shift of CF_3 groups in $LiNTf_2$ to -80 ppm (Figure 4 in main text).

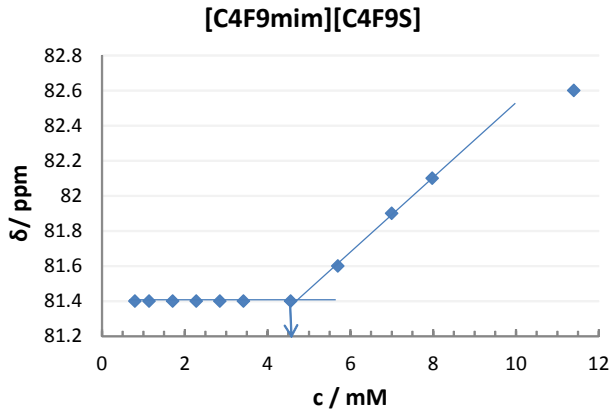


Figure 1 ESI: ^{19}F NMR chemical shifts δ of the terminal -CF_3 groups in the $[C_4F_9mim][C_4F_9S]$ as a function the surfactant concentration.

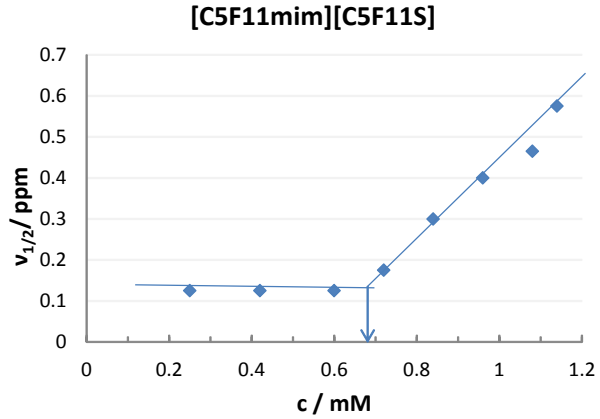


Figure 2 ESI: Half line width $\Delta\nu_{1/2}$ of ^{19}F NMR chemical shifts for the terminal $-CF_3$ group in the $[C_5F_{11}mim][C_5F_{11}S]$ as a function the surfactant concentration.

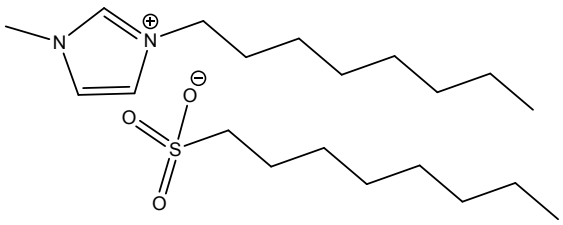


Figure 3ESI: Chemical structure of catanionic surfactant $[C_8H_{17}mim][C_8H_{17}S]$.[1]

1. M. Blesic, M. Swadzba-Kwasny, J. D. Holbrey, J. N. C. Lopes, K. R. Seddon and L. P. N. Rebelo, *Physical Chemistry Chemical Physics*, 2009, 11, 4260-4268.