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ORIGINAL ARTICLE

Synthesis and surface-active properties of fluorinated cyclic PEGyl succinate derivatives

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Abstract Equimolar reaction of PEG with maleic anhydride in favoring conditions to cyclization is described. The obtained cyclic compounds were submitted to radical addition of 2-*F*-alkylethanethiol to furnish fluorinated loops. Amphiphilic properties of the latter were investigated by measuring their surface tension and critical micellar concentration CMC. These new amphiphilic compounds may exhibit some interesting interactions with appropriate cations at the surface cells.

Keywords Crown ethers · Fluorine · Surfactant

Introduction

Crown ethers [1, 2] and derivatives are known to play a vital role in many processes of interest in both fundamental and applied sciences. Due to their selective cationic binding affinities and their adjustable hydrophobicities, crown ethers are used in analytical separations, the recovery or removal specific species, ion selective electrodes and biological mimics [3–7]. Succinate crown ethers [8] have been used for the preparation of large cyclic ether–esters using ring-chain reactions [9], these cyclic oligomers of such ether–esters should demonstrate complexing behavior with metal ions in a similar way to that of crown ethers [10] and they could be of use in ion separation techniques, e.g., in waste-water decontamination [11].

Addition of lipophilic long-chain alkyl group to crown ether, results in the formation of amphiphilic derivatives, forming micelles or complex supramolecular structures in water [12–17].

Here we report the synthesis of some *F*-alkylated cyclic polyethylene glycol succinate and we evaluate their surface properties via surface tension measurements.

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Experimental

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker AC 300 at 300, 75 and 282 MHz, respectively. TMS was used as standard reference for ^{1}H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR. The IR spectra were recorded on a Brüker IFS 66V/S spectrometer. Surface tension measurements (γ_s) were performed by Krüss K9 digital tensiometer, the solution contained 0.1% (w/w) of amphiphile in water and was measured at 25 °C. High resolution mass spectra (HRMS) were taken on AMD-604 apparatus.

Preparation of Polyethyleneglycol Maleate **1**: general procedure

A solution of maleic anhydride (0.981 g, 10 mmol), polyethylene glycol (10 mmol) and HOTs (0.15 g) in a 20 mL of dioxane and 60 mL of toluene was refluxed with azeotropic removal of water, using a Dean–Stark apparatus. After 72 h (TLC CH_2Cl_2/CH_3OH: 98/2) of stirring at reflux, the mixture was concentrated under vacuum and the crude compound **1** was purified on column chromatography.

*Triethyleneglycol Maleate (**1a**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C=O} = 1725$, $\nu_{C=C} = 1638$. ^1H NMR ($CDCl_3$): δ(ppm) 3.65–3.77 (m, 8H, $CH_2(CH_2OCH_2)_2CH_2$), 4.37 (m, 4H, $2CO_2CH_2$), 6.27 (s, 2H, CH=CH). ^{13}C NMR ($CDCl_3$): δ(ppm) 63.70, 68.80 (s, 4C, $CH_2(CH_2OCH_2)_2CH_2$), 68.82 (s, 2C, $2CO_2CH_2$), 129.59 (s, 2C, CH=CH), 165.09 (s, 2C, $2CO_2$). HRMS (EI) calculated for $C_{10}H_{14}O_6$: 230.0790, found: 230.0793.

*Tetraethyleneglycol Maleate (**1b**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C=O} = 1726$, $\nu_{C=C} = 1637$. ^1H NMR ($CDCl_3$): δ(ppm) 3.65–3.78 (m, 12H, $CH_2(CH_2OCH_2)_3CH_2$), 4.36 (m, 4H, $2CO_2CH_2$), 6.27 (s, 2H, CH=CH). ^{13}C NMR ($CDCl_3$): δ(ppm) 64.38, 67.04, 70.67 (s, 6C, $CH_2(CH_2OCH_2)_3CH_2$), 71.63. (s, 2C, $2CO_2CH_2$), 129.59 (s, 2C, CH=CH), 165.10 (s, 2C, $2CO_2$ HRMS (EI) calculated for $C_{12}H_{18}O_7$: 274.1053, found: 274.1057.

*Pentaethyleneglycol Maleate (**1c**)*

Eluent of purification CH_2Cl_2/CH_3OH: 96/4 IR (cm^{-1}): $\nu_{C=O} = 1728$, $\nu_{C=C} = 1640$. ^1H NMR ($CDCl_3$): δ(ppm) 3.58–3.75 (m, 16H, $CH_2(CH_2OCH_2)_4CH_2$), 4.34 (m, 4H, $2CO_2CH_2$), 6.29 (s, 2H, CH=CH). ^{13}C NMR ($CDCl_3$): δ(ppm) 64.30, 68.79, 70.54, 70.57, (s, 8C, $CH_2(CH_2OCH_2)_4CH_2$), 70.87 (s, 2C, $2CO_2CH_2$), 129.87 (s, 2C, CH=CH), 165.17 (s, 2C, $2CO_2$). HRMS (EI) calculated for $C_{14}H_{22}O_8$: 318.1315, found: 318.1311.

*Hexaethyleneglycol Maleate (**1d**)*

Eluent of purification CH_2Cl_2/CH_3OH: 96/4 IR (cm^{-1}): $\nu_{C=O} = 1728$, $\nu_{C=C} = 1637$. ^1H NMR ($CDCl_3$): δ(ppm) 3.61–3.76 (s, 20H, $CH_2(CH_2OCH_2)_5CH_2$), 4.38 (m, 4H, $2CO_2CH_2$), 6.31 (s, 2H, CH=CH). ^{13}C NMR ($CDCl_3$): δ(ppm) 64.40, 68.65, 68.80, 70.57, 70.60 (s, 10C, $CH_2(CH_2OCH_2)_5CH_2$), 70.85 (s, 2C, $2CO_2CH_2$), 129.70 (s, 2C, CH=CH), 165.15 (s, 2C, $2CO_2$). HRMS (EI) calculated for $C_{16}H_{26}O_9$: 362.1577, found: 362.1580.

Preparation of Polyethyleneglycol 2-(Alkylsulfanyl) Succinate **2**: general procedure

In a 25 mL round bottomed flask was placed under N_2 atmosphere a mixture of maleate crown ether **1** (2 mmol), thiol (2.2 mmol) and AIBN (0.131 g, 0.8 mmol). The mixture was then stirred at 80 °C for 6 h (TLC CH_2Cl_2/CH_3OH: 97/3). After cooling to room temperature, the obtained compound was purified on column chromatography.

*Triethyleneglycol 2-(Octylsulfanyl) Succinate (**2a**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C=O} = 1737$. ^1H NMR ($CDCl_3$): δ(ppm) 0.89 (t, 3H, CH_3), 1.27 (s, 10H, $CH_3(CH_2)_5$), 1.60 (m, 2H, CH_2CH_2S), 2.68 (m, 2H, CH_2S), 2.68–3.10 (m, 2H, CO_2CH_2CH), 3.57–3.75 (m, 8H, $CH_2(CH_2OCH_2)_2CH_2$), 3.73 (m, 1H, $SCHCO_2$), 4.05–4.35 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 14.08 (s, 1C, CH_3), 28.80 (s, 1C, CH_3CH_2), 29.11 (s, 1C, $CH_3CH_2CH_2$), 29.12 (s, 1C, $CH_3(CH_2)_2CH_2$), 29.18 (s, 1C, $CH_3(CH_2)_3CH_2$), 29.31 (s, 1C, $CH_2CH_2CH_2S$), 29.68 (s, 1C, CH_2CH_2S), 22.62 (s, 1C, CO_2CH_2CH), 36.88 (s, 1C, CH_2S), 41.72 (s, 1C, $SCHCO_2$), 63.86, 64.52, 68.71, 68.91 (s, 4C, $CH_2(CH_2OCH_2)_2CH_2$), 69.49, 69.81 (s, 2C, $2CO_2CH_2$), 169.81, 170.81 (s, 2C, $2CO_2$). HRMS (ESI) calculated for: $(C_{18}H_{32}O_6S,Na)^+$: calculated: 399.1811, found: 399.1817.

*Triethyleneglycol 2-[2-(F-hexyl)ethylsulfanyl] Succinate (**2a'**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C-F} = 1143$, $\nu_{C=O} = 1737$. ^1H NMR ($CDCl_3$) δ(ppm) 2.41 (m, 2H, CF_2CH_2), 2.91 (m, 2H, CH_2S), 2.81–3.11(m, 2H, CO_2CH_2CH), 3.57–3.75 (m, 8H, $CH_2(CH_2OCH_2)_2CH_2$), 3.75 (m, 1H, $SCHCO_2$), 4.20–4.50 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$) δ(ppm) 22.59 (s, 1C, CO_2CH_2CH), 31.72 (t, 1C, CF_2CH_2, $^2JCF = 21.810$ Hz), 36.49 (s, 1C, CH_2S), 41.72 (s, 1C, $SCHCO_2$), 63.86, 64.52, 68.71, 68.91 (s, 4C, $CH_2(CH_2OCH_2)_2CH_2$), 69.49, 69.81, (s, 2C, $2CO_2CH_2$), 169.85, 170.82 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$) δ(ppm) −80.78 (m, 3F, CF_3), −115.29 (m, 2F, $CF_{2\alpha}$), −122.84 (m, 2F, $CF_{2\beta}$), −123.82 (m, 2F, $CF_{2\gamma}$), −124.29 (m, 2F, $CF_{2\delta}$), −127.13 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{18}H_{19}F_{13}O_6S,Na)^+$: calculated: 633.0587, found: 633.0593.

*Triethyleneglycol 2-[2-(F-octyl)ethylsulfanyl] Succinate (**2a"**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C-F} = 1139$, $\nu_{C=O} = 1735$. ^1H NMR ($CDCl_3$): δ(ppm) 2.44 (m, 2H, CF_2CH_2), 2.93 (m, 2H, CH_2S), 2.71–3.11(m, 2H, CH_2CH), 3.67–3.74 (m, 8H, $CH_2(CH_2OCH_2)_2CH_2$), 3.75 (m, 1H, $SCHCO_2$), 4.25–4.45 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 22.54 (s, 1C, $CHCH_2$), 31.72 (t, 1C, CF_2CH_2, $^2JCF = 22.037$ Hz), 36.49 (s, 1C, CH_2S), 41.72 (s, 1C, $SCHCO_2$), 63.86, 64.52, 68.70, 68.90 (s, 4C, $CH_2(CH_2OCH_2)_2CH_2$), 69.49, 69.81 (s, 2C, $2CO_2CH_2$), 169.85, 170.82 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm)

−81.68 (m, 3F, CF_3), −115.23 (m, 2F, $CF_{2\alpha}$), −122.61 (m, 2F, $CF_{2\beta}$), −122.65 (m, 4F, $2CF_{2\gamma}$), −123.64 (m, 2F, $CF_{2\delta}$), −123.26 (m, 2F, $CF_{2\xi}$), −127.05 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{20}H_{19}F_{17}O_6S,Na)^+$: calculated: 733.0528, found: 733.0535.

*Tetraethyleneglycol 2-(Octylsulfanyl) Succinate (**2b**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C=O} = 1732$. ^1H NMR ($CDCl_3$): δ(ppm) 0.89 (t, 3H, CH_3), 1.27 (s, 10H, $CH_3(CH_2)_5$), 1.60 (m, 2H, CH_2CH_2S), 2.68 (m, 2H, CH_2S), 2.68–3.10 (m, 2H, CO_2CH_2CH), 3.62–3.78 (m, 12H, $CH_2(CH_2OCH_2)_3CH_2$), 3.73 (m, 1H, $SCHCO_2$), 4.06–4.40 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 14.08 (s, 1C, CH_3), 28.80 (s, 1C, CH_3CH_2), 29.11 (s, 1C, $CH_3CH_2CH_2$), 29.12 (s, 1C, $CH_3(CH_2)_2CH_2$), 29.18 (s, 1C, $CH_3(CH_2)_3CH_2$), 29.31 (s, 1C, $CH_2CH_2CH_2S$), 29.68 (s, 1C, CH_2CH_2S), 31.63 (s, 1C, CH_2S), 22.62 (s, 1C, CO_2CH_2CH), 41.72 (s, 1C, $SCHCO_2$), 64.26, 64.94, 68.81, 68.95, 70.59, 70.72 (s, 6C, $CH_2(CH_2OCH_2)_3CH_2$), 70.02, 70.90 (s, 2C, $2CO_2CH_2$) 170.24, 171.20 (s, 2C, $2CO_2$). HRMS (ESI) calculated for: $(C_{20}H_{36}O_7S,Na)^+$: calculated: 443.2074, found: 443.2081.

*Tetraethyleneglycol 2-[2-(F-hexyl)ethylsulfanyl] Succinate (**2b'**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C-F} = 1138$, $\nu_{C=O} = 1732$. ^1H NMR ($CDCl_3$): δ(ppm) 2.41 (m, 2H, CF_2CH_2), 2.94 (m, 2H, CH_2S), 2.77–3.15 (m, 2H, CO_2CH_2CH), 3.62–3.78 (s, 12H, $CH_2(CH_2OCH_2)_3CH_2$), 3.78 (m, 1H, $SCHCO_2$), 4.18–4.55 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 22.52 (s, 1C, CO_2CH_2CH), 31.68 (t, 1C, CF_2CH_2, $^2JCF = 22.037$ Hz), 36.49 (s, 1C, CH_2S) 41.93 (s, 1C, $SCHCO_2$), 64.26, 64.94, 68.81, 68.95, 70.59, 70.72 (s, 6C, $CH_2(CH_2OCH_2)_3CH_2$), 71.02, 70.90 (s, 2C, $2CO_2CH_2$), 169.85, 170.82 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.69 (m, 3F, CF_3), −115.12 (m, 2F, $CF_{2\alpha}$), −122.79 (m, 2F, $CF_{2\beta}$), −123.78 (m, 2F, $CF_{2\gamma}$), −124.25 (m, 2F, $CF_{2\delta}$), −127.04 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{20}H_{23}F_{13}O_7S,Na)^+$: calculated: 677.0849, found: 677.0843.

*Tetraethyleneglycol 2-[2-(F-octyl)ethylsulfanyl] Succinate (**2b"**)*

Eluent of purification CH_2Cl_2/CH_3OH: 98/2 IR (cm^{-1}): $\nu_{C-F} = 1136$, $\nu_{C=O} = 1737$. ^1H NMR ($CDCl_3$): δ(ppm) 2.42 (m, 2H, CF_2CH_2), 2.95 (m, 2H, CH_2S), 2.67–3.19 (m, 2H, CO_2CH_2CH), 3.65–6.78 (s, 12H, $CH_2(CH_2OCH_2)_3CH_2$), 3.78 (m, 1H, $SCHCO_2$), 4.25–4.45 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 22.60 (s, 1C, CO_2CH_2CH), 31.71 (t, 1C, CF_2CH_2, $^2JCF = 22.565$ Hz), 36.59 (s, 1C, CH_2S), 41.93 (s, C, $SCHCO_2$), 64.30, 64.97, 68.84, 68.97, 70.63, 70.76 (s, 6C, $CH_2(CH_2OCH_2)_3CH_2$), 71.04, 70.92 (s, 2C, $2CO_2CH_2$), 169.91, 170.75 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.74 (m, 3F, CF_3), −115.29 (m, 2F, $CF_{2\alpha}$), −122.82 (m, 2F, $CF_{2\beta}$), −122.88 (m, 4F, $2CF_{2\gamma}$), −123.68 (m, 2F, $CF_{2\delta}$), −124.28 (m, 2F, $CF_{2\xi}$), −127.07 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{22}H_{23}F_{17}O_7S,Na)^+$: calculated: 777.0785, found: 777.0791.

*Pentaethyleneglycol 2-(Octylsulfanyl) Succinate (**2c**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C=O} = 1735$. ^1H NMR ($CDCl_3$): δ(ppm) 0.89 (t, 3H, CH_3), 1.27 (s, 10H, $CH_3(CH_2)_5$), 1.60 (m, 2H, CH_2CH_2S), 2.68 (m, 2H, CH_2S), 2.68–3.10 (m, 2H, CO_2CH_2CH), 3.62–3.65 (m, 16H, $CH_2(CH_2OCH_2)_4CH_2$), 3.73 (m, 1H, $SCHCO_2$), 4.20–4.45 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 14.08 (s, 1C, CH_3), 28.82 (s, 1C, CH_3CH_2), 29.14 (s, 1C, $CH_3CH_2CH_2$), 29.15 (s, 1C, $CH_3(CH_2)_2CH_2$), 29.18 (s, 1C, $CH_3(CH2)_3CH_2$), 29.31 (s, 1C, $CH_2CH_2CH_2S$), 29.68 (s, 1C, CH_2CH_2S), 36.88 (s, 1C, CH_2S), 22.64 (s, 1C, CO_2CH_2CH), 41.72 (s, 1C, $SCHCO_2$), 64.22, 64.82, 68.84, 68.78, 70.11, 70.60, 70.65, 70.83 (s, 8C, $CH_2(CH_2OCH_2)_4CH_2$), 70.92, 71.07 (s, 2C, $2CO_2CH_2$), 170.40, 171.64 (s, 2C, $2CO_2$). HRMS (ESI) calculated for: $(C_{22}H_{40}O_8S,Na)^+$: calculated: 487.2336, found: 487.2342.

*Pentaethyleneglycol 2-[2-(F-hexyl)ethylsulfanyl] Succinate (**2c'**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C-F} = 1138$, $\nu_{C=O} = 1735$. ^1H NMR ($CDCl_3$): δ(ppm) 2.43 (m, 2H, CF_2CH_2), 2.93 (m, 2H, CH_2S), 2.75–3.12 (m, 2H, CH_2CH), 3.62–3.65 (m, 16H, $CH_2(CH_2OCH_2)_4CH_2$), 3.76 (m, 1H, $SCHCO_2$), 4.20–4.45 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 22.67 (s, 1C, $CHCH_2$), 31.90 (t, 1C, CF_2CH_2, $^2JCF = 21.659$ Hz), 36.41 (s, 1C, CH_2S), 42.40 (s, 1C, $SCHCO_2$), 64.22, 64.82, 68.84, 68.78, 70.11, 70.60, 70.65, 70.83 (s, 8C, $CH_2(CH_2OCH_2)_4CH_2$), 70.92, 71.07 (s, 2C, $2CO_2CH_2$), 169.89, 170.97 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.79 (m, 3F, CF_3), −115.23 (m, 2F, $CF_{2\alpha}$), −122.85 (m, 2F, $CF_{2\beta}$), −123.83 (m, 2F, $CF_{2\gamma}$), −124.31 (m, 2F, $CF_{2\delta}$), −127.11(m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{22}H_{27}F_{13}O_8S,Na)^+$: calculated: 721.1111, found: 721.1117.

*Pentaethyleneglycol 2-[2-(F-octyl)ethylsulfanyl] Succinate (**2c"**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C-F} = 1137$, $\nu_{C=O} = 1733$. ^1H NMR ($CDCl_3$): δ(ppm) 2.45 (m, 2H, CF_2CH_2), 2.89 (m, 2H, CH_2S), 2.69–3.11 (m,

2H, CO_2CH_2CH), 3.62–3.65 (m, 16H, $CH_2(CH_2OCH_2)_4CH_2$), 3.76 (m, 1H, $SCHCO_2$), 4.20–4.40 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 23.31 (s, 1C, CO_2CH_2CH), 31.56 (t, 1C, CF_2CH_2, $^2JCF = 21.886$ Hz), 36.24 (s, 1C, CH_2S), 42.24 (s, 1C, $SCHCO_2$), 64.07, 64.67, 68.60, 68.80, 70.43, 70.48, 70.66, 70.76 (s, 8C, $CH_2(CH_2OCH_2)_4CH_2$), 70.91, 71.58 (s, 2C, $2CO_2CH_2$), 169.71, 170.78 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.73 (m, 3F, CF_3), −115.26 (m, 2F, $CF_{2\alpha}$), −122.79 (m, 2F, $CF_{2\beta}$), −122.74 (m, 4F, $2CF_{2\gamma}$), −123.69 (m, 2F, $CF_{2\delta}$), −124.25 (m, 2F, $CF_{2\xi}$), −127.05 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{24}H_{27}F_{17}O_8S,Na)^+$: calculated: 821.1047, found: 821.1053.

*Hexaethyleneglycol 2-(Octylsulfanyl) Succinate (**2d**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C=O} = 1736$. ^1H NMR ($CDCl_3$): δ(ppm) 0.89 (t, 3H, CH_3), 1.27 (s, 10H, $CH_3(CH_2)_5$), 1.60 (m, 2H, CH_2CH_2S), 2.68 (m, 2H, CH_2S), 2.68–3.10 (m, 2H, CO_2CH_2CH), 3.62–3.71 (m, 20H, $CH_2(CH_2OCH_2)_5CH_2$), 3.73 (m, 1H, $SCHCO_2$), 4.08–4.40 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 14.08 (s, 1C, CH_3), 28.82 (s, 1C, CH_3CH_2), 29.14 (s, 1C, $CH_3CH_2CH_2$), 29.16 (s, 1C, $CH_3(CH_2)_2CH_2$), 29.18 (s, 1C, $CH_3(CH_2)_3CH_2$), 29.31 (s, 1C, $CH_2CH_2CH_2S$), 29.68 (s, 1C, CH_2CH_2S), 36.88 (s, 1C, CH_2S), 22.72 (s, 1C, CO_2CH_2CH), 41.72 (s, 1C, $SCHCO_2$), 70.87, 70.90 (s, 2C, $2CO_2CH_2$), 64.45, 64.73, 64.99, 68.90, 68.98, 70.64, 70.75, 70.78, 70.79, 70.80 (s, 10C, $CH_2(CH_2OCH_2)_5CH_2$), 70.87, 70.90 (s, 2C, $2CO_2CH_2$), 170.80, 171.46 (s, 2C, $2CO_2$). HRMS (ESI) calculated for: $(C_{24}H_{44}O_9S,Na)^+$: calculated: 531.2598, found: 531.2592.

*Hexaethyleneglycol 2-[2-(F-hexyl)ethylsulfanyl] Succinate (**2d'**)*

Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}) $\nu_{C-F} = 1137$, $\nu_{C=O} = 1736$. ^1H NMR ($CDCl_3$): δ(ppm) 2.42 (m, 2H, CF_2CH_2), 2.94 (m, 2H, CH_2S), 2.74–3.11 (m, 2H, CO_2CH_2CH), 3.62–3.71 (m, 20H, $CH_2(CH_2OCH_2)_5CH_2$), 3.78 (m, 1H, $SCHCO_2$), 4.20–4.40 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 22.60 (s, 1C, CH_2), 31.68 (t, 1C, CF_2CH_2, $^2JCF = 21.735$ Hz), 22.66 (s, 1C, CO_2CH_2CH), 36.32 (s, 1C, CH_2S), 42.25 (s, 1C, $SCHCO_2$), 64.45, 64.73, 64.99, 68.90, 68.98, 70.64, 70.75, 70.78, 70.79, 70.84 (s, 10C, $CH_2(CH_2OCH_2)_5CH_2$), 70.87, 70.90 (s, 2C, $2CO_2CH_2$), 169.97, 170.96 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.73 (m, 3F, CF_3), −115.21 (m, 2F, $CF_{2\alpha}$), −122.84 (m, 2F, $CF_{2\beta}$), −123.81 (m, 2F, $CF_{2\gamma}$), −124.29 (m, 2F, $CF_{2\delta}$), −127.09 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{24}H_{31}F_{13}O_9S,Na)^+$: calculated: 765.1373, found: 765.1380.

*Hexaethyleneglycol 2-[2-(F-octyl)ethylsulfanyl] Succinate (**2d"**)*

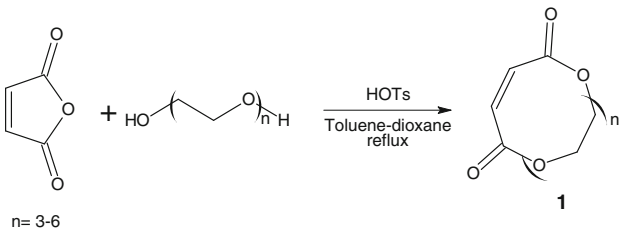
Eluent of purification CH_2Cl_2/CH_3OH: 97/3 IR (cm^{-1}): $\nu_{C-F} = 1134$, $\nu_{C=O} = 1733$. ^1H NMR ($CDCl_3$): δ(ppm) 2.49 (m, 2H, CF_2CH_2), 2.93 (m, 2H, CH_2S), 2.79–3.10 (m, 2H, CO_2CH_2CH), 3.62–3.75 (m, 20H, $CH_2(CH_2OCH_2)_5CH_2$), 3.78 (m, 1H, $SCHCO_2$), 4.25–4.35 (m, 4H, $2CO_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) 23.36 (s, 1C, CO_2CH_2CH), 31.73 (t, 1C, CF_2CH_2, $^2JCF = 21.961$ Hz), 36.36 (s, 1C, CH_2S), 42.29 (s, 1C, $SCHCO_2$), 64.45, 64.63, 65.00, 68.91, 69.02, 70.78, 70.81, 70.86, 70.88, 70.91 (s, 10C, $CH_2(CH_2OCH_2)_5CH_2$), 71.16, 71.28 (s, 2C, $2CO_2CH_2$), 169.97, 170.97 (s, 2C, $2CO_2$). ^{19}F NMR ($CFCl_3$): δ(ppm) −81.75 (m, 3F, CF_3), −115.29 (m, 2F, $CF_{2\alpha}$), −122.81 (m, 2F, $CF_{2\beta}$), −122.76 (m, 4F, $2CF_{2\gamma}$), −123.70 (m, 2F, $CF_{2\delta}$), −124.27 (m, 2F, $CF_{2\xi}$), −127.11 (m, 2F, $CF_{2\omega}$). HRMS (ESI) calculated for: $(C_{26}H_{31}F_{17}O_9S,Na)^+$: calculated: 865.1309, found: 865.1304.

Results and discussion

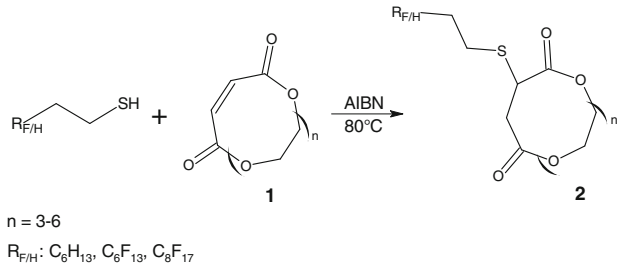
The equimolar reaction of maleic anhydride with polyethylene glycol in dilute solution of 1,4-dioxane-toluene led to the corresponding cyclic polyethylene glycol maleate **1** (Scheme 1) in moderate to acceptable yields (Table 1).

Maleate crown ether yields depended directly upon the number of ethylene oxide group (CH_2CH_2O); these yields decreased with the increase of *n*.

The solvent free radical addition of 2-*F*-alkylethanethiol to compound **1** afforded the fluorinated surfactant **2**



Scheme 1 Cyclic polyethylene glycol maleate **1** preparation



Scheme 2 Fluorinated cyclic PEGyl succinate derivatives **2**

Table 1 Cyclic PEG maleate **1** prepared

Crown ether **1**	n	Yield (%)
1a	3	52
1b	4	44
1c	5	37
1d	6	30

Table 2 Surfactants **2** prepared

PEG succinate **2**	*n*	$R_{F/H}$	Yield (%)	γ_s^a (mN m^{-1}) ± SD
2a	3	C_6H_{13}	94	32.10 ± 0.04
2b	4	C_6H_{13}	91	32.88 ± 0.03
2c	5	C_6H_{13}	90	33.52 ± 0.03
2d	6	C_6H_{13}	88	34.16 ± 0.02
2a'	3	C_6F_{13}	92	20.12 ± 0.04
2b'	4	C_6F_{13}	90	20.92 ± 0.04
2c'	5	C_6F_{13}	89	21.22 ± 0.03
2d'	6	C_6F_{13}	86	22.18 ± 0.03
2a"	3	C_8F_{17}	89	17.90 ± 0.06
2b"	4	C_8F_{17}	88	19.58 ± 0.05
2c"	5	C_8F_{17}	86	20.34 ± 0.04
2d"	6	C_8F_{17}	85	20.80 ± 0.04

[a] Aqueous 0.1% (w/w) solution at 25 °C

(Scheme 2) in high yields (Table 2) [18]. In the same way, hexane-thiol gave the corresponding hydrocarbon derivative **2**.

Values of surface tension γ_s of surfactants **2** aqueous solutions are given. Compared to hydrocarbon analogous, the fluorinated surfactants **2a'-d'** exhibit better surface activity.

Curves showing the variation of surface tension as a function of amphiphilic concentration of **2c** and **2c'** are displayed in Fig. 1. Each curve shows a break

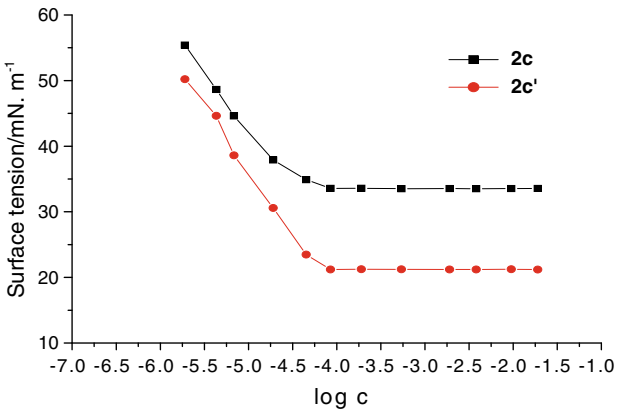


Fig. 1 Plot of surface tension as a function of the logarithm of the concentration (in mol L^{-1}) of surfactants **2c** and **2c'** in water at 25 °C

corresponding to a CMC around $6.3.10^{-5}$ mol L^{-1}, whatever the type of chain. Therefore, the micellization process occurs at very low concentrations.

The dependence of the surface activity on the structure of amphiphiles **2** has been studied taking into consideration the length of the alkyl chain and the size of the macrocyclic. Table 2 shows that surface tension values decrease with the increasing of alkyl chaine length [19–21]. This observation is in agreement with Tanford theory [22].

However, surface tension values increase with the increasing of the macrocyclic size. Actually, in the larger macrocyclic size, the number of ethylene oxide, and consequently the HLB (Hydrophile–Lipophile Balance) is higher. It is well known that the higher the HLB value the more water soluble surfactant is. So, the enhanced water solubility of the surfactant lowers the surface activity of this latter [21, 23].

Conclusions

In this work a novel crown ethers amphiphiles were synthesized and characterized. The dependence of the surface activity of these new amphiphiles in aqueous solutions has been studied according to the type and length of alkyl chain and the size of the macrocyclic. The host-guest properties, especially the alkali metal compelling abilities and phase transfer catalysis experiments of the new crown ethers derivatives, are currently under investigation.

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