# One *F*-octyl versus two *F*-butyl chains in surfactant aggregation behavior

A. Damé[a,b], , E. Taffin de Givenchy[a], S. Y. Dieng[b], M. Oumar[b] F. Guittard[a]

[a] Université de Nice-Sophia Antipolis, Laboratoire de Chimie des Matériaux Organiques et Métalliques, CMOM, équipe de Chimie Organique aux interfaces, Parc Valrose, 06108 Nice Cedex 2, France
[b] Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal

**Precursor monotailed 4** : **x = 4 and n =1** ; yellowish liquid ; yield : 72% ; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^1$H NMR (600MHz, $CDCl_3$), δ (ppm): 1.9–2.3 [4H, m, $C_4F_9$-**$(CH_2)_2$**-]; 3.31 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_3)_2$]; 3.7 [6H, s, -CH-$(CO_2$**$CH_3$**$)_2$] ; $^{19}$F NMR (600MHz, $CDCl_3$) δ (ppm): -81.78 (3F, t, $CF_3$), -115.20 (2F, q, $(CF_2)_\alpha$), -125.01 (2F, s, $(CF_2)_\beta$), -126.70 (2F, s, $(CF_2)_\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$…

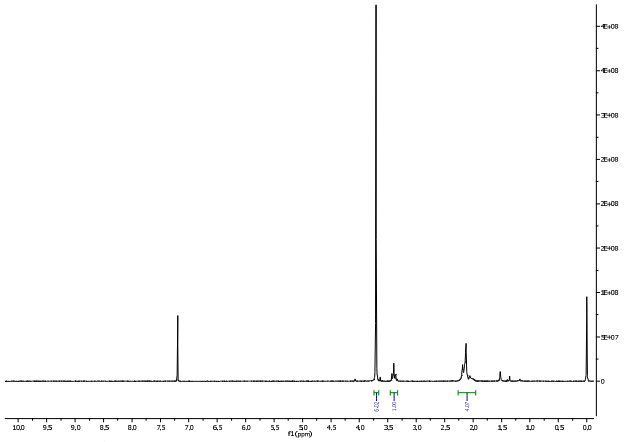

Figure 1: $^1$H NMR spectra of compound 4

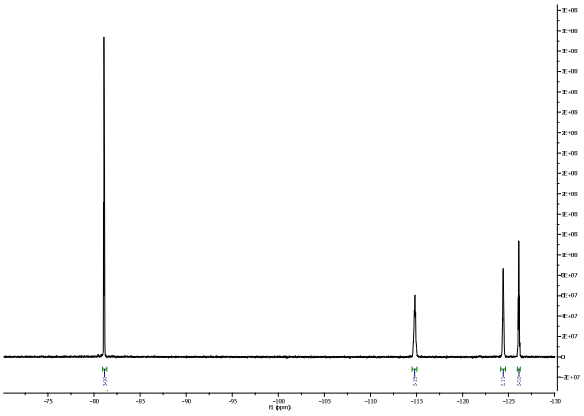

Figure 2: $^{19}$F NMR spectra of compound 4

**Precursor monotailed 5: x = 4 and n = 2**; yellowish liquid ; yield : 76% ; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^1$H NMR (600MHz, $CDCl_3$), δ (ppm): 1.2 [6H, t, -CH-$(CO_2CH_2$**$CH_3$**$)_2$]; 1.9-2.4 [4H, m, $C_4F_9$-**$(CH_2)_2$**-]; 3.35 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_2CH_3)_2$]; 4.3 [4H, q, -CH-$(CO_2$**$CH_2$**$CH_3)_2$]; $^{19}$F NMR (600MHz, $CDCl_3$) δ (ppm): -81.78 (3F, t, $CF_3$), -115.30 (2F, q, $(CF_2)_\alpha$), -125.01 (2F, s, $(CF_2)_\beta$), -126.70 (2F, s, $(CF_2)_\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$

**Precursor monotailed 6: x = 6 and n = 1**; yellowish liquid ; yield : 74.3; IR ($cm^{-1}$) : 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^1$H NMR (600MHz, $CDCl_3$), δ (ppm): 1.9–2.3 [4H, m, $C_4F_9$-**$(CH_2)_2$**-]; 3.31 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_3)_2$]; 3.7 [6H, s, -CH-$(CO_2$**$CH_3$**$)_2$] ; $^{19}$F NMR (600MHz, $CDCl_3$) δ (ppm) : -81.2 (3F, t, CF3), -114.30 (2F, q, $(CF_2)_\alpha$), -121.6 (2F, s, $(CF_{2n})_\beta$), -122.6, (2F, s, $(CF_2)\delta$), -123.3 (2F, s, $(CF_2)\gamma$), -125.9 (2F, s, $(CF_2)\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…

**Precursor monotailed 7: x = 6 and n = 2**; yellowish liquid ; yield : 77.1% ; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^1$H NMR (600MHz, $CDCl_3$), δ (ppm): 1.2 [6H, t, -CH-$(CO_2CH_2$**$CH_3$**$)_2$]; 1.9-2.4 [4H, m, $C_4F_9$-**$(CH_2)_2$**-]; 3.35 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_2CH_3)_2$]; 4.3 [4H, q, -CH-$(CO_2$**$CH_2$**$CH_3)_2$]; $^{19}$F NMR (600MHz, $CDCl_3$) δ (ppm) : -81.2 (3F, t, CF3), -114.30 (2F, q, $(CF_2)_\alpha$), -121.6 (2F, s, $(CF_{2n})_\beta$), -122.6, (2F, s, $(CF_2)\delta$), -123.3 (2F, s, $(CF_2)\gamma$), -125.9 (2F, s, $(CF_2)\omega$)
for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…

**Precursor monotailed 8: x = 8 and n = 1**; white solid; yield: 78.8; IR ($cm^{-1}$) : 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^1$H NMR (600MHz, $CDCl_3$), δ (ppm): 1.9–2.3 [4H, m, $C_4F_9$-**$(CH_2)_2$**-]; 3.31 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_3)_2$]; 3.7 [6H, s, -CH-$(CO_2$**$CH_3$**$)_2$] ; $^{19}$F NMR (600MHz, $CD_3OD$) δ (ppm): -81.9 (3F), -115.2 (2F), -122.4 (6F), -123.4, (2F), -123.5 à -124.20 (2F), -127.03 (2F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…

**Precursor monotailed <u>9</u>: x = 8 and n = 2;** yellowish liquid ; yield : 70.5% ; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1730 et 1740 ($\nu_{C=O)}$, 1050 ($\nu_{C-O)}$ ; $^{1}H$ NMR (600MHz, $CDCl_3$), δ (ppm): 1.2 [6H, t, -CH-$(CO_2CH_2\mathbf{CH_3})_2$]; 1.9-2.4 [4H, m, $C_4F_9$-$\mathbf{(CH_2)_2}$-]; 3.35 [1H, t, -$(CH_2)$-**CH**-$(CO_2CH_2.CH_3)_2$]; 4.3 [4H, q, -CH-$(CO_2\mathbf{CH_2}CH_3)_2$]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.9 (3F), -115.2 (2F), -122.4 (6F), -123.4, (2F), -123.5 à -124.20 (2F), -127.03 (2F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…

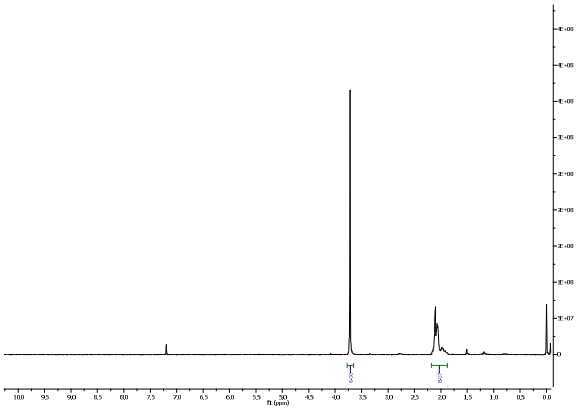

Figure 3: $^{1}H$ NMR spectra of compound 13

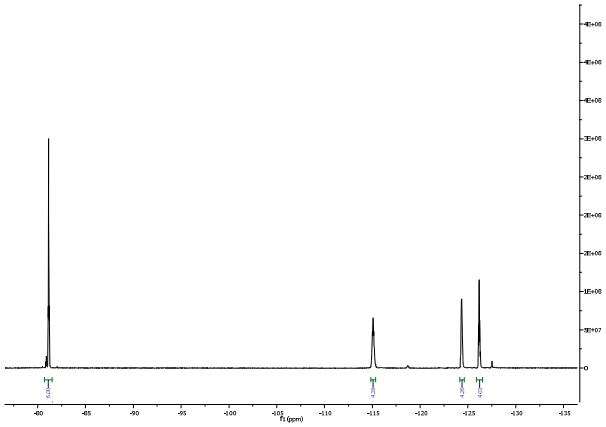

Figure 4: $^{19}F$ NMR spectra of compound 13

**Precursor detailed <u>13</u>**: **x=z=4 and n = 1**; colorless liquid; yield: 43.9%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1735 et 1740 ($\nu_{C=O);}$ 1050 ($\nu_{C-O)}$; $^{1}H$ NMR (600MHz, $CDCl_3$); δ (ppm): 1.8-2.25 [8H, m, $2C_4F_9$-$\mathbf{(CH_2)_2}$-]; 3.7 [6H, s $(CO_2\mathbf{CH_3})_2$]; $^{19}F$ NMR , (600MHz, $CDCl_3$) δ (ppm): -81.6 (6F, t, $2CF_3$), -115.20 (q, 4F, $2(CF_2)_\alpha$), -125.01 (s, 4F, $2(CF_2)_\beta$), -126.6 (4F, s, $2(CF_2)_\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$…

**Precursor detailed <u>14</u>**: **x=z=4 and n = 2**; colorless liquid; yield: 43.9%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1735 et 1740 ($\nu_{C=O);}$ 1050 ($\nu_{C-O)}$; $^{1}H$ NMR (600MHz, $CDCl_3$); δ (ppm): 1.2 [6H, t -$(CO_2CH_2\mathbf{CH_3})_2$]; 1.8-2.25 [8H, m, $2C_4F_9$-$\mathbf{(CH_2)_2}$-]; 4.3 [4H, q, -$(CO_2\mathbf{CH_2}CH_3)_2$]; $^{19}F$ NMR , (600MHz, $CDCl_3$) δ (ppm): -81.6 (6F, t, $2CF_3$), -115.20 (q, 4F, $2(CF_2)_\alpha$), -125.01 (s, 4F, $2(CF_2)_\beta$), -126.6 (4F, s, $2(CF_2)_\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$…

**Compound PFM-C4 <u>10</u>**: white solid; yield: 90%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O);}$ 1130 ($\nu_{C-O)}$; $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.8-2.4 [4H, m, $C_4F_9$-$\mathbf{(CH_2)_2}$-]; 3.0-3.2 [1H, t, -$(CH_2)$-**CH**-$(CO_2^-)_2$]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.2 (3F, t, CF3), -115.20 (2F, q, $(CF_2)_\alpha$), -125.01 (2F, s, $(CF_2)_\beta$), -126.70 (2F, s, $(CF_2)_\omega$) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$… MS: ESI negative mode; m/z (%) = 348.9 (100) ($[M\text{-}Na^+]^+$); MS/MS: CID to 25%); m/z = 304.9 ($[M\text{-}Na^+ \text{-}CO_2]^+$).

**Compound PFM-C6 <u>11</u>** : white solid; yield: 82%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O);}$ 1130 ($\nu_{C-O)}$; $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.9-2.3 [4H, m, $C_4F_9$-$\mathbf{(CH_2)_2}$-]; 2.9-3.25 [1H, t, -$(CH_2)$-**CH**-$(CO_2^-)_2$]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.2 (3F, t, CF3), -114.30 (2F, q, $(CF_2)_\alpha$), -121.6 (2F, s, $(CF_{2n})_\beta$), -122.6, (2F, s, $(CF_2)\delta$), -123.3 (2F, s, $(CF_2)\gamma$), -125.9 (2F, s, $(CF_2)\omega$)
for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…; MS: ESI negative mode; m/z (%) = 448.8 (100) ($[M\text{-}Na^+]^+$); MS/MS: CID to 25%); m/z = 404.8 ($[M\text{-}Na^+ \text{-}CO_2]^+$).

**Compound PFM-C8 <u>12</u>** : white solid; yield: 92%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O);}$ 1130 ($\nu_{C-O)}$; $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.9-2.4 [4H, m, $C_4F_9$-$\mathbf{(CH_2)_2}$-]; 3.0-3.25 [1H, t, -$(CH_2)$-**CH**-$(CO_2^-)_2$]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.9 (3F), -115.2 (2F), -122.4 (6F), -123.4, (2F), -123.5 à -124.20 (2F), -127.03 (2F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma - (CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…; MS: ESI negative mode; m/z (%) = 548.8 (100) ($[M\text{-}Na^+]^+$); MS/MS: CID to 25%); m/z = 504.8 ($[M\text{-}Na^+ \text{-}CO_2]^+$).

**Compound PFM-2C44 <u>17</u>** white solid; yield: 82.2%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O);}$ 1130 ($\nu_{C-O)}$; $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.8-2.25 [8H, m, $2C_4F_9$-$\mathbf{(CH_2)_2}$-]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.2 (6F), -115.20 (4F), -125.01 (4F), -126.70 (4F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)_\beta$- $(CF_2)_\alpha$-$CH_2$…
MS: ESI negative mode; m/z (%) = 594.8 (100) ($[M\text{-}Na^+]^+$); MS/MS: CID to 25%); m/z = 550.8 ($[M\text{-}Na^+ \text{-}CO_2]^+$).

**Compound PFM-2C46 <u>18</u> :** white solid; yield: 81.5%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O;}$ 1130 ($\nu_{C-O}$); $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.8-2.3 [8H, m, $C_4F_9$-**$(CH_2)_2$**- et $C_6F_{13}$-**$(CH_2)_2$**- ]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.2 (6F), -115.5 (4F), -122.70 (2F), -123.4 à -124.5 (4F), -125.2 (2F), -127.5 (4F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma$ – $(CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$…; MS: ESI negative mode; m/z (%) = 694.8 (100) ([M-$Na^+$]$^+$); MS/MS: CID to 25%); m/z = 650.8 ([M-$Na^+$ -$CO_2$]$^+$).

**Compound PFM-2C66 <u>19</u>** white solid; yield: 92%; IR ($cm^{-1}$): 2776-2948 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 1590 et 1389 ($\nu_{C=O;}$ 1130 ($\nu_{C-O}$); $^{1}H$ NMR ($CD_3OD$); δ (ppm): 1.8-2.4 [8H, m, 2$C_6F_{13}$-**$(CH_2)_2$**-]; $^{19}F$ NMR (600MHz, $CD_3OD$) δ (ppm): -81.2 (6F), -115.6 (4F), -122.40 (4F), -123.4 à -124.5 (8F), -127.5 (4F) for $CF_3$-$(CF_2)_\omega$-$(CF_2)\gamma$ – $(CF_2)\delta$ - $(CF_{2n})_\beta$ - $(CF_2)_\alpha$-$CH_2$ …; MS: ESI negative mode; m/z (%) = 794.7 (100) ([M-$Na^+$]$^+$); MS/MS: CID to 25%); m/z = 750.8 ([M-$Na^+$ -$CO_2$]$^+$).