Giant brain-like aggregates from new fluorocarbon/hydrocarbon hybrid cationic surfactants.

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1) ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and MS for all the synthesized surfactants.

Tertiary amine 4: colorless liquid; IR (cm^{-1}): 2776-2948 ($\nu_{C—H}$), 1100-1460 ($\nu_{C—F}$), 847-950 ($\nu_{N—C}$); ^{1}H NMR ($CDCl_3$) δ (ppm): 2.18 (6H, s, [N(**CH_3)$_2$**]); 2.56 (4H, m, [C_4F_9-**CH_2**-CH_2-S-CH_2-**CH_2**-N(CH_3)$_2$]); 2.69 (4H, m, [-**CH_2**-S-**CH_2**-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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…yield : 78 %

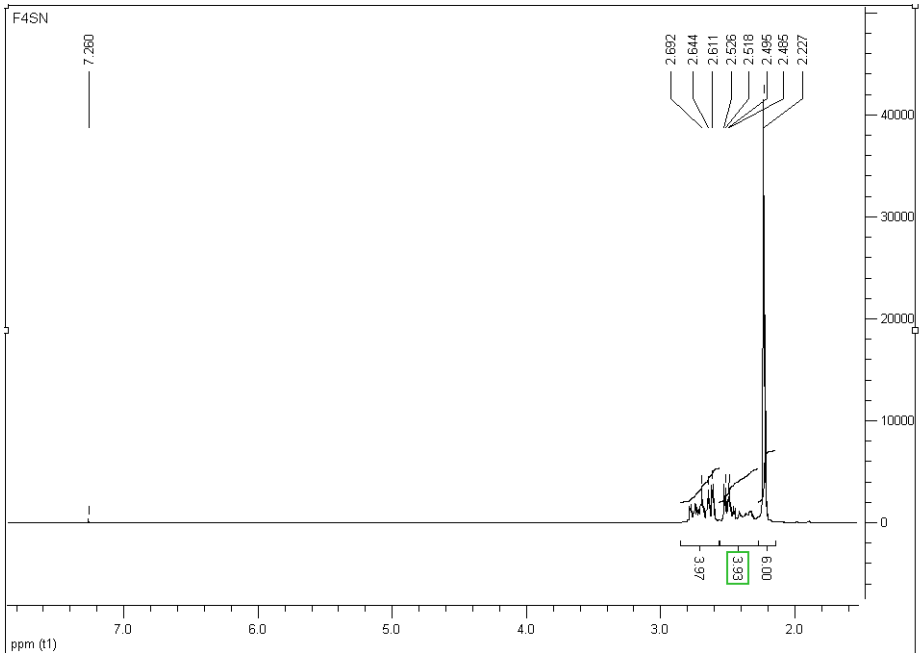

Figure 1. ^{1}H NMR spectra of compound **4**

Tertiary amine 5: colorless liquid; IR (cm^{-1}): 2776-2948 ($\nu_{C—H}$), 1100-1460 ($\nu_{C—F}$), 847-952 ($\nu_{N—C}$); ^{1}H NMR ($CDCl_3$) δ (ppm): 2.20 (6H, s,) [N(**CH_3)$_2$**]); 2.58 (4H, m, [C_4F_9-**CH_2**-CH_2-S-CH_2-**CH_2**-N(CH_3)$_2$]); 2.71 (4H, m, [-**CH_2**-S-**CH_2**-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.43 (3F, s, CF_3), -114.88 (2F, s, $(CF_2)_\alpha$), -122.36 (2F, s, $(CF_2)_\beta$), -123.81 to -124.12 (4F, s, $(CF_2)_{2\gamma}$), -126.52 (2F, s, $(CF_2)_\omega$) for CF_3-$(CF_2)_\omega$-$(CF_2)_{2\gamma}$-$(CF_2)_\beta$- $(CF_2)_\alpha$-CH_2…. Yield: 82 %

Tertiary amine 6: colorless liquid; IR (cm^{-1}): 2776-2948 ($\nu_{C—H}$), 1100-1459 ($\nu_{C—F}$), 871-954 ($\nu_{N—C}$); -^{1}H NMR ($CDCl_3$) δ (ppm): 2.18 (6H, s, [N(**CH_3)$_2$**]); 2.47 (4H, m, [C_4F_9-**CH_2**-CH_2-S-CH_2-**CH_2**-N(CH_3)$_2$]); 2.64 (4H, m, [-**CH_2**-S-**CH_2**-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.12 (2F, s, $(CF_2)_\alpha$), -122.70 (2F, s, $(CF_2)_\beta$), -123.50 to -124.20 (8F, s, $(CF_2)_{2\gamma}$), -127.03 (2F, s, $(CF_2)_\omega$) for CF_3-$(CF_2)_\omega$-$(CF_2)_{4\gamma}$-$(CF_2)_\beta$- $(CF_2)_\alpha$-CH_2…. Yield: 64 %

Compound S-F_4H_4: white solid; IR (Cm^{-1}): 2880-2973 ($\nu_{C—H}$), 1100-1400 ($\nu_{C—F}$), 848-962 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ (ppm), 0.99 (3H, t, [(CH_2)-**CH_3**]); 1.42 (2H, m, [-(**CH_2**)-CH_3]); 1.71 (2H, m, [**CH_2**-(CH_2)-CH_3]); 2.45 (2H, m, [C_4F_9-**CH_2**-]); 3.02 (4H, m, [-**CH_2**-S-**CH_2**-]); 3.46 (6H, s, [-N^+(**CH_3)$_2$**]); 3.63 (2H, m, [N^+-**CH_2**-C_2H_4-CH_3]); 3.89 (2H, m, [-N^+-**CH_2**-CH_2-S-]); ^{19}F NMR (CD_3OD) δ (ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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 positive mode; m/z (%) = 408.1 (100) ([M-Br]$^+$); MS/MS: CID to 25%); m/z = 307.1 ([M-Br^--$C_6H_{15}N$]$^+$). Yield: 72 %

Compound S-F_4H_6: white solid; IR (Cm^{-1}): 2868-2939 ($\nu_{C—H}$), 1100-1466 ($\nu_{C—F}$), 847-926 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ (ppm): 0.83 (3H, t, [(CH_2)-**CH_3**]); 1.29 (6H, m, [-(**CH_2**)$_3$-CH_3]); 1.67 (2H, m, [**CH_2**-(CH_2)$_3$-CH_3]); 2.48 (2H, m, [C_4F_9-**CH_2**-]); 2.82 (4H,

m, [-**CH$_2$**-S-**CH$_2$**-]); 3.02 (6H, s, [-N$^+$(**CH$_3$**)$_2$]); 3.21 (2H, m, [N$^+$-**CH$_2$**-CH$_2$-(CH$_2$)$_3$-CH$_3$]); 3.44 (2H, m, [-N$^+$-**CH$_2$**-CH$_2$-S-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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 positive mode; m/z (%) = 436.1 (100) ([M-Br]$^+$); MS/MS: CID to 25%); m/z = 307.1 ([M-Br$^-$-$C_8H_{19}N$]$^+$). Yield: 68 %

Compound S-F$_4$H$_8$: white solid; IR (Cm^{-1}): 2864-2937 ($\nu_{C—H}$), 1134-1350 ($\nu_{C—F}$), 873-954 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ(ppm): 0.78 (3H, t, [$(CH_2)_5$-**CH$_3$**]); 1.25 (10H, m, [-(**CH$_2$**)$_5$-CH_3]); 1.65 (2H, m, [**CH$_2$**-$(CH_2)_5$-CH_3]); 2.45 (2H, m, [C_4F_9-**CH$_2$**-]); 2.79 (4H, m, [-**CH$_2$**-S-**CH$_2$**-]); 2.99 (6H, s, [-N$^+$(**CH$_3$**)$_2$]); 3.19 (2H, m, [N$^+$-**CH$_2$**-CH$_2$-$(CH_2)_5$-CH_3]); 3.44 (2H, m, [-N$^+$-**CH$_2$**-CH$_2$-S-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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 positive mode; m/z (%) = 464.1 (100) ([M-Br]$^+$); MS/MS: CID to 25%); m/z = 307.1 ([M-Br$^-$-$C_{10}H_{23}N$]$^+$). Yield: 60 %

Compound S-F$_4$H$_{10}$: white solid; IR (Cm^{-1}): 2861-2935 ($\nu_{C—H}$), 1134-1409 ($\nu_{C—F}$), 884-1012 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ(ppm): 0.84 (3H, t, [(CH_2)-**CH$_3$**]); 1.25 (14H, m, [-(**CH$_2$**)$_7$-CH_3]); 1.72 (2H, m, [**CH$_2$**-$(CH_2)_7$-CH_3]); 2.53 (2H, m, [C_4F_9-**CH$_2$**-]); 2.86 (4H, m, [-**CH$_2$**-S-**CH$_2$**-]); 3.07 (6H, s, [-N$^+$(**CH$_3$**)$_2$]); 3.30 (2H, m, [N$^+$-**CH$_2$**-CH$_2$-$(CH_2)_7$-CH_3]); 3.52 (2H, m, [-N$^+$-**CH$_2$**-CH$_2$-S-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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 positive mode; m/z (%) = 492.2 (100) ([M-Br]$^+$); MS/MS: CID to 25%); m/z = 307.1 ([M-Br$^-$-$C_{12}H_{27}N$]$^+$). Yield: 67 %

Compound S-F$_4$H$_{12}$: white solid; IR (Cm^{-1}): 2860-2939 ($\nu_{C—H}$), 1134-1409 ($\nu_{C—F}$), 884-1012 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ(ppm): 0.98 (3H, t, [$(CH_2)_9$-**CH$_3$**]); 1.38 (18H, m, [-(**CH$_2$**)$_9$-CH_3]); 1.85 (2H, m, [**CH$_2$**-$(CH_2)_9$-CH_3]); 2.64 (2H, m, [C_4F_9-**CH$_2$**-]); 2.96 (4H, m, [-**CH$_2$**-S-**CH$_2$**-]); 3.21 (6H, s, [-N$^+$(**CH$_3$**)$_2$]); 3.40 (2H, m, [N$^+$-**CH$_2$**-CH$_2$-$(CH_2)_9$-CH_3]); 3.70 (2H, m, [-N$^+$-**CH$_2$**-CH$_2$-S-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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: positive mode; m/z (%) = 520.2 (100) ([M-Br]$^+$); MS/MS: CID to 25%); m/z = 307.1 ([M-Br$^-$-$C_{14}H_{31}N$]$^+$). Yield: 54 %

Compound S-F$_4$H$_{14}$: white solid; IR (Cm^{-1}): 2836-2923 ($\nu_{C—H}$), 1134-1409 ($\nu_{C—F}$), 884-1012 ($\nu_{N—C}$); ^{1}H NMR (CD_3OD) δ(ppm): 0.84 (3H, t, [$(CH_2)_{11}$-**CH$_3$**]); 1.29 (22H, m, [-(**CH$_2$**)$_{11}$-CH_3]); 1.72 (2H, m, [**CH$_2$**-$(CH_2)_{11}$-CH_3]); 2.49 (2H, m, [C_4F_9-**CH$_2$**-]); 2.85 (4H, m, [-**CH$_2$**-S-**CH$_2$**-]); 3.29 (6H, s, [-N$^+$(**CH$_3$**)$_2$]); 3.34 (2H, m, [N$^+$-**CH$_2$**-CH$_2$-$(CH_2)_{11}$-CH_3]); 3.55 (2H, m, [-N$^+$-**CH$_2$**-CH$_2$-S-]); ^{19}F NMR (CD_3OD) δ(ppm): -81.78 (3F, s, CF_3), -115.20 (2F, s, $(CF_2)_\alpha$), -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 positive mode; m/z (%) = 548.1 (100) ([M-Br]$^+$); MS/MS: CID to 25%) ; m/z = 307.1 ([M-Br$^-$-$C_{16}H_{35}N$]$^+$). Yield: 24 %

2) Variation of Log(CMC) as a function of the number of carbon atoms in the hydrophobic chains