Supporting Information

Perfluoroalkylated Linear Polyglycerols and their Supramolecular Assemblies in Aqueous Solution

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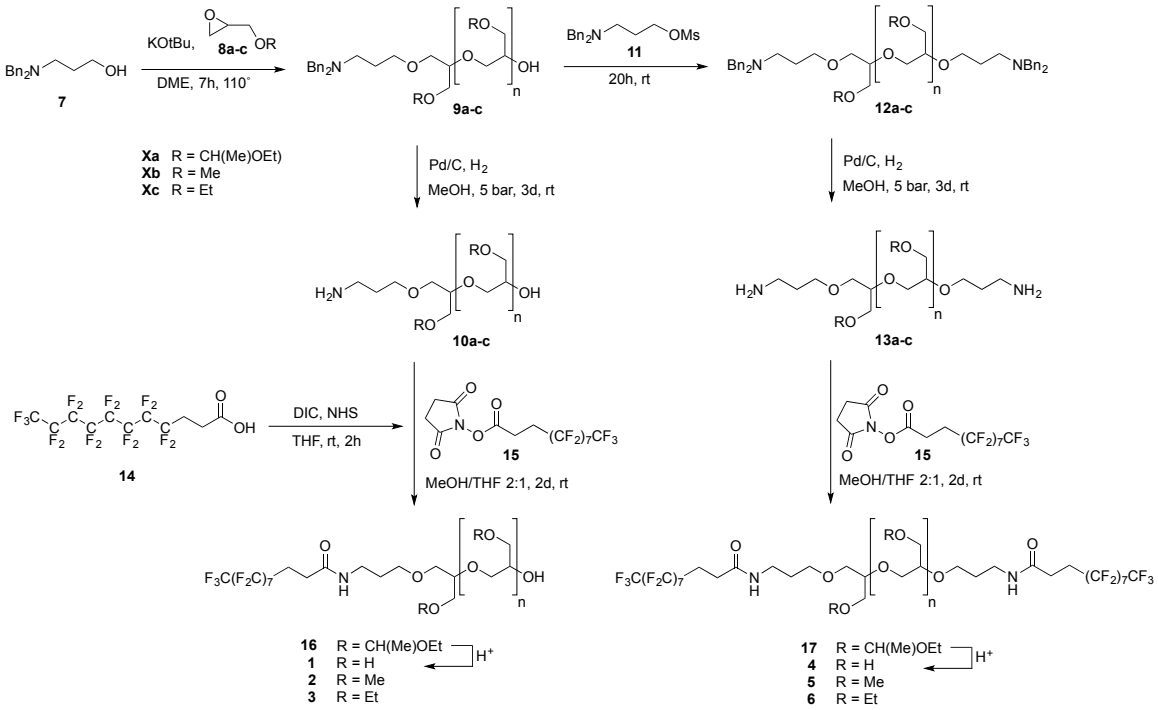
Content

1. Syntheses of linear polygycerols (LPGs)



Scheme S1 – Syntheses of LPG amphiphiles and bolaamphiphiles.

General procedure for the synthesis of monofunctionalized LPGs:

The linear polyglycerols LPG(OMe), LPG(OEt), as well as LPG(OEE), which is the precursor for LPG(OH), were prepared by living anionic polymerization with 3-dibenzylamino-1-propanol as initiator via reaction with the respective oxirane monomer.[1] 3-(dibenzylamino)-propan-1-ol was synthesized according to the literature.[2] The initiator **7** (2.2 g, 8.6 mmol) was dissolved in 1M KO*t*Bu in THF (8.2 mL, 8.2 mmol) under argon atmosphere and heated to 80 ˚C for 30 min until full deprotonation of the functionalized alcohol occurred. The generated *t*-BuOH and the solvent were removed in high vacuum. The remaining alcoholate initiator was completely dried, re-dissolved in dry DME, and heated to 110 ˚C under argon atmosphere. Each of the freshly distilled monomers, glycidyl methyl ether **8b** (12.3 g, 140 mmol) for LPG(OMe), glycidyl ethyl ether **8c** (14.3 g, 140 mmol) for LPG(OEt), or ethoxyethyl glycidyl ether **8a** (20.4 g, 140 mmol) for LPG(OEE), were added to the alcoholate DME solution and polymerized for 24 h at 110 ˚C under argon atmosphere. The reaction was quenched by the addition of water, concentrated under reduced pressure, and subsequently dried in high vacuum. For purification, the obtained yellow oil was dissolved in Et_2O and centrifuged to separate the insoluble salts. The Et_2O from the decanted top layers was removed in vacuo, and the dibenzylaminopropanol-functionalized LPG (**9a-c**) was obtained as a slightly yellow oil in 80% yield.

Compound 9a [Bn_2N-LPG(OEE)-OH]**:** ^{1}H-NMR: (400 MHz, MeOD, TMS): δ (ppm) = 1.19 (t, J = 7.04 Hz 3H, OCH_2CH_3), 1.28 (d, J = 5.24 Hz, 3H, OCH_2CH_3), 1.73-1.80 (m, 2H, $CH_2CH_2CH_2$), 2.51 (t, 2H, J = 6.9 Hz, NCH_2), 3.31-3.68 (m, 8H, 2x OCH, 3x OCH_2), 4.71-4.75 (m, 2H, OCH, OCH_2), 7.21-7.37 (m, 10H, Bn_2N). MS (MALDI-TOF): M_n / M_W = 1.06, M_n = 2030.9 [M (n = 13)+Na]$^+$.

Compound 9b [Bn_2N-LPG(OMe)-OH]: ^{1}H-NMR: (400 MHz, $CDCl_3$, TMS): δ (ppm) = 1.73-1.80 (m, 2H, $CH_2CH_2CH_2$), 2.48 (t, 2H, J = 7.02 Hz, NCH_2), 3.31-3.62 (m, 8H, OCH, OCH_3, 2x OCH_2), 7.19-7.35 (m, 10H, Bn_2N). MS (MALDI-TOF): M_n / M_W = 1.04, Mn = 1334.9 [M (n = 13)+Na]$^+$, M_W = 1525.

Compound 9c [Bn_2N-LPG(OEt)-OH]: ^{1}H-NMR: (400 MHz, MeOD, TMS): δ (ppm) = 1.17 (t, J = 7.14 Hz 3H, OCH_2CH_3), 1.70-1.80 (m, 2H, $CH_2CH_2CH_2$), 2.49 (t, 2H, J = 7.0 Hz, NCH_2), 3.40-3.70 (m, 7H, 1x OCH, 3x OCH_2), 7.15-7.36 (m, 10H, Bn_2N). MS (MALDI-TOF): M_n / M_W = 1.04, M_n = 1525.9 [M (n = 13)+Na]$^+$, M_W = 1559.

General procedure for the synthesis of bifunctional LPGs:

In order to create LPGs with two terminal amino groups, the above-described reactions were quenched with the mesylated version of the polymerization starter, which had been previously prepared. To prepare the quencher 3-(dibenzylamino)-propan-1-ol **7** (4.3 g, 16.6 mmol) was dissolved in 20 mL THF and TEA (1.9 g, 18.3 mmol) was added. After cooling to 0 ˚C, methanesulfonyl chloride was added slowly and the reaction mixture was stirred for 2 h at room temperature. The precipitate was filtered off, 50 mL DCM were added, and the organic phase was washed with distilled water and brine and dried with sodium sulfate. After solvent evaporation in vacuo 5.4 g of the quencher **11** were obtained as orange oil (98%).
To quench the respective LPG polymerization 3-(dibenzylamino)propyl methanesulfonate **11** dissolved in dry DME (3.4 g, 10.3 mmol) was added, cooled to room temperature and stirred for 20 h. Purification was performed as described above. The substitution of the terminal alcohol with a protected amino function produced the symmetric LPG diamines **12a-c** in 70% yield.
The LPG amines **9a-c** and LPG diamines **12a-c** were deprotected via hydrogenation in MeOH with Pd/C (10% w/w) as catalyst. This reaction mixture was transferred to a pressure cylinder and allowed to proceed under 5 bar hydrogen atmosphere at room temperature for 3 days. The mixture was filtered through celite® to remove the catalyst, and the filtrate was concentrated under reduced pressure. The amino-functionalized **10a** LPG(OEE)-NH_2, **10b** LPG(OMe)-NH_2 and **10c** LPG(OEt)-NH_2 and diamino-functionalized **13a** LPG(OEE)-$(NH_2)_2$, **13b** LPG(OMe)-$(NH_2)_2$ and **13c** LPG(OEt)-$(NH_2)_2$ were obtained as slightly yellow, viscous oils in quantitative yield after drying in high vacuum.

Compound 10a [LPG(OEE)-(NH_2)]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 7.04 Hz, 3H, OCH_2CH_3), 1.28 (d, J = 5.24 Hz, 3H, OCH_2CH_3), 1.70-1.77 (m, 2H, $CH_2CH_2CH_2$), 2.74 (t, 2H, J = 6.94 Hz, NCH_2), 3.51-3.68 (m, 7H, OCH, 3x OCH_2), 4.71-4.75 (q, J = 5.24 Hz, 1H, OCH).
Compound 10b [LPG(OMe)-(NH_2)]: ^{1}H-NMR: (500 MHz, MeOD-d4, TMS): δ (ppm) = 1.73-1.78 (m, 2H, $CH_2CH_2CH_2$), 2.78 (t, 2H, J = 6.85 Hz, NCH_2), 3.31-3.79 (m, 8H, OCH, OCH_3, 2x OCH_2).
Compound 10c [LPG(OEt)-(NH_2)]: (400 MHz, MeOD, TMS): δ (ppm) = 1.19 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.70-1.80 (m, 2H, $CH_2CH_2CH_2$), 2.77 (t, 2H, J = 6.7 Hz, NCH_2), 3.40-3.70 (m, 7H, 1x OCH, 3x OCH_2).
Compound 13a [LPG(OEE)-$(NH_2)_2$]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 7.04 Hz, 3H, OCH_2CH_3), 1.28 (d, J = 5.24 Hz, 3H, OCH_2CH_3), 1.70-1.77 (m, 4H, 2x $CH_2CH_2CH_2$), 2.74 (t, 4H, J = 6.94 Hz, 2x NCH_2), 3.51-3.68 (m, 7H, OCH, 3x OCH_2), 4.71-4.75 (q, J = 5.24 Hz, 1H, OCH).
Compound 13b [LPG(OMe)-$(NH_2)_2$]: ^{1}H-NMR: (500 MHz, MeOD-d4, TMS): δ (ppm) = 1.73-1.78 (m, 4H, 2x $CH_2CH_2CH_2$), 2.78 (t, 4H, J = 6.85 Hz, 2x NCH_2), 3.31-3.79 (m, 8H, OCH, OCH_3, 2x OCH_2).

Compound 13c [LPG(OEt)-(NH_2)$_2$]: (400 MHz, MeOD, TMS): δ (ppm) = 1.19 (t, J = 7.0 Hz, 3H, $OCH_2CH_{3,}$), 1.70-1.80 (m, 4H, 2x $CH_2CH_2CH_2$), 2.77 (t, 4H, J = 6.7 Hz, 2x NCH_2), 3.40-3.70 (m, 7H, 1x OCH, 3x OCH_2).

2. Synthesis of polyglycerol amphiphiles

The mono- and diamino functionalized LPGs **10a-c** and **13a-c** were coupled with perfluoroalkyl moieties **14** via amide bond formation. First, the carboxylic group of the 2*H*,2*H*,3*H*,3*H*-perfluoroundecanoic acid **14** (5.0 g, 2.0 mmol) was activated by coupling *N*-hydroxysuccinimid (NHS) (1.3 g, 2.2 mmol) with DIC (1.4 g, 2.2 mmol) in THF at rt for 2 h. After solvent evaporation the product **15** was purified by washing with trifluorotoluene to yield a white solid (4.5 g, 75%).

In a second step, the NHS activated perfluoroundecanoic acid **15** (1.1 eq. per terminal amine), the respective LPG were dissolved in MeOH/THF 2:1 and triethylamine (1 eq. per terminal amine) was added. The mixture was stirred for 2 days at room temperature and purified by dialysis in regenerated cellulose membrane with 1 kDa MWCO in THF to yield yellow oil (80%).

To obtain the final product of the hydroxyl side chain amphiphiles **1** LPG(OH)-(R_{f8}) and **4** LPG(OH)-(R_{f8})$_2$ the acetal-protected side chains of **16** LPG(OEE)-(R_{f8}) and **17** LPG(OEE)-(R_{f8})$_2$ were deprotected. Under acidic conditions, the ethoxyethyl group, attached to the side chain oxygen of each repeating unit, was cleaved off as Et_2O. The deprotection afforded the hydroxy side-chain linear polyglycerol.[3] Therefore, LPG(OEE)-(R_{f8})$_{1/2}$ (3.6 g, 1.2 mmol) was dissolved in 50 mL THF and 3 drops of hydrochloric acid (6M) were added. A white precipitate was observed immediately. The mixture was further stirred for two hours at room temperature, the supernatant was decanted, THF was removed in vacuo, and product **1** and **4** were further purified by washing with HFE-7100. After drying in high vacuum a white resin was obtained (2.3 g, 85%).

Compound 16 [LPG(OEE)-(R_{f8})]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 6.84 Hz, 3H, $OCH_2CH_{3,}$), 1.28 (d, J = 5.08 Hz, 3H, $OCHCH_{3,}$), 1.74-1.81 (m, 2H, $CH_2CH_2CH_2$), 2.45-2.60 (m, 4H, $CF_2CH_2CH_2$), 3.45-3.95 (m, 7H, 2x OCH, 3x OCH_2), 4.70-4.80 (q, J = 5.08 Hz, 1H, OCH). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6): δ (ppm) = -82.4 (m, CF_3), -115.7 (CF_2), -116.0 (CF_2), -122.7 (CF_2), -122.9 (CF_2), -123.8 (CF_2), -124.5 (CF_2), -127.3 (CF_2).

Compound 17 [LPG(OEE)-(R_{f8})$_2$]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 6.84 Hz, 3H, $OCH_2CH_{3,}$), 1.28 (d, J = 5.08 Hz, 3H, $OCHCH_{3,}$), 1.74-1.81 (m, 4H, 2x $CH_2CH_2CH_2$), 2.45-2.60 (m, 8H, 2x $CF_2CH_2CH_2$), 3.45-3.95 (m, 7H, 2x OCH, 3x OCH_2), 4.70-4.80 (q, J = 5.08 Hz, 1H, OCH). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6): δ (ppm) = -82.4 (m, CF_3), -115.7 (CF_2), -116.0 (CF_2), -122.7 (CF_2), -122.9 (CF_2), -123.8 (CF_2), -124.5 (CF_2), -127.3 (CF_2).

Compound 1 [LPG(OH)-(R_{f8})]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.75-1.81 (m, 2H, $CH_2CH_2CH_2$), 2.45-2.55 (m, 4H, $CF_2CH_2CH_2$), 3.50-3.80 (m, 5H, OCH, 2x OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6): δ (ppm) = -82.4 (m, CF_3), -115.8 (CF_2), -115.9 (CF_2), -122.7 (CF_2), -122.9 (CF_2), -123.7 (CF_2), -124.5 (CF_2), -127.3 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.02, Mn = 1689.8 $[M (n = 13)+Na]^+$

Compound 2 [LPG(OMe)-(R_{f8})]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.70-1.79 (m, 2H, $CH_2CH_2CH_2$), 2.45-2.58 (m, 4H, $CH_2CH_2C_{f8}$), 3.34-3.70 (m, 8H, OCH, OCH_3, 2x

OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6,): δ (ppm) = -82.2 (t, *J*= 10.4 Hz, CF_3), -115.5 (CF_2), -122.6 (CF_2), -122.8 (CF_2), -123.6 (CF_2), -124.4 (CF_2), -127.2 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.02, Mn = 1802.8 $[M (n = 15)+Na]^+$

Compound 3 [LPG(OEt)-(R_{f8})]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 7.0 Hz, 3H, OCH_2CH_3,), 1.72-1.81 (m, 2H, $CH_2CH_2CH_2$), 2.45-2.65 (m, 4H, $CF_2CH_2CH_2$), 3.40-3.72 (m, 7H, 1x OCH, 3x OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, TMS): δ (ppm) = -82.2 (m, CF_3), -115.5 (CF_2), -122.5 (CF_2), -122.8 (CF_2), -123.6 (CF_2), -124.4 (CF_2), -127.2 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.05, Mn = 1555.7 $[M (n = 11)+Na]^+$

Compound 4 [LPG(OH)-(R_{f8})$_2$]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.75-1.81 (m, 4H, 2x $CH_2CH_2CH_2$), 2.45-2.55 (m, 8H, 2x $CF_2CH_2CH_2$), 3.50-3.80 (m, 5H, OCH, 2x OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6): δ (ppm) = -82.4 (m, CF_3), -115.8 (CF_2), -115.9 (CF_2), -122.7 (CF_2), -122.9 (CF_2), -123.7 (CF_2), -124.5 (CF_2), -127.3 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.02, Mn = 2151.5 $[M (n = 13)+H]^+$

Compound 5 [LPG(OMe)-(R_{f8})$_2$]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.70-1.79 (m, 4H, 2x $CH_2CH_2CH_2$), 2.45-2.58 (m, 8H, 2x $CH_2CH_2C_{f8}$), 3.34-3.70 (m, 8H, OCH, OCH_3, 2x OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, C_6F_6,): δ (ppm) = -82.2 (t, *J*= 10.4 Hz, CF_3), -115.5 (CF_2), -122.6 (CF_2), -122.8 (CF_2), -123.6 (CF_2), -124.4 (CF_2), -127.2 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.02, Mn = 2277.9 $[M (n = 15)+H]^+$

Compound 6 [LPG(OEt)-(R_{f8})$_2$]: ^{1}H-NMR: (400 MHz, MeOD-d4, TMS): δ (ppm) = 1.19 (t, J = 7.0 Hz, 3H, OCH_2CH_3,), 1.72-1.81 (m, 4H, 2x $CH_2CH_2CH_2$), 2.45-2.65 (m, 8H, 2x $CF_2CH_2CH_2$), 3.40-3.72 (m, 7H, 1x OCH, 3x OCH_2). ^{19}F-NMR (400 MHz, MeOD-d4, TMS): δ (ppm) = -82.2 (m, CF_3), -115.5 (CF_2), -122.5 (CF_2), -122.8 (CF_2), -123.6 (CF_2), -124.4 (CF_2), -127.2 (CF_2). MS (MALDI-TOF): M_n / M_W = 1.04, Mn = 2190.9 $[M (n = 12)+H]^+$

3. Synthesis of Disperse Red 4,4,4-trifluorobutanoate (DR-CF_3) 18

Disperse Red 1 (1.1 g, 3.52 mmol) and 4,4,4-trifluorobutanoic acid (500 mg, 3.52 mmol) were dissolved in 100 mL DCM. ECDI (1.35 g, 7.04 mmol) and DMAP (540 mg, 4.4 mmol) were added to the solution and stirred for 72 h at room temperature. After the mixture was repeatedly washed with pure water, the solvent was removed under vacuum to yield a red residue. The raw product was further purified by column chromatography (Hex:EtAc 3:2) to yield the desired compound (1.34 g, 84%).

18 DR-CF_3: ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.38 – 8.28 (m, 2H, Ar-H), 7.93 (ddd, J = 9.2, 4.8, 2.4 Hz, 4H, Ar-H), 6.81 (dd, J = 9.8, 2.5 Hz, 2H, Ar-H), 4.35 (t, J = 6.3 Hz, 2H, NCH_2CH_2), 3.71 (t, J = 6.3 Hz, 2H, NCH_2CH_2), 3.54 (q, J = 7.1 Hz, 3H, CH_3), 2.61 – 2.55 (m, 2H, $CH_2CH_2CF_3$), 2.52 – 2.37 (m, 2H, $CH_2CH_2CF_3$), 1.27 (t, J = 7.1 Hz, 2H, NCH_2CH_3) ppm. ^{19}F-NMR (400 MHz, $CDCl_3$, δ): -66.89 (t, *J* = 10.4 Hz, CF_3) ppm. MS (ESI-TOF): m/z= 439.16 $[M+H]^+$, 461.14 $[M+Na]^+$

4. Calculation of Davies HLB values

The HLB values of nonionic surfactants are typically calculated as Griffin values, which are the mass ratio of hydrophilic to hydrophobic moiety and do not account for the specific hydrophilicity and hydrophobicity of each functional group.
To include the specific properties of LPG side chain hydrophilicity and perfluorocarbon hydrophobicity, we calculated Davies HLB values for the presented amphiphiles as shown below:

HLB = 7 + Σ (hydrophilic group contributions) – Σ (hydrophobic group contributions)

Table S1 – HLB contributions of the respective amphiphile functional groups.[4-6]

Functional group	HLB contribution
$-(CH_2)_2OH$	0.95
$-(CH_2)_2OMe$	0.47
$-(CH_2)_2OEt$	0.33
$-(CH_2)_2O-$	0.33
$-CF_2-$, $-CF_3$	0.87

1. LPG(OH)-R_f
7 + 0.95 (x 15) (OH side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 8) (R_F)
= 7 + 14.25 + 5 - 7= ~ 19

2. LPG(OMe)-R_f
7 + 0.47 (x 15) (OMe side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 8) (R_F)
= 7 + 7.05 + 5 - 7= ~ 12

3. LPG(OEt)-R_f
7 + 0.33 (x 15) (OEt side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 8) (R_F)
= 7 + 5 + 5 - 7= ~ 10
4. LPG(OH)-$(R_f)_2$
7 + 0.95 (x 15) (OH side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 16) (R_F)
= 7 + 14.25 + 5 - 14= ~ 12

5. LPG(OMe)-$(R_f)_2$
7 + 0.47 (x 15) (OMe side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 16) (R_F)
= 7 + 7.05 + 5 - 14= ~ 5

6. LPG(OEt)-$(R_f)_2$
7 + 0.33 (x 15) (OEt side chain) + 0.33 (x 15) (LPG backbone) - 0.87 (x 16) (R_F)
= 7 + 5 + 5 - 14= ~ 3

5. Aggregate size analysis

The hydrodynamic diameters (D_h) were determined by dynamic light scattering (DLS) using Zetasizer Nano-ZS from Malvern Instruments equipped with a 633 nm He–Ne laser. The polydispersity index (PDI) was used as a measure of the width of size distribution. A PDI less than 0.3 indicates a homogenous population for colloidal systems. Each sample was measured three times and the results are expressed as a mean ± standard deviation.

6. Cryo-TEM Sample Preparation

Samples for cryo-TEM were prepared by placing an aliquot of the sample solution on commercially available holey carbon covered copper grids (R 1/4 batch of Quantifoil Micro Tools GmbH, Jena, Germany). The supernatant fluid was blotted until an ultra-thin film was obtained, which spanned the holes of the support film. The grids were immediately vitrified in liquid ethane using a spring-loaded plunging device. The vitrified samples were then transferred into the electron microscope under liquid nitrogen using a Gatan cryo-holder and stage (model 626, Gatan Inc., California, USA). Microscopy was performed at 94 K sample temperature with a Philips CM12 transmission electron microscope (FEI, Oregon, USA) at a primary magnification of 58,300 x (100 kV, LaB6-illumination). Images were recorded on Kodak® SO-163 negative film and digitized with an Epson Perfection V750 PRO scanner (EPSON Deutschland GmbH, Meerbusch, Germany) at a final pixel resolution of 0.363 nm.

7. AFM Sample Preparation

Freshly cleaved mica was glued to metal disks and a 20 µl of the sample solution 0.25 wt% LPG(OH)-$(R_{f8})_2$ (**4**) was deposited in the middle and incubated for at least 15 minutes. Before measurement, calibration of the cantilever spring constant was performed using the thermal noise method.[7] AFM tips SNL-10 (Bruker) with a tip radius of 2-10 nm cantilever with spring constant values 0.3-0.5 N/m were used. After incubation, the sample was rinsed with 1-3 ml Milli-Q water and 10 µl were deposited on the mica surface. The sample surface was never allowed to dry. The sample was then mounted onto the AFM piezo tube and a fluid cell was assembled. During imaging, the amplitude set point was adjusted to minimize the normal forces onto the sample, but still within a range appropriate enough to maintain good image quality. Scan rates of 0.6 - 0.8 Hz were used during mapping with 512 points per scan.

8. Figures and Tables

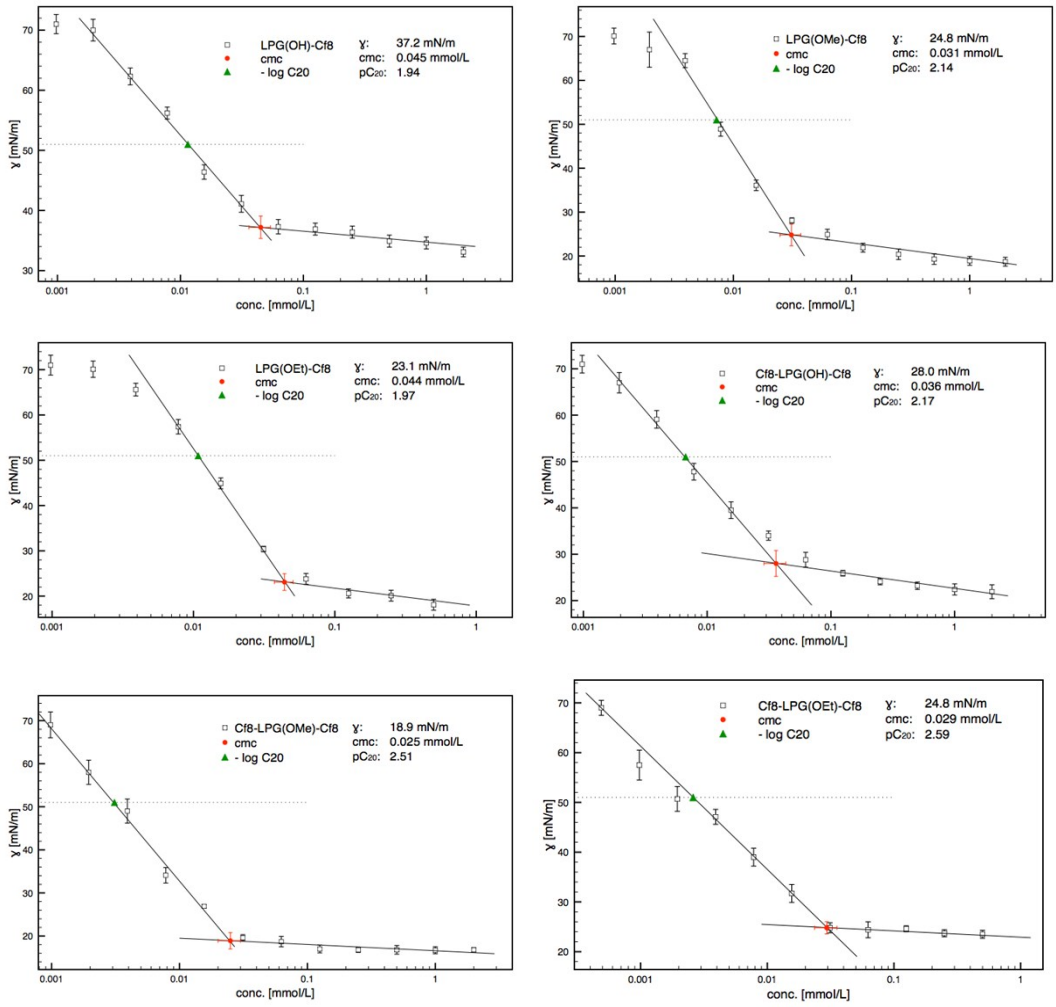


Fig. S1 - Surface tension measurements to determine CMC and γ_{CMC} via pendent drop method.

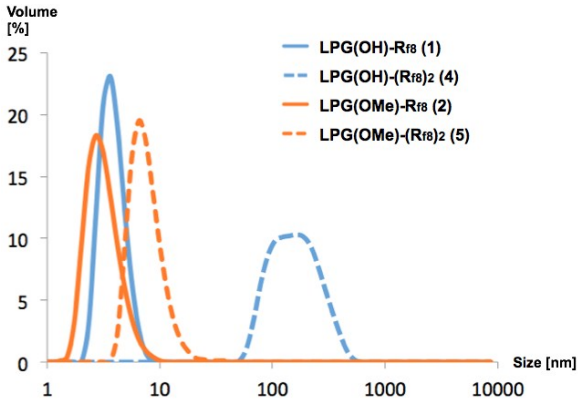


Figure S2 – Hydrodynamic diameters of 0.1 wt% LPG(OH)-C_{f8}, LPG(OH)-$(C_{f8})_2$, LPG(OMe)-C_{f8}, LPG(OMe)-$(C_{f8})_2$ solutions, directly dissolved in water determined by DLS.

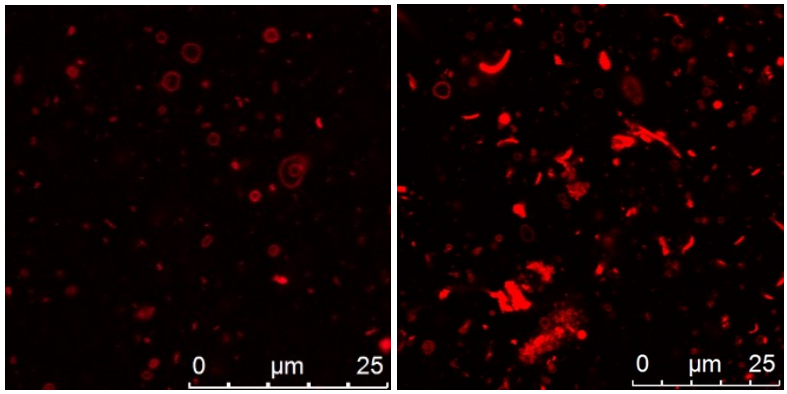


Fig. S3 - Fluorescence microscopy of an aqueous solution of methoxy amphihile 5 with encapsulated rhodamine below (left) and above LCST (45°C, right)

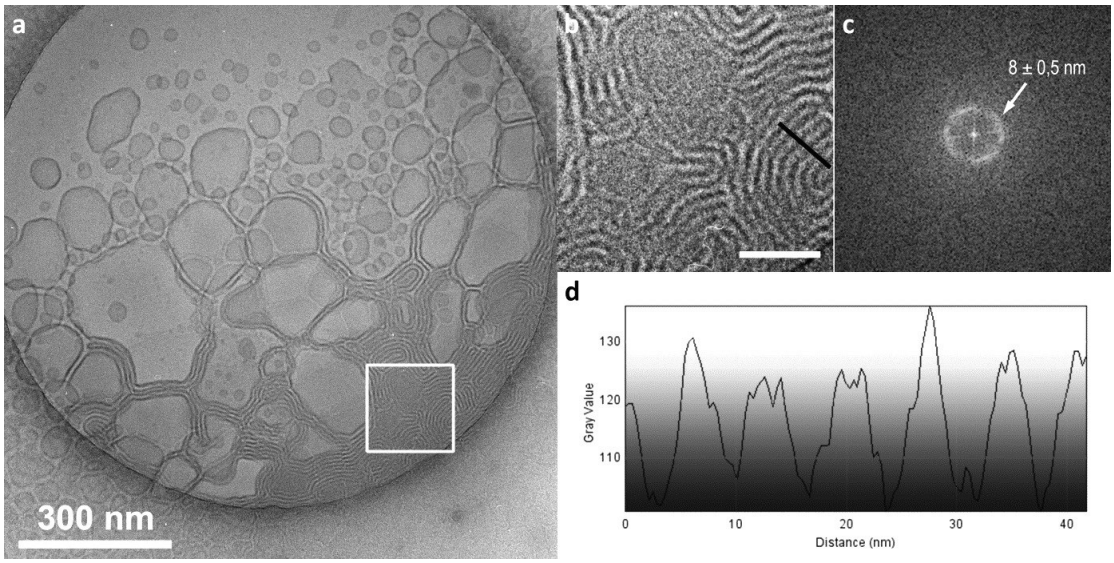


Fig. S4 – a) Cryo-TEM image of a 0.25 wt% aqueous solution of LPG(OMe)-R_{f8} (2), which was prepared according to the film hydration method. Lamellar structures are created by high material density. The white frame marks the corresponding image detail (b, scale represents 50 nm). c) The reflexes corresponding to a repetitive distance of the membranes of 8 ± 0.5 nm. d) The line plot along the black line in (b) shows the electron density of those areas.

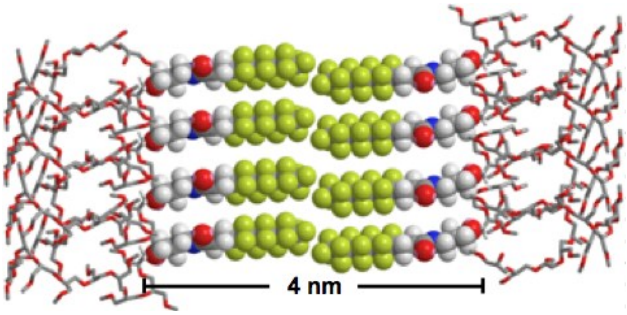


Fig. S5 – Model of a LPG(OMe)-R_{f8} membrane. The double-layered arrangement of the molecules leads to a 4 nm thick perfluoroalkyl induced bilayer in the center of the membrane. The complete refolding of the LPG(OMe) polymer chain results in a width of about 2 nm on each side, which agrees well with the determined width of the total membrane thickness of 8 nm.

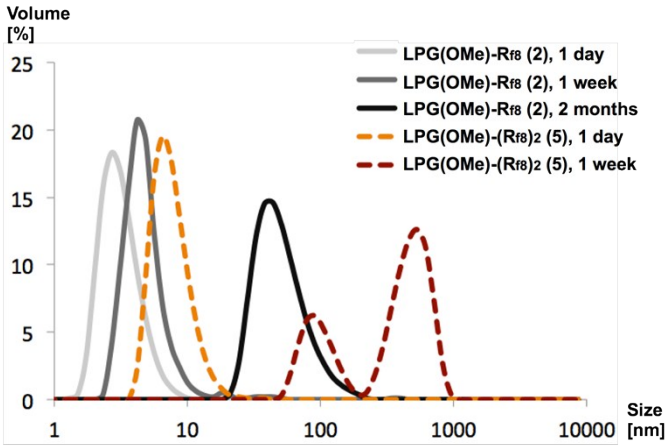


Fig. S6 - DLS measurements of aged methoxy amphiphiles (2 and 5). The formation of larger aggregates after 1 week for bolaamphiphile 5 and after 2 months for amphiphile 2 is visible.

Table S2 – Dye encapsulation values in mol% carrier displayed as diagram Fig. 5.

Structure	DR	DR-CF_3
LPG(OH)-Cf_8	0.16	3.9
LPG(OMe)-Cf_8	0.30	1.6
LPG(OH)-$(Cf_8)_2$	2.1	1.2
LPG(OMe)-$(Cf_8)_2$	0.59	0.55

9. NMR and MS data

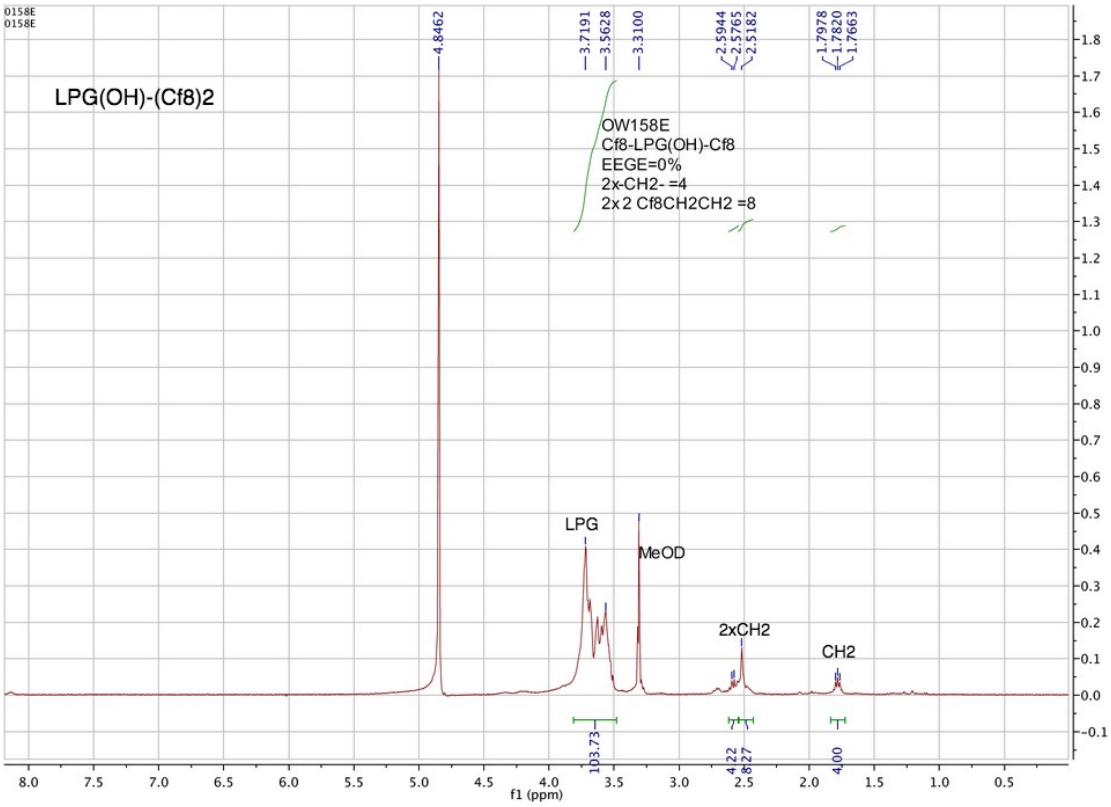


Fig. S7 – ^{1}H-NMR hydroxy amphiphile 4.

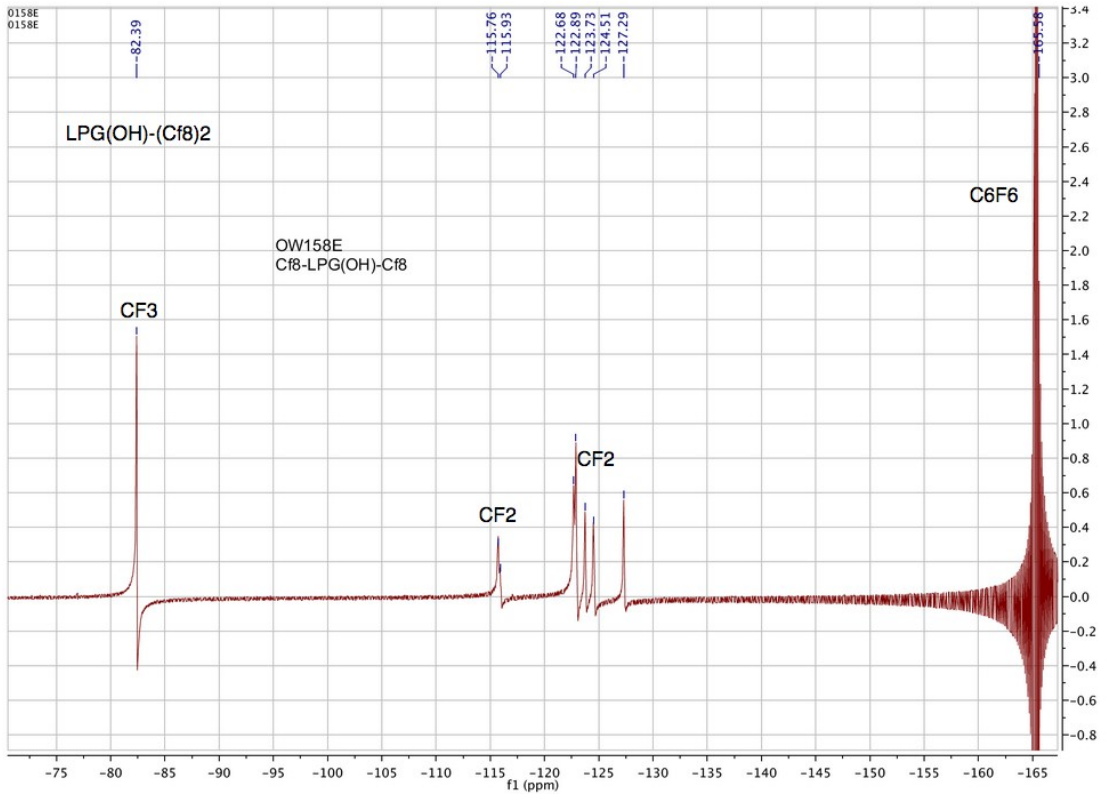


Fig. S8 – ^{19}F-NMR hydroxy amphiphile 4.

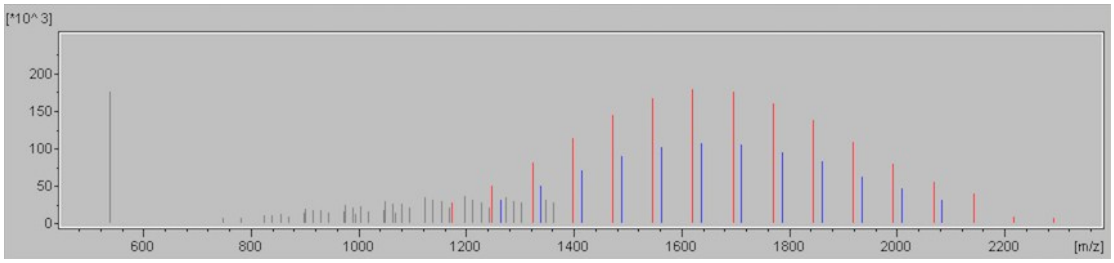


Fig. S9 – MS (MALDI-TOF): Hydroxy amphiphile 1: M_n / M_W = 1.02, Mn = 1689.8 [M (n = 13)+Na]$^+$.

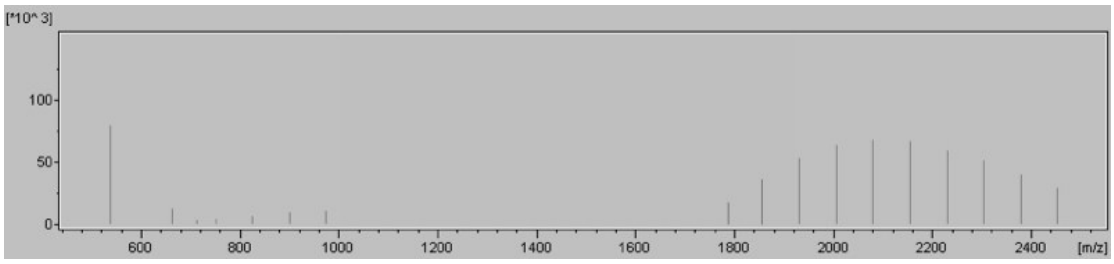


Fig. S10 – MS (MALDI-TOF): Hydroxy amphiphile 4: M_n / M_W = 1.02, Mn = 2151.5 [M (n = 13)+H]$^+$.

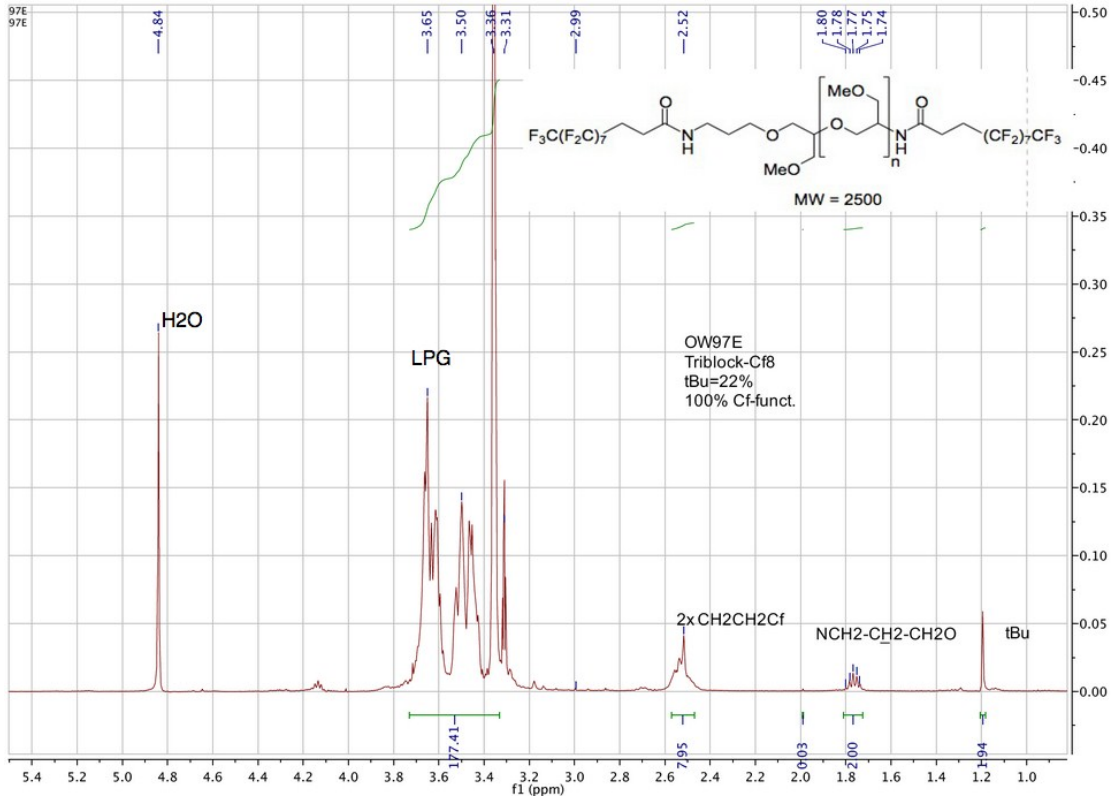


Fig. S11 – ^{1}H-NMR methoxy amphiphile 5.

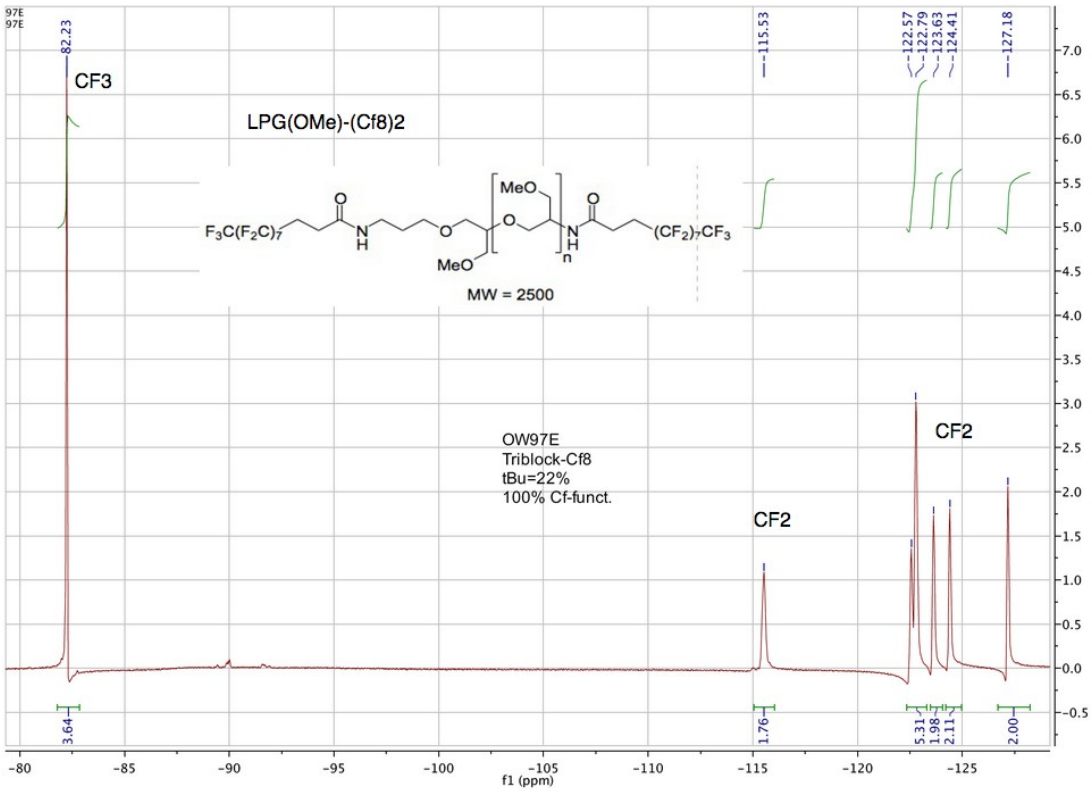


Fig. S12 – ^{19}F-NMR methoxy amphiphile 5.

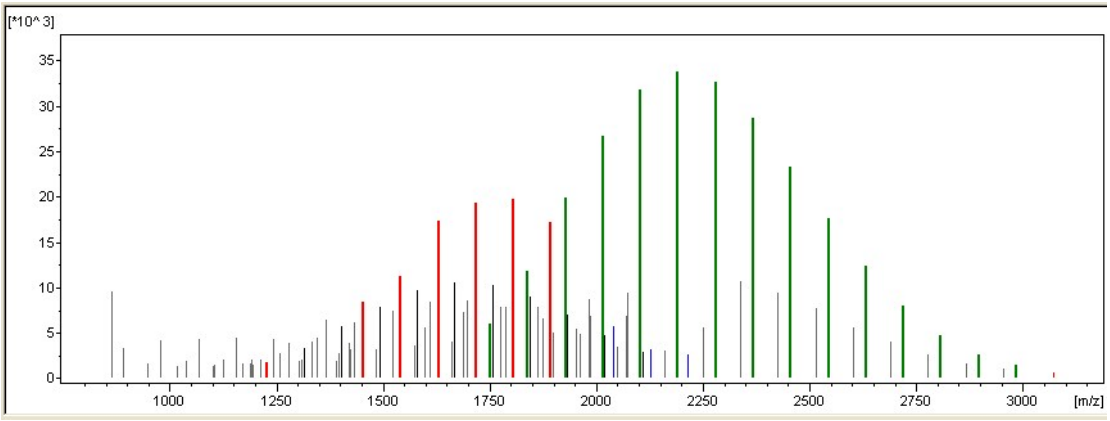


Fig. S13 – MS (MALDI-TOF): Methoxy amphiphiles: MS (MALDI-TOF): 2 mono-R_{f8}: M_n / M_W = 1.02, Mn = 1802.8 [M (n = 15)+Na]$^+$ (red), 5 di-R_{f8}: M_n / M_W = 1.02, Mn = 2277.9 [M (n = 15)+H]$^+$ (green).

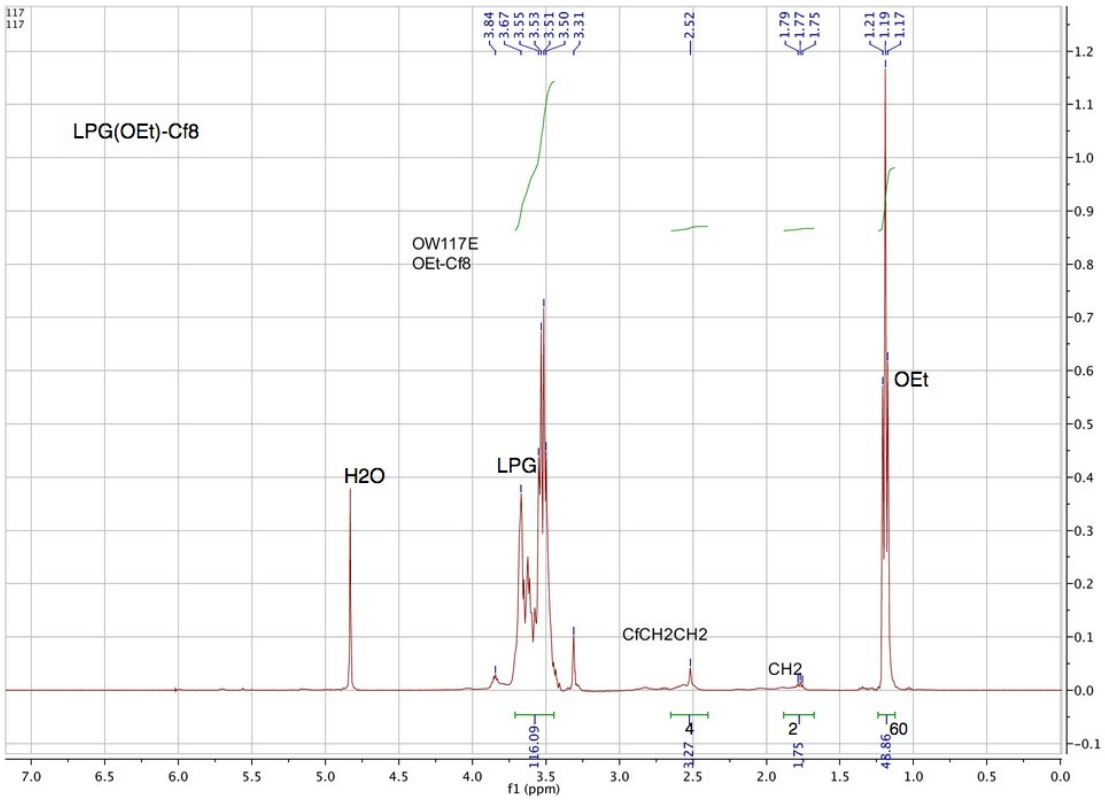


Fig. S14 – ^{1}H-NMR ethoxy amphiphile 3.

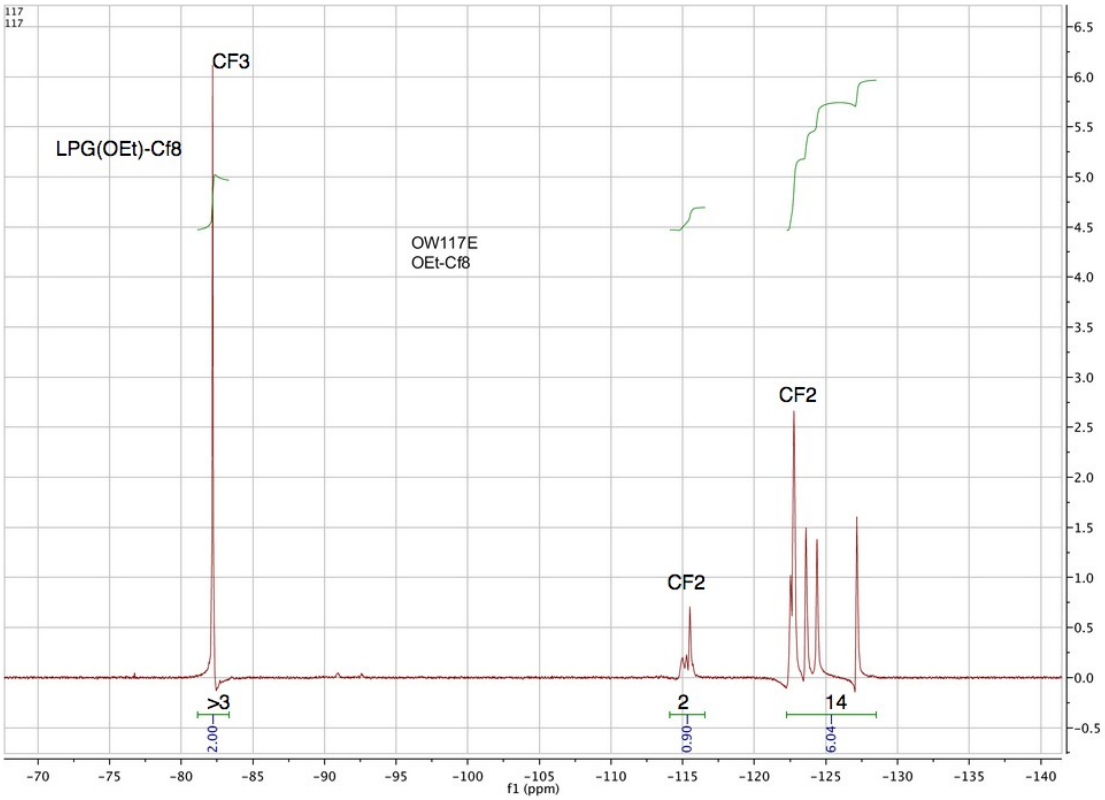


Fig. S15 – ^{19}F-NMR methoxy amphiphile 3.

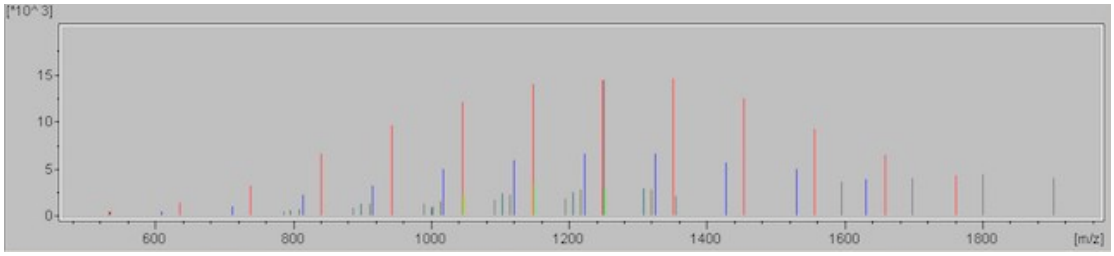


Fig. S16 – MS (MALDI-TOF): Ethoxy amphiphile 3: M_n / M_W = 1.05, Mn = 1555.7 $[M (n = 11)+Na]^+$.

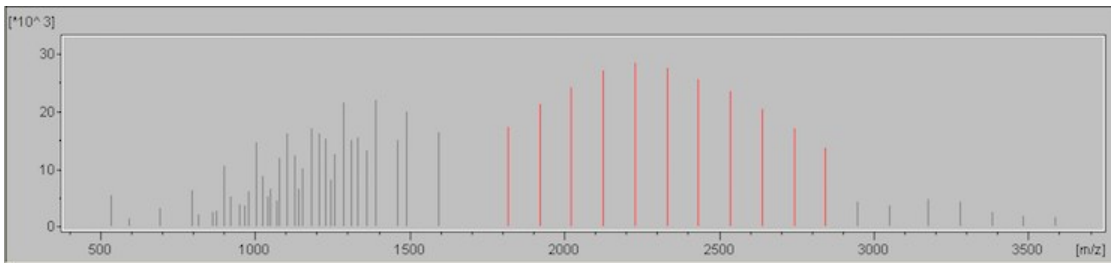


Fig. S17 – MS (MALDI-TOF): Ethoxy amphiphile 6: M_n / M_W = 1.04, Mn = 2190.9 $[M (n = 12)+H]^+$.

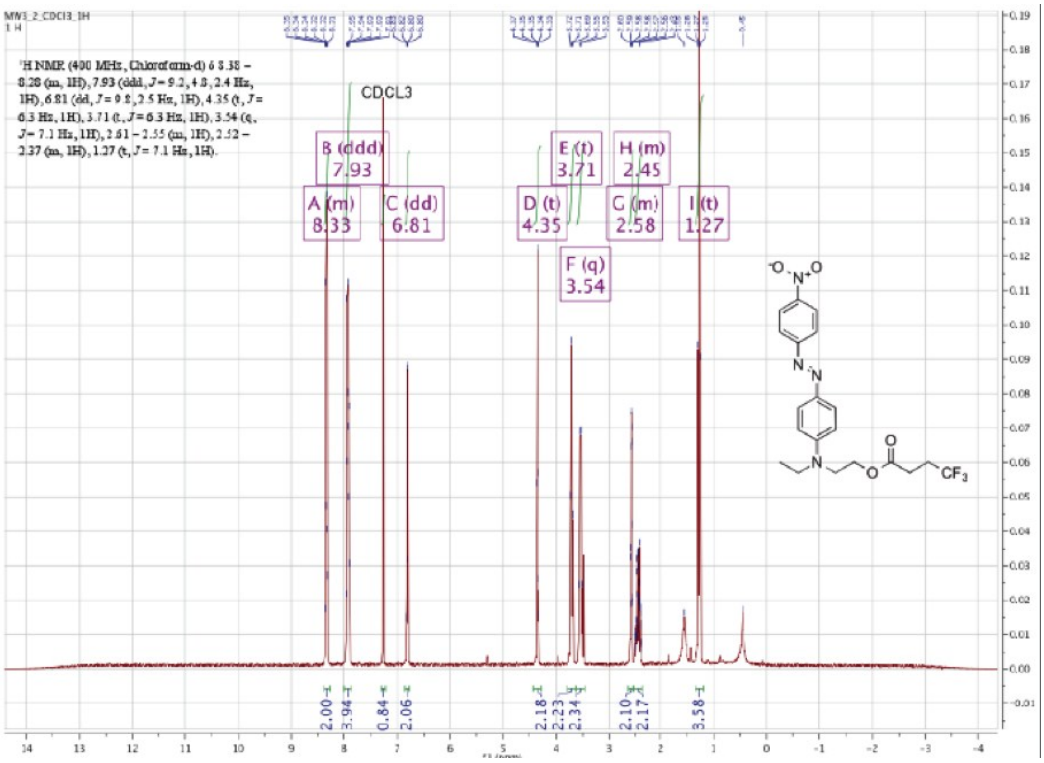


Fig. S18 – ^{1}H-NMR DR-CF_3 18.

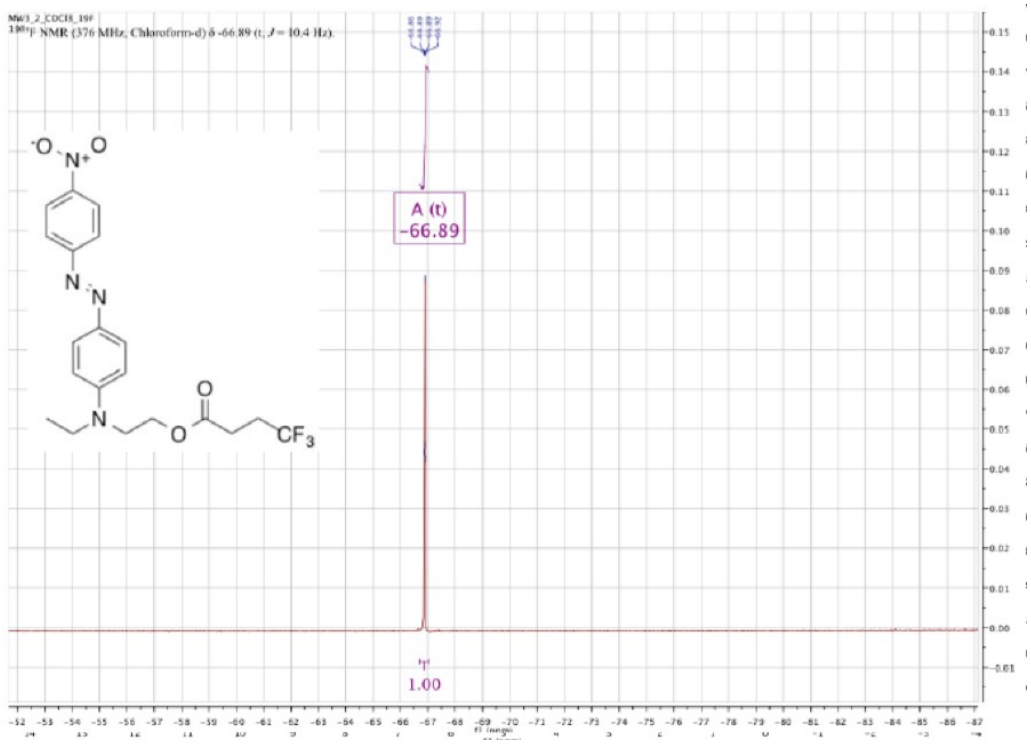


Fig. S19 – ^{19}F-NMR of DR-CF_3 18.

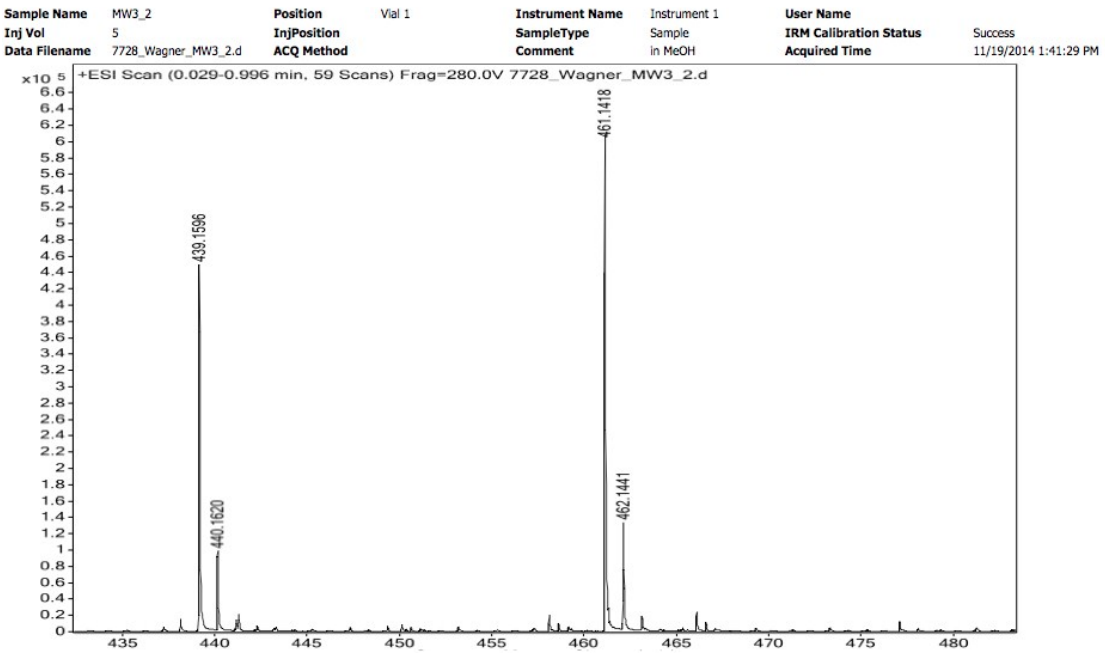


Fig. S20 – MS (ESI-TOF) of DR-CF_3 18: m/z= 439.16 $[M+H]^+$, 461.14 $[M+Na]^+$.

10. References

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