Supplementary Material (ESI) for Chemical Communications

Supplementary Information

A triblock fluorous surfactant as a specific gelator for perfluorocarbons

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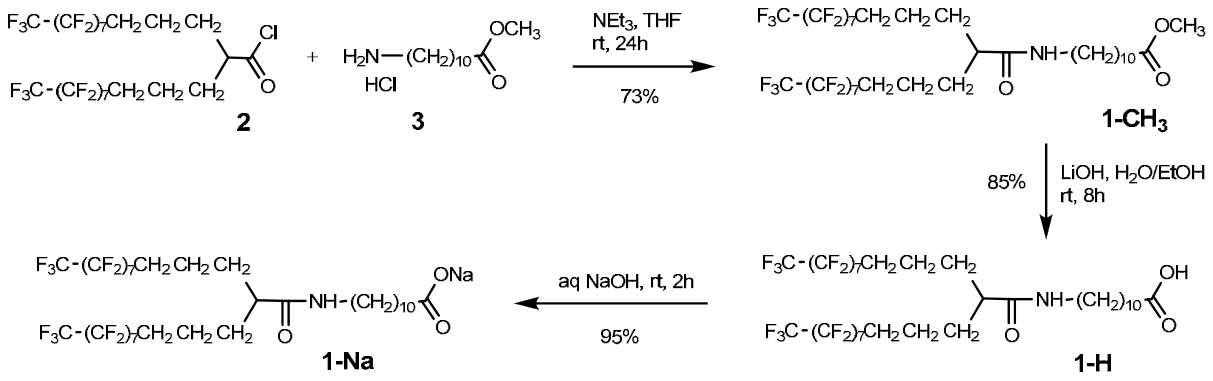
General: NMR analysis were carried out on spectrometers Bruker AC-250 FT (250 MHz for proton, 63 MHz for carbon) and Bruker DPX-300 (300 MHz for proton, 75.5 MHz for carbon). The chemical shifts (δ) for carbon and proton are given compared to the internal reference (TMS) and are expressed in ppm. MALDI-MS spectra were recorded in the positive mode by using a 2,5-dihydroxy-benzoic acid in dioxane as matrix. Infrared spectrum was recorded directly on powder of **1-Na** on a Perkin Elmer Spectrum 100 FTIR spectrometer at room temperature equipped with a Pike Miracle™ single reflection ATR system. The spectrum (from 4000 to 650 cm^{-1}) was obtained from 20 scans, with a resolution of 1 cm^{-1}. Melting points were uncorrected. All commercially available materials were used without further purification unless otherwise stated. THF was distilled over sodium/benzophenone.

Synthesis of 1-Na:



- Synthesis of 11-[N-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-tridecanoyl]amino undecanoate, 1-CH_3

A mixture of Methyl 11-aminoundecanoate hydrochloride **3** (82 mg, 0.326 mmol) and triethylamine (100 mg, 0.99 mmol) were dissolved in dry CH_2Cl_2 (20 mL) under nitrogen and then cooled at 0°C. Then a THF solution of 6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecanoic chloride[1] **2** (326 mg, 0.326 mmol) was added over 30 min. The mixture was stirred at room temperature overnight. Solvent was removed under reduced pressure. The residue was then dissolved in 20 mL CH_2Cl_2, washed with 1N HCl solution, dried over Na_2SO_4 and then filtered. Removal of the solvent yielded 284 mg (73%) of **1-CH_3** as a white powder. Mp 56-58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.56 (t, ^3J = 6.05 Hz, 1H), 3.66 (s, 3H), 3.27 (m, 2H), 2.29 (t, , ^3J = 7.5, 2H), 2.03 (m, 5H), 1.88-1.40 (m, 12H), 1.40-1.10 (m, 12H); ^{13}C NMR (62.9 MHz $CDCl_3$) δ = 174.7, 174.5, 51.7, 48.1, 39.9, 34.4, 32.7, 31.2, 30.0, 29.7 (2C), 29.6, 29.5, 29.4, 27.3, 25.3, 18.8; MS MALDI: m/z = 1200.6 [M+Na^+]; elemental anal. Calcd. For $C_{36}H_{37}NO_3F_{34}$: C, 36.72; H, 3.17, found C, 36.49; H, 3.01.

- Synthesis of 11-[N-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10, 11,11,11-heptadecafluoroundecyl)-tridecanoyl]amino undecanoic acid, 1-H

Ester **1-CH_3** (140mg, 0.12 mmol) and lithium hydroxide (34 mg, 1.42 mmol) were dissolved in 10 mL ethanol and 5 mL water, and stirred at 20°C for 8h. Ethanol was removed and the solution was acidified to pH = 5 with 1 N hydrochloride solution and then stirred for 2h. The

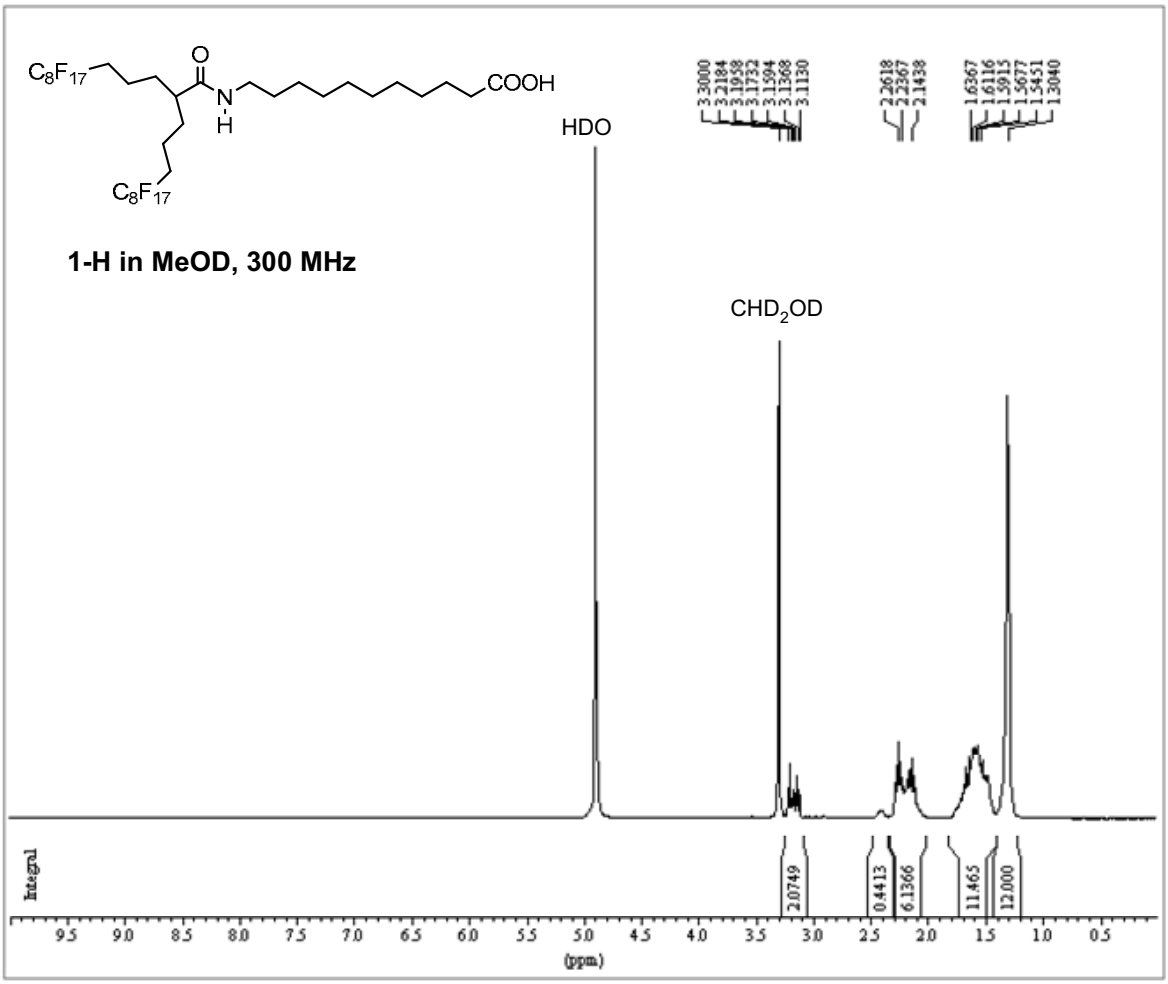
product was extracted with dichloromethane, the organic layer was dried over Na_2SO_4 and evaporated in vacuum to afford 119 mg (yield: 85%) of acid **1-H** as a colorless viscous oil. ^1H NMR (250 MHz, $CDCl_3$,) δ = 5.57 (t, J = 5.80, 1H), 3.28 (m, 2H), 2.34 (t, J = 7.33, 2H), 2.03 (m, 5H), 1.85-1.40 (m, 12H), 1.40-1.10 (m, 12H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 174.5, 174.3, 47.8, 39.5, 33.7, 32.3, 30.8, 29.6, 29.5, 29.2, 29.0, 28.9, 28.8, 26.8, 24.6, 18.4; MS MALDI: m/z = 1186.7 [$M+Na^+$].

- Synthesis of 11-[N-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-tridecanoyl]-aminoundecanoate sodium salt, 1-Na

Acid **1-H** (119 mg, 0.1 mmol) dissolved in 10 mL methanol was added to 100 mg of a 1N sodium hydroxide solution. The mixture was stirred at room temperature for 2h. Then the solvent was removed under vacuum. The product was washed with dichloromethane and dried to yield 115 mg of sodium salt **1-Na** in 95% yield as a white solid. Mp 195-197 °C; FT-IR: 3309, 2925, 2853, 1640, 1563, 1466, 1441, 1421, 1371, 1332, 1236, 1198, 1143, 1134, 1116, 1033, 746, 736, 722, 704 cm^{-1}.

Reference:

1 J. Loiseau, M. Lescanne, A. Colin, F. Fages, J.-B. Verlhac and J.-M. Vincent, *Tetrahedron*, 2002, **58**, 4049.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O
N
H
COOH
C8F17
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3.1958
3.1732
3.1594
3.1368
3.1130
2.2618
2.2367
2.1438
1.6367
1.6116
1.5915
1.5677
1.5451
1.5040
HDO
1-H in MeOD, 300 MHz
CHD2OD
Integral
2.0749
0.4413
6.1366
11.465
12.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)