Electronic Supplementing Information for

Frustrated Self-Assembly of Dendron and Dendrimer-Based Supramolecular Liquid Crystals

Raffaele Mezzenga[1,2,], Janne Ruokolainen[3], Nadia Canilho[1], Edis Kasëmi[4], Dieter A. Schlüter[4], Won Bo Lee[5], Glenn H. Fredrickson[5]*

[1]Department of Physics and Fribourg Center for Nanomaterials, Ch. du. Musée 3, CH-1700 Fribourg (Switzerland)

[2]Nestlé Research Center, Vers-Chez-les-Blancs, 1000, Lausanne 26 (Switzerland)

[3]Department of Engineering Physics, Helsinki University of Technology, Espoo, Finland

[4]Swiss Federal Institute of Technology, Department of Materials, Institute of Polymers, ETH-Zurich, HCI J 541, CH-8093, Zurich, (Switzerland)

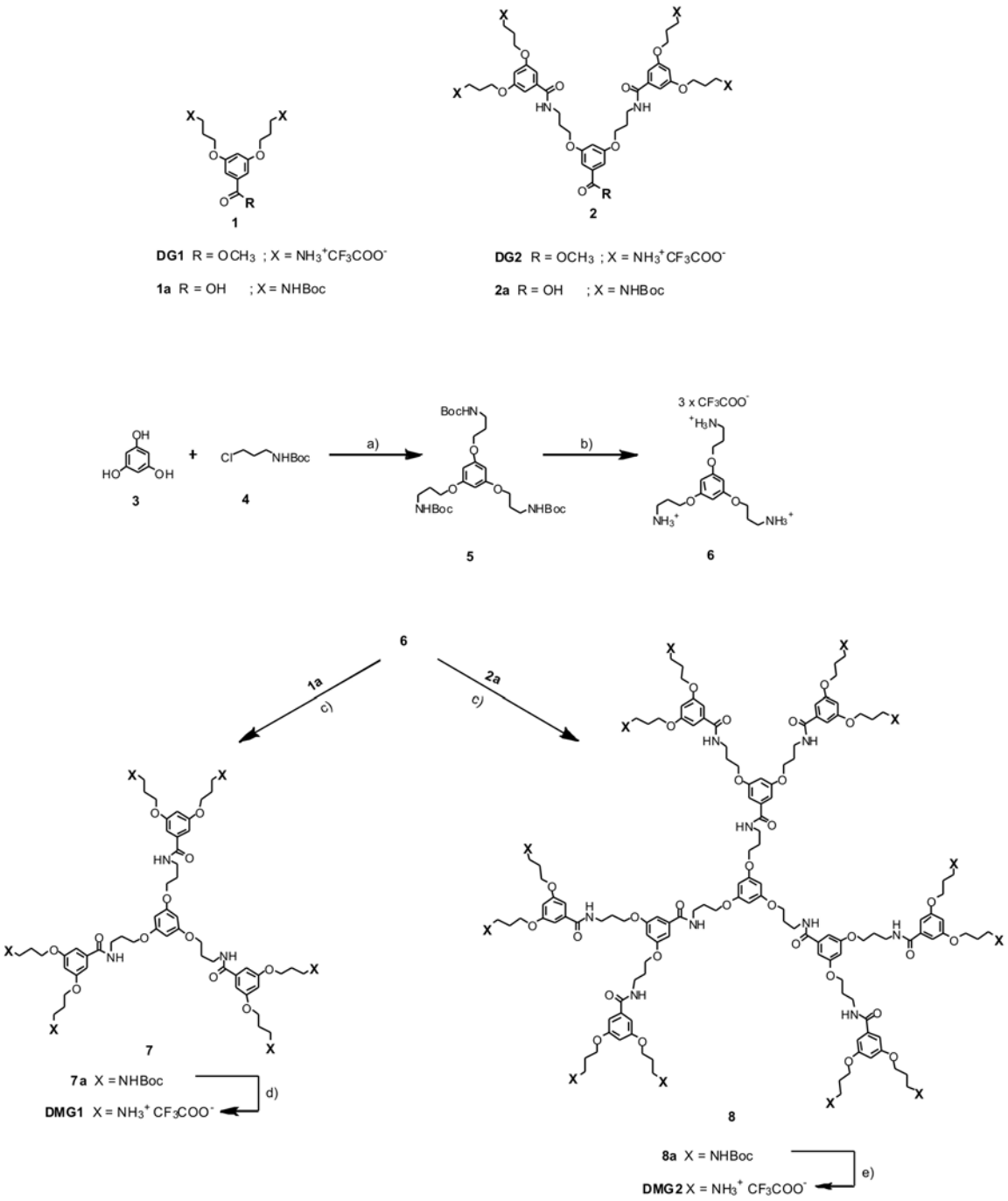
[5]Materials Research Laboratory, University of California, Santa Barbara, CA 93106

1. Synthesis of DG1, DG2, DMG1 and DMG2 dendritic structures

Scheme S1 depicts the synthetic procedure performed regarding dendrimers. The main reactions used are amide-coupling reactions (for dendrimer assembly) and standard protection-deprotection protocols. Although the synthetic steps are conventional and relatively easy to perform in good yield and purity, a few comments regarding synthetic issues are necessary.

The synthesis started with the Williamson-type etherification of commercially available 1,3,5-trihydroxybenzene **3** with Boc-protected 3-chloropropylamin **4** in diethyl ketone. This afforded the Boc-protected core molecule **5** on a 20 gram scale in 50% overall yield, indicative of a relatively high conversion per coupling step. The quantitative deprotection of **5** with neat TFA furnished brownish solid **6** to which then 4.5 – 5.5 equivalents of Boc-protected G1 dendrons **1a** and **2a** were attached by employing standard amide coupling reactions based on Hydroxybenzotriazole (HOBt) and *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) in DCM and DMF, respectively. Successive column chromatography purifications using different solvents mixtures gave dendrimers **7a** and **8a** in 52 – 65% yield. Reaction of **7a** and **8a** with large excess of TFA furnished positively charged **DMG1** and **DMG2** dendrimers having 6 and 12 free ammonium groups at the periphery, respectively.

The purity of the novel compounds was investigated by ^{1}H and ^{13}C NMR as well as mass spectroscopy and correct or almost correct data from combustion analysis. Although dendrimers are known to have a tendency to aggregate into larger clusters and thus give complex NMR spectra, these particular dendrimers did not cause any problems and the observed signals could be reliably integrated and assigned (see Synthetic Details).



Scheme S1 Reagents and conditions: a) **3**, **4** K_2CO_3 18-C-6, tetrabutylammonium iodide (TBAI), diethyl ketone, reflux, 18h (51%), b) **5**, TFA, 12h, (95%); c) **6**, **1a** or **2a**, HOBt, EDC, DCM/MeOH or DMF/MeOH, -20°C, 24h, (52-65%); d) **7a**, TFA, 24h, (93%); 2) **8a**, TFA, 36h, (90%).

1a. Synthetic Details

General: Compounds **DG1**, **DG2**, **1a** and **1b,** were synthesized according to literature methods.[1] Other reagents were purchased from Aldrich, Across or Fluka.Tetrahydrofuran (THF) and triethylamine (TEA). They were refluxed over Na with benzophenone as indicator; dichloromethane (DCM) was dried by distilling over CaH_2. All other reagents and solvents were used as received. All reactions were performed under nitrogen atmosphere. Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm/ 230-400 mesh) was used as the stationary phase for column chromatography. Whenever possible, reactions were monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminum plates $60F_{254}$ (Merck). Compounds were detected by UV light (254 nm or 366 nm) and/or by treatment with a solution of ninhydrine in ethanol followed by heating. If not otherwise noted, ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and AV 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers at room temperature using chloroform-d as a solvent. High-resolution mass spectral (HRMS) analyses were performed by the MS-service of the Laboratorium für Organische Chemie at ETH Zürich. MALDI-MS were run on an IonSpec Ultra instrument where 2,5-dihydroxybenzoic acid (DHB), 2-[(2E)-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB) or 3-hydroxypyridine 2-carboxylic acid (3-HPA) served as the matrix. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. The samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules.

1,3,5-Tris [(tert-butoxycarbonylamino)propoxy)]benzene (5)

A solution of benzene-1,3,5-triol **3** (8.82 g, 70 mmol), 3-(*tert*-butyloxycarbonyl amino)propyl chloride **4** (49 g, 254 mmol), potassium carbonate (57.86 g, 419 mmol), 18-crown-6 (6.7 g, 25.37 mmol), TBAI (11.24 g, 30.45mmol) and sodium iodide (2.66 g, 17.76 mmol) in 1L of freshly distilled diethyl ketone was refluxed for 18 h. The solution was filtered, washed successively with saturated aqueous sodium hydrogen carbonate and brine, dried with magnesium sulphate, and evaporated *in vacuo*. Chromatographic separation (silica gel, DCM/methanol 30/1) yielded **5** as colorless liquid which then crystallized to solid (20.93 g, 51%).

R_f = 0.24 (DCM/MeOH 30/1); M.p. = 114 °C; ^{1}H NMR: δ = 1.46 (s, 27 H; Boc), 1.96 (m, 6 H; CH_2), 3.29 (t, 6 H; C$\underline{H_2}$NH), 3.95 (t, 6 H; PhOCH_2), 4.82 (t, 3 H, NH), 6.05 (s, 3 H, Ph) ppm.;^{13}C NMR: δ = 28.13 (C($\underline{C}H_3)_3$), 29.49 (CH_2), 38.02 (CH_2N), 65.69 (OCH_2), 79.22 ($\underline{C}(CH_3)_3$), 94.07, 161.63 (Ar), 156.02 (CO) ppm.;ESI: *m/z* (rel - %): 620.11 (100) $[M + Na]^+$, 636.11 (10) $[M + K]^+$; Elemental analysis (%) calcd. for $C_{30}H_{51}N_3O_9$ (597.75): C 60.28, H 8.60, N 7.03; found: C 60.16, H 8.63, N 6.96.

1,3,5-Tris(3-aminopropoxy)benzene tristrifluoroacetate (6)

To a solution of **5** (20 g, 33.45 mmol) in 100 ml of DCM, TFA (40 mL, 61.2 g, 536 mmol) was added. After stirring for 12 h, 30 mL of methanol was added and mixture was left stirring for 12 d. Evaporation of solvent without further purification gave brownish solid **6** (20.31 g, 95 %).

M.p. = 152 °C; ^{1}H NMR (CD_3OD): δ = 2.08 (m, 6 H; CH_2), 3.10 (t, 6 H; C$\underline{H_2}$NH), 4.02 (t, 6 H; PhOCH_2), 6.14 (s, 3 H, Ph) ppm. ;^{13}C NMR (CD_3OD): δ = 26.91 (CH_2), 37.14 (CH_2N), 64.88 (OCH_2), 94.07, 160.45 (Ar) ppm.; ESI: *m/z* (rel - %): 638.21 (100) $[M + H]^+$; Elemental analysis (%) calcd. for $C_{21}H_{30}N_3O_9F_9$ (639.47) C 39.44, H 4.73, N 6.57; found: C 39.62, H 4.72, N 6.47.

1,3,5-Tris(3-{3,5-bis[3-(tert-butoxycarbonylamino)propoxy]benzamido} propoxy) benzene (7a)

N-Hydroxybenzotriazole (2.77 g, 20.50 mmol) was added to a solution of acid **1a** (8 g, 17.08 mmol) in dry DCM (500 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (4.32 g, 22.55 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (5.31 g, 52.5 mmol) and **6** (2.33 g, 3.5 mmol) in methanol (10 mL) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 16 h, and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Two successive chromatographic separations (silica gel, DCM/MeOH 20/1 and Hexane/Ethylacetate 1/10) yielded **7a** as a colorless foam (3.74 g, 65 %).
R_f = 0.11 (DCM/MeOH 30/1); M.p. = 89 °C; ^{1}H NMR: δ = 1.44 (s, 54 H; Boc), 1.95 (m, 12 H; CH_2), 2.09 (m, 6 H; CH_2) 3.29 (t, 12 H; C$\underline{H_2}$NH), 3.62 (m, 6 H; C$\underline{H_2}$NH), 4.01 (m, 18 H; $PhOCH_2$), 4.92 (br, 6 H; NH), 6.07 (s, 3 H; Ph_{core}), 6.53 (t, 3 H; Ph), 6.91(dd, 6 H; Ph), 7.05 (t, 3 H; NH) ppm.; ^{13}C NMR: δ = 28.42 (C($\underline{C}H_3)_3$), 28.85, 29.50 (CH_2), 37.87 (CH_2N), 65.84, 66.39 (OCH_2), 79.30 ($\underline{C}(CH_3)_3$), 94.32 (Ph_{core}), 104.41, 105.72, 136.73, 156.31, 160.52 (Ar), 159.94 (CONH), 167.40 (CO) ppm.; HRMS-MALDI: *m/z* (rel-%): 1671.90 (100) $[M + Na]^+$, 1686.87 (20) $[M + K]^+$.; Elemental analysis (%) calcd. for $C_{84}H_{129}N_9O_{24}$ (1648.99): C 61.18, H 7.88, N 7.64; found: C 60.91, H 8.06, N 7.62.

1,3,5-Tris{3-[3,5-bis(3-aminopropoxy)benzamido]propoxy}benzene hexatrifluroacetate (DMG1)

To a solution of **DG1** (3.54 g, 2.14 mmol) in 150 ml of DCM, 24 mL of TFA (36.71 g, 322 mmol) was added. After stirring for 24 h, 30 mL of methanol was added and mixture was left stirring for 12 d. Evaporation of solvent without further purification gave brownish sticky liquid **DG1a** (3.5 g, 93 %).
^{1}H NMR (CD_3OD): 2.07 (m, 6 H; CH_2), 2.17 (m, 12 H; CH_2), 3.17 (t, 12 H; C$\underline{H_2}$NH), 3.56 (t, 6 H; C$\underline{H_2}$NH), 4.00 (m, 6 H; $PhOCH_2$), 4.15 (m, 12 H; $PhOCH_2$), 6.11 (s, 3

H; Ph_{core}), 6.74 (t, 3 H; Ph), 7.04 (dd, 6 H; Ph) ppm.; ^{13}C NMR (CD_3OD): δ = 26.91, 28.79 (CH_2), 37.07 (CH_2N), 65.12, 65.55 (OCH_2), 93.79 (Ph_{core}), 104.34, 105.76, 136.50, 159.79, 160.79 (Ar), 168.39 (CO) ppm.; MALDI-TOF: *m/z* 1199.76 [(M – $5CF_3COOH$) + K]$^+$.; Elemental analysis (%) calcd. for $C_{66}H_{87}N_9O_{24}F_{18}$ (1732.43): C 45.76, H 5.06, N 7.28; found: C 44.91, H 5.44, N 6.95.

1,3,5-Tris{3-[3,5-bis(3-{3,5-bis[3-(tert-butoxycarbonylamino)propoxy] benzamido}propoxy)benzamido]propoxy}benzene (8a)

N-Hydroxybenzotriazole (1.25 g, 9.24 mmol) was added to a solution of acid **8** (9 g, 7.7 mmol) in dry DMF (300 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (1.94 g, 10.16 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (3.64 g, 36 mmol) and **6** (1.53 g, 2.4 mmol) in methanol (10 mL) was added dropwise at -10°C. The resulting mixture was warmed to room temperature, stirred for 24 h, and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulphate and the solvent removed in vacuo. Two successive chromatographic separations (silica gel, DCM/MeOH 20/1 and Hexane/Ethylacetate 1/10) yielded **8a** as a colorless foam (4.67 g, 52 %).

R_f = 0.35 (DCM/MeOH 10/1); M.p. = 108 – 109 °C; ^1H NMR: δ = 1.40 (s, 108 H; Boc), 1.86, 2.00 (m, 42 H; CH_2), 3.22, 3.51 (t, 42 H; C$\underline{H_2}$NH), 3.89 (m, 42 H; $PhOCH_2$), 5.12 (br, 12 H; NH), 5.96 (s, 3 H; Ph_{core}), 6.38 (t, 3 H; Ph), 6.45 (dd, 6 H; Ph), 6.84 (t, 6 H; Ph), 6.90 (dd, 12 H; Ph), 7.47 (t, 3 H; NH) ppm.; ^{13}C NMR: δ = 28.44 (C($\underline{C}H_3)_3$), 28.68, 28.92, 29.50 (CH_2), 37.49, 37.75 (CH_2N), 65.77, 66.10, 66.41 (OCH_2), 79.19 ($\underline{C}(CH_3)_3$), 94.36 (Ph_{core}), 104.38, 105.80, 136.56, 136.41, 156.19, 156.24, 156.31, 159.79 (Ar), 159.90, 160.49 (CONH), 167.53, 167.58 (CO) ppm.; MALDI-TOF: *m/z* (rel-%): 3771.91 (60) [M + Na]$^+$, 3787.91 (10) [M + K]$^+$.; Elemental analysis (%) calcd. for $C_{192}H_{285}N_{21}O_{54}$ (3751.47): C 61.47, H 7.66, N 7.84; found: C 61.26, H 7.68, N 7.57.

1,3,5-Tris[3-(3,5-bis{3-[3,5-bis(3-aminopropoxy)benzamido]propoxy} benzamido)propoxy]benzene dodecatrifluroacetate (DMG2)

To a **8a** (2.18 g, 0.583 mmol), 25 mL of neat TFA (38 g, 333 mmol) was added. After stirring for 24 h, 20 mL of methanol was added and mixture was left stirring for 12 d. Evaporation of solvent without further purification gave brownish solid **DMG2** (2 g, 90 %).

M.p. = 96 – 98°C; ^{1}H NMR (CD_3OD): δ = 1.89, 1.93, 2.00 (m, 42 H; CH_2), 3.01, 3.17, 3.39 (m, 42 H; C$\underline{H_2}$NH), 3.82, 3.91, 3.97 (m, 42 H; $PhOCH_2$), 5.91 (s, 3 H; Ph_{core}), 6.48 (t, 3 H; Ph), 6.56 (t, 6 H; Ph), 6.82 (dd, 6 H; Ph), , 6.87 (dd, 12 H; Ph), 7.48, 8.44 (t, br 3 H; NH) ppm.; ^{13}C NMR (CD_3OD): δ = 28.30, 30.07, 30.15 (CH_2), 38.99, 38.47, 38.56 (CH_2N), 66.51, 67.11, 67.24 (OCH_2), 95.29 (Ph_{core}), 105.67, 105.76, 106.96, 107.2, 137.74, 137.83, 161.16, 161.57 (Ar), 169.75, 169.92 (CO) ppm.:HR-MALDI: *m/z* (rel-%): 2552 (100) [M – 12 CF_3COOH]$^{+}$.

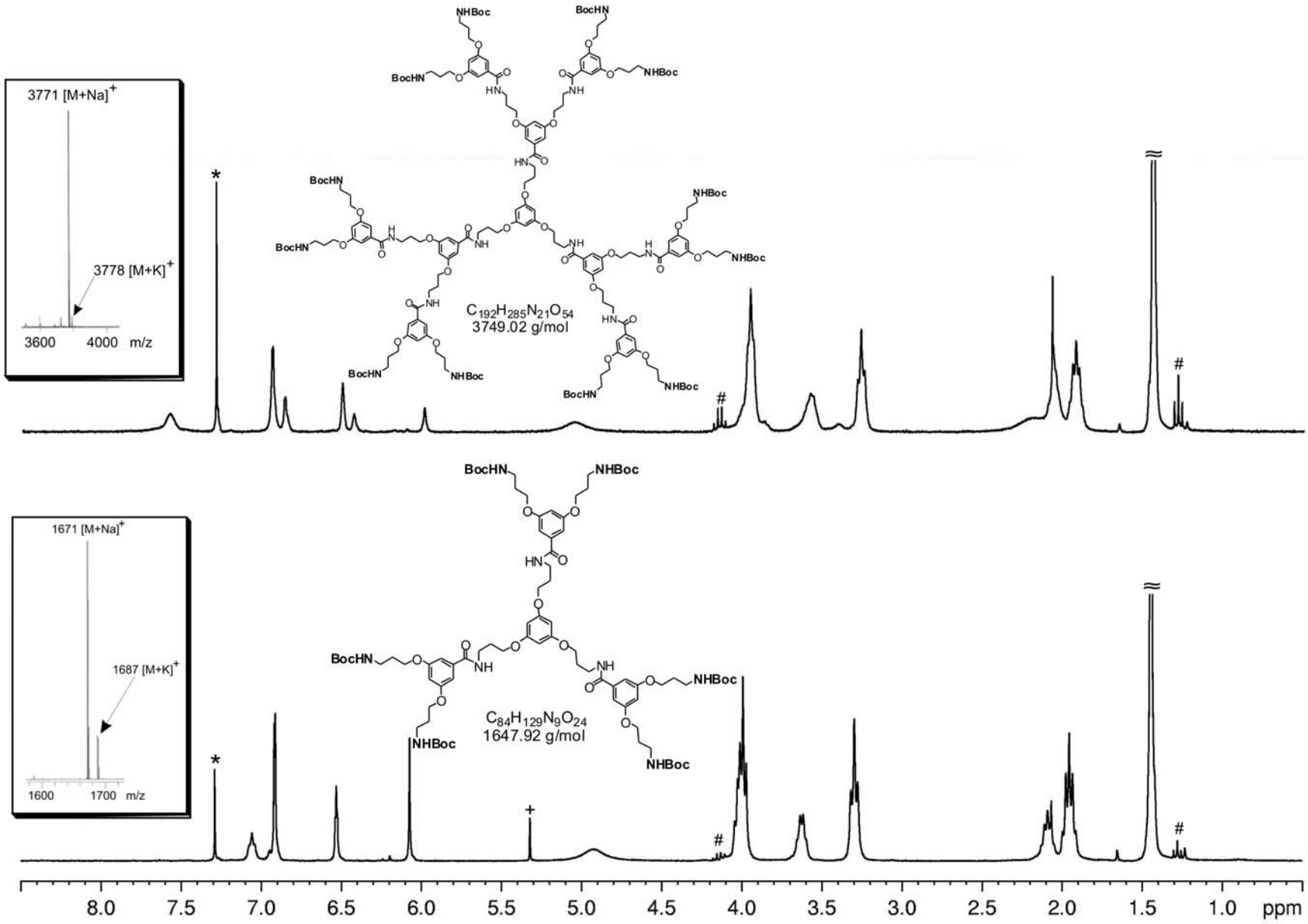


Figure S1. 300 MHz ^{1}H-NMR spectrum of the **7a** and **8a** dendrimers measured in $CDCl_3$ at 25°C together with their corresponding maldi-tof mass spectrum (*: chloroform, #: ethylacetate, and +: DCM).

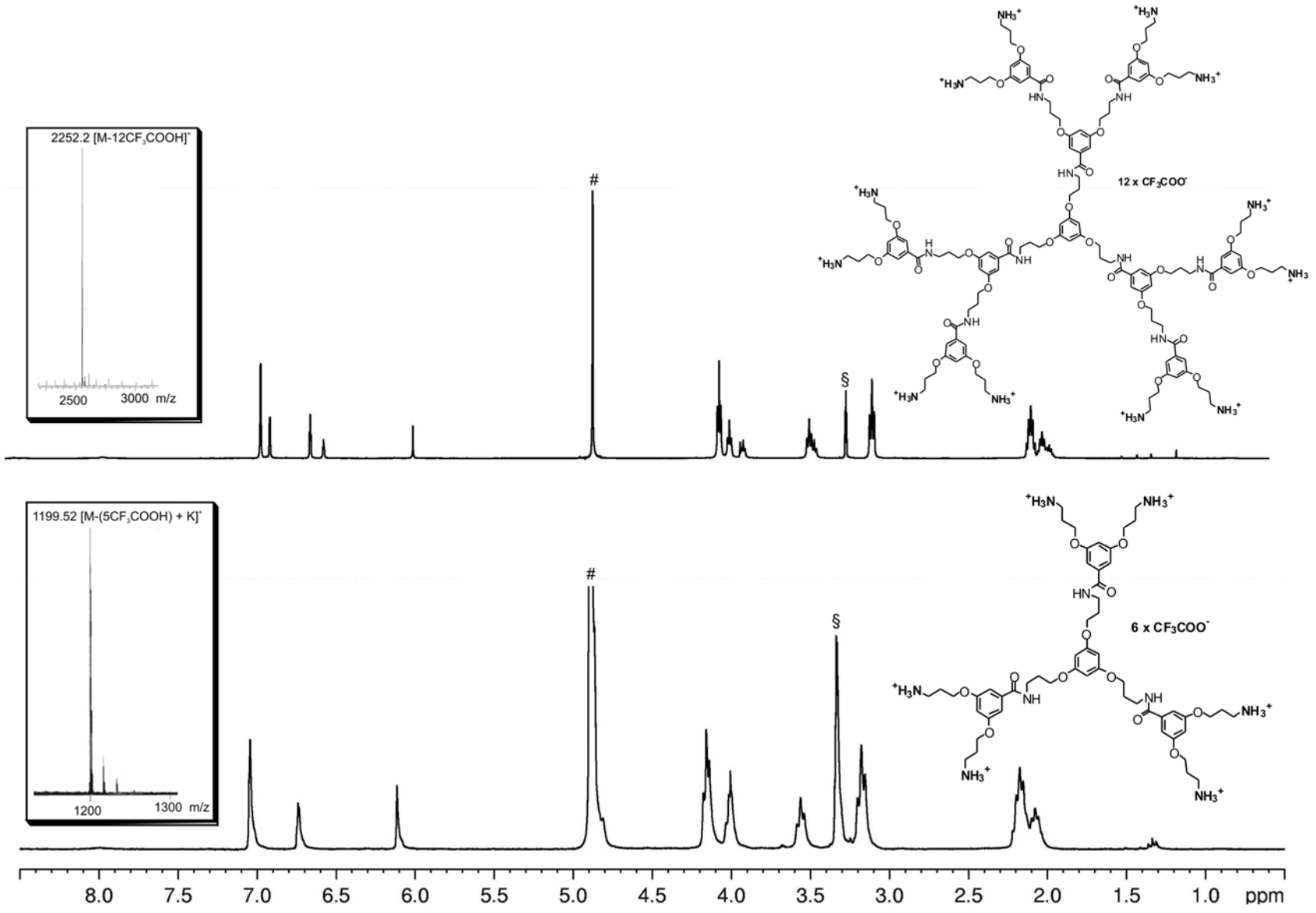


Figure S2. 500 MHz ^{1}H-NMR spectrum of the **DMG1** and **DMG2** dendrimers measured in CD_3OD at 25°C together with their corresponding maldi-tof mass spectrum (**#** : water and §: methanol).

2. Preparation of DG1-C_x, DG2-C_x, DMG1-C_x and DMG2-C_x complexes

Between 30 to 50 mg of deprotected dendron and dendrimers G1 and G2 carrying respectively at the periphery 2, 4, 6 and 12 charged ammonium groups and the same number of trifluoroacetic acid counter ions, were dissolved in 20 ml of water. In order to prepare the ionic complexes at the stoichiometric ratio, an equivalent molar mass of monoalkyl and dialkyl sulfate salt surfactants were individually dissolved in water in the case of C8, C12, C14 and sulphate butyl oleate (SBO) and in a mixture of 1-butanol/water/ethanol (88 wt %, 11 wt %, 1.3 wt %) for C18 due to its poor solubility in water. The pH of all the solutions were maintain at or below 3,45 to prevent the deprotonation of the acidic counter ion which could compete with the interactions between the dendritic periphery and the surfactant polar head causing a decrease in the complexation yield. The volume of the surfactant solutions was adjusted in order to maintain the surfactant concentrations below the critical micelle concentration (cmc). The complexes were obtained by adding dropwise the surfactant-rich solution in the corresponding dendritic solutions under continuous stirring. The dendritic solutions became quickly turbid and the complex aggregates eventually precipitated out of the supernatant solution. Ultracentrifugation was also used to enhance precipitation of the aggregates. The complexes made with C8, C12, C14 and SBO were rinsed with acidic water at pH below 3.45 and centrifuged, complexes made with C18 were only centrifuged owing there poor solubility in organic solvents. The pure complexes were collected and dried under vacuum at 35°C over one night. In all complexes 19F NMR analyses gave no residual trifluroacetate peak even after a large number of scanning and amplification of the signal, in support of a full exchange with sulfate alkyl tails. Elemental analysis and ^{1}H-NMR for both the dendron DG1 and DG2 and dendrimer DMG1 and DMG2 confirmed a nearly-stoichiometric complexation of the dendritic structures with the various sulfate surfactants (see Figure S3, Figure S4 and Table S1).

3. Thermal Annealing of DG1-C_x, DG2-C_x, DMG1-C_x and DMG2-C_x complexes

The annealing treatment was applied over three days under high vacuum (10^{-8} mbar) at typically 50 °C for the columnar phases and 80 °C for the lamellae phases. Those temperatures were selected because they are comprised between the melting temperature of the surfactant alkyl tails and the ordered-disordered temperature transition of the respective liquid crystalline phases, so to allow attaining thermodynamically stable structures.

4. Physical Characterization of of DG1-C_x, DG2-C_x, DMG1-C_x and DMG2-C_x complexes

SAXS and WAXS.

Simultaneous wide and small-angle X-rays scattering (SWAXS) experiments were performed using a SAXSess instrument (Anton Paar) with a line collimation setup. The system used a Cu Kα radiation source (λ = 0.1542 nm) and the generated beam was attenuated by a semitransparent nickel foil beam stop. A highly sensitive SWAXS imaging plate slide at 263.3 mm from the sample is used to collect the signal under vacuum. The sample holder was temperature controlled in the range comprised between 10 and 200 °C. Powder samples were clamped in between two mica foils and sandwiched in a steel sample holder for solids samples. Diffraction data shown in the present paper were acquired for 30 mn exposure and corrected by subtracting the mica background. All the scattering signals were treated with SAXSquant software by Anton Paar. Figure S5a shows the SAXS signals of DG1 prior to complexation, demonstrating its crystalline nature. Figure S5b obtained at room temperature for DMG1 complexed with C8, C12 and C18. DMG1-C8 present a broad peak characteristic of comb-like amorphous systems, while DMG1-C12 and DMG1-C18 present a liquid crystalline arrangement corresponding to a columnar hexagonal phase with a lattice period *a* of 3.7 nm and a lamellar phase with a layer spacing *d* of 4.7 nm, respectively. On Figure S6 the SWAXS signal of DMG1 and DG2 complexed with SBO are

also given. Differently from all the other samples, which were glassy or waxy, the SBO-complexes presented a liquid-like behaviour.

In order to determine the alkyl tail volume fraction reported in the Table 1 of the main text, dendron and dendrimer densities were measured through a Accupyc 1330 helium pycnometer from Micromeritics. The measurement method is based on Archimede's principle of fluid displacement and Boyle's law to determine the envelope volume of a solid. A reference volume was first measured with the empty cell at room temperature. Then ca 1g of extremely dried dendron and dendrimer were introduced in the cell and twenty cycles of measurements were acquired to yield accurate estimations of densities. The densities values reported by Table 1 in the main text are the averages values out of 20 series of measurements. Based on the measured densities, the alkyl tail volume fractions, ϕ_{ST}, were calculated for each ionic complexes following the expressions 1 and 2, respectively used in the case of dendron ionic complexes and dendrimer ionic complexes:

$$\phi_{ST} = \frac{\frac{2^j M_T}{\rho_S}}{\frac{M_D + 2^j M_H}{\rho_D} + \frac{2^j M_T}{\rho_S}} \qquad (1)$$

$$\phi_{ST} = \frac{\frac{3*(2^j M_T)}{\rho_S}}{\frac{M_D + 3*(2^j M_H)}{\rho_D} + \frac{3*(2^j M_T)}{\rho_S}} \qquad (2)$$

j gives the dendron/dendrimer generation, M_T, M_D and M_H represent the molecular masses of the surfactant alkyl tails, the dendron/dendrimer and the surfactant polar head, respectively. ρ_S and ρ_D are the densities of the surfactant and the dendron/dendrimer measured with the helium pycnometer. In the above calculations, volume fractions of the alkyl tail are calculated by considering the molar mass of the surfactant polar head as being part of the more polar dendron/dendrimer backbones.

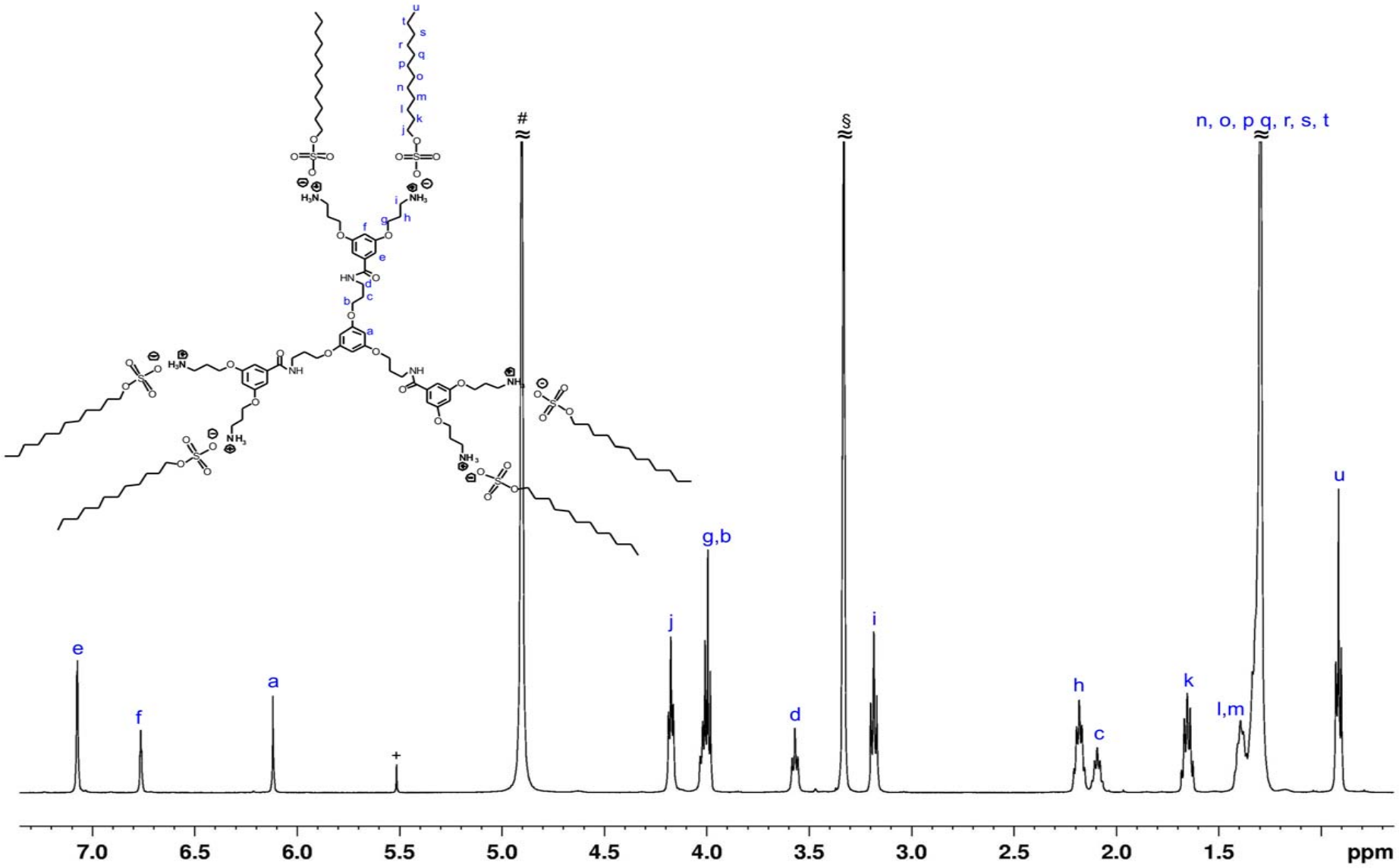


Figure S3. 500 MHz ^{1}H-NMR spectrum of the **DMG1-C12** complex measured in CD_3OD at 25°C (+: DCM, # : water and §: methanol).

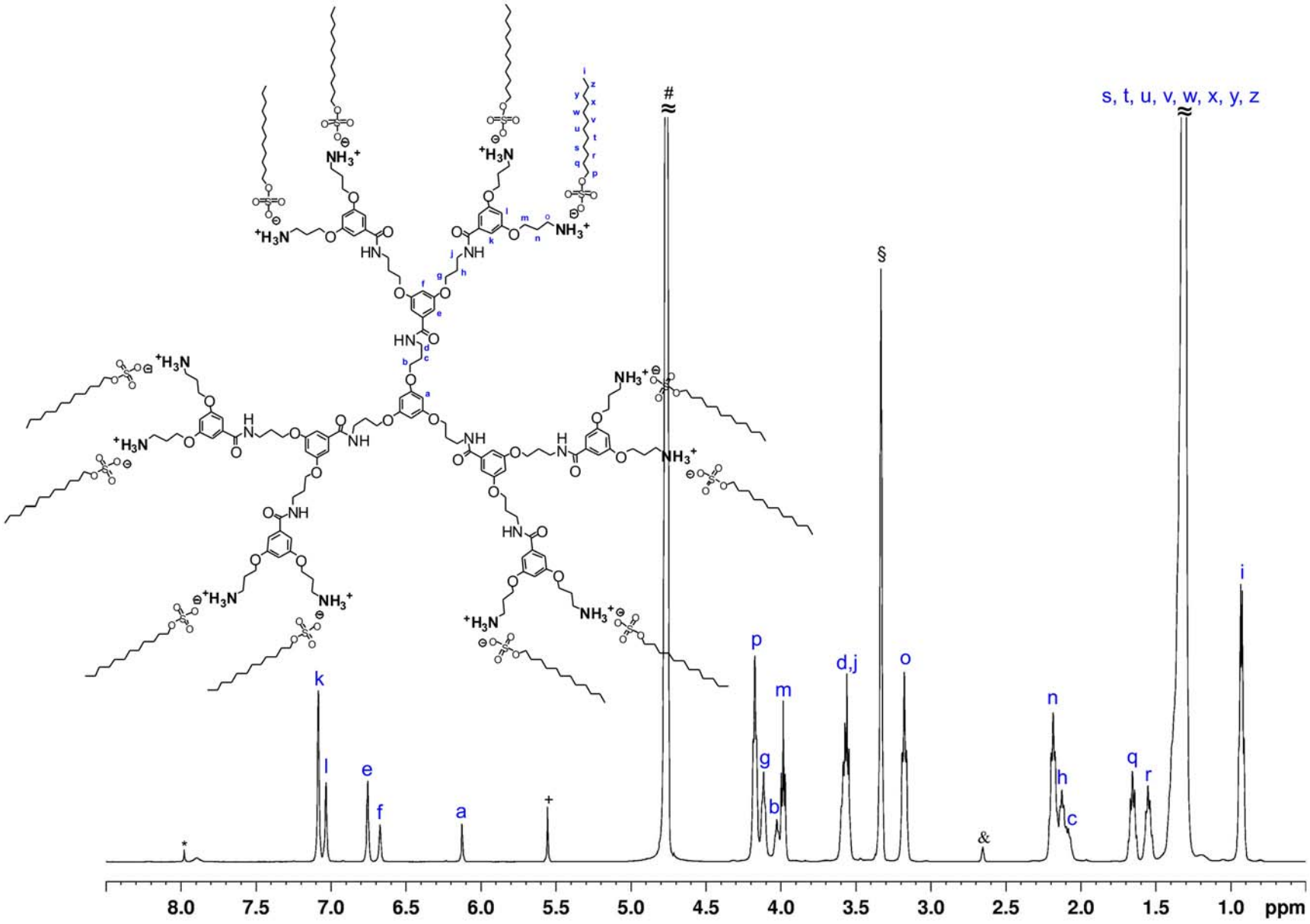


Figure S4. 500 MHz ^{1}H-NMR spectrum of the **DMG2-C12** complex measured in mixture of $CD_3OD/CDCl_3/(CD_3)_2SO$ (80/10/10 v/v) at 25°C.(+: DCM, # : water, §: methanol, *: chloroform and &: DMSO).

	Calc./Found (%) **C**	Calc./Found (%) **H**	Calc./Found (%) **N**
DG2-SBO	61.32/59.84	9.43/9.27	3.25/2.82
DMG1-SBO	61.46/62.50	9.59/9.40	3.36/2.85
DMG2-SBO	61.58/63.58	9.38/9.30	3.70/3.11
DG2-C14	58.81/57.03	9.15/9.10	4.29/4.54
DMG2-C12	57.68/54.09	8.79/8.45	5.12/5.23

Table S1. Elemental analysis results obtained for **DG2, DMG1** and **DMG2** complexed with **SBO** and for **DG2** and **DMG2** complexed with **C14** and **C12**, respectively.

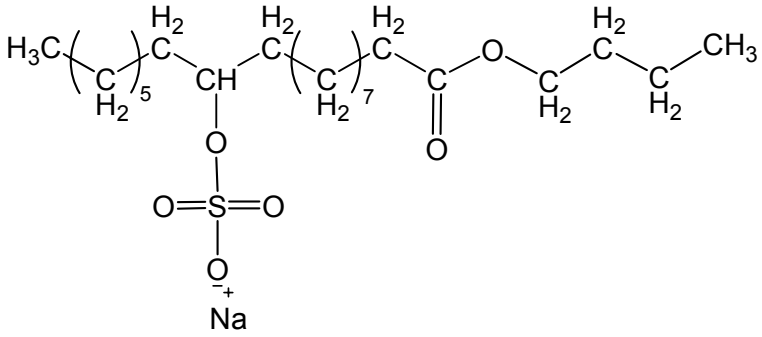
While all the complexes based on dendrons and dendrimers and C8, C12, C14 and C18 showed a hard glassy nature, irrespectively of the amorphous (C8, C12, C14) or crystalline (C18) nature of the alkyl tails, in the case of complexes with sulphate butyl oleate (SBO), soft, liquid-like or waxy complexes were obtained. SBO bears two non symmetric tails where one is extended by an alkyl acetate group which impedes crystallization of the chains, as shown in Scheme S2. This has the effect of increasing the volume fraction of the pendant chains to 0.65-0.71, depending on which dendron/dendrimer is attached to.

Therefore, the findings with SBO support structures in which the liquid-like pendant chains occupy the continuous domain and the glassy dendrons/dendrimers occupy the discrete domains, in agreement with simulations shown in Figure 4 of the main text. In fact, these samples, had such a liquid-like pronounced behaviour that sections successfully cryo-microtomed at -180°C did not survive the staining procedure, making impossible the direct identification of domains by TEM.

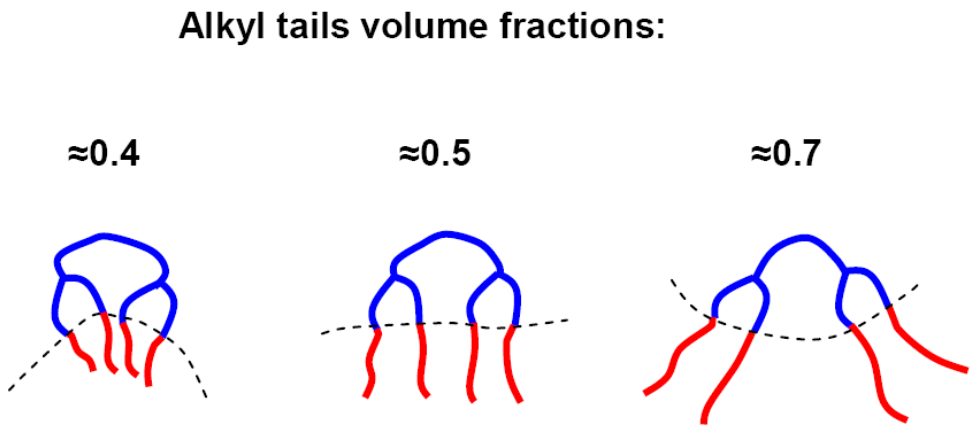
Scheme S3 gives a sketch of the evolution in curvature of the dendron/alkyl tails interface upon increasing the length/volume fraction of the side chains. Table S2 gives the lattice parameters as measured by SAXS for the for the various dendron/dendrimer-alkyl tail complexes investigated.

	DG2	DMG1	DMG2
C8	a= 3,8 b= 2,4	Amorphous	Amorphous
C12	3,6	3,7	3,8
C14	4,5	4,4	5,7
C18	4,6	4,7	5

Table S2. Lattice parameters expressed in nm, for the various dendron/dendrimer-alkyl tail complexes investigated



Scheme S2. Molecular Structure of Sulphate Butyl Oleate



Scheme S3. Sketch of the progressive changes in dendron/side chains interface curvature from "inverted" to "flat" to "direct" configurations upon increasing alkyl tail volume fraction (or chain lengths).

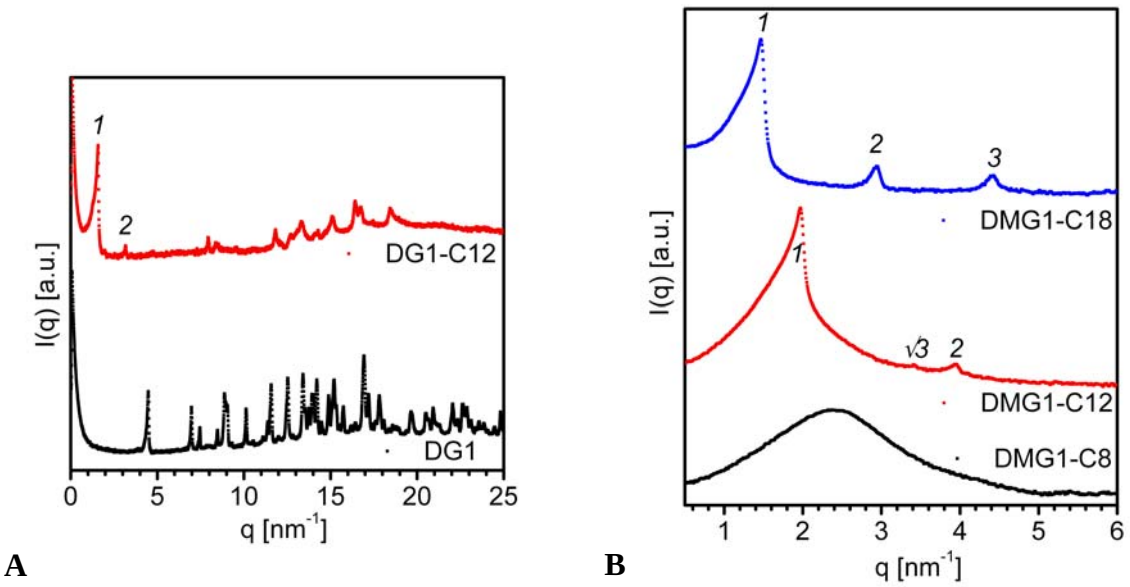


Figure S5. *(a)* SAXS profiles of uncomplexed **DG1** and **DG1-C12** demonstrating the compound crystalline of **DG1**. *(b)* SAXS diffraction profiles at room temperature for the **DMG1** complexed with **C8, C12** and **C18** corresponding respectively to an amorphous state (DMG1-C8), columnar hexagonal packing (DMG1-C12) and a lamellar phase (DMG1-C18).

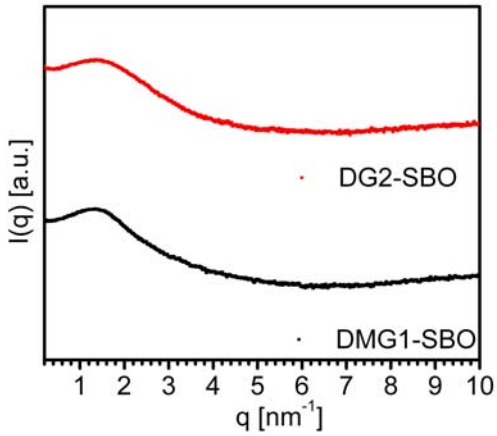


Figure S6. SAXS profiles at room temperature for **DMG1** and **DG2** complexed with **SBO.**

5. Self-Consistent Field Theory Simulations

Self-consistent field theory (SCFT) calculations were performed for the dendron and dendrimer structures shown in Figure 4 of the main text. SCFT is based on a mesoscopic model of polymer chains that fully captures polymer connectivity and architecture, but employs a simplified model of segmental interactions and local chain statistics.[2] The interacting many-chain model is converted to a statistical field theory, which is analyzed within the mean-field approximation.[3-4] SCFT has been successfully applied to a wide variety of inhomogeneous polymer systems such as polymer alloys and block copolymers.[4-6]

In the present work, the dendron and dendrimer molecules are described as suitably branched (flexible) Gaussian chains with dissimilar segments interacting locally via Flory-Huggins type contact interactions (Flory parameter, χ) and an incompressibility constraint on the total segment density. We chose to fix χ =0.05 and the *end-to-end* chain length (spanning the free end of a lipid tail across the dendron/dendrimer to the end of a second lipid tail), N=1000, in the comparison molecules to establish appropriate length and interaction energy scales for potential mesophases. Specifically, this incompatibility between dendron segments and alkyl tails (χN=50) is strong enough to produce mesophases where the two components are highly segregated. Having fixed N, the remaining architectural parameter in the model is the volume fraction of alkyl tails in the molecule, f_C. It is important to note that the constraint of fixed N does not imply the three molecules are compared at the same overall molecular weight. Indeed, at the same N, the G2 dendrimer has 1.5 times the molecular weight of the G2 dendron.

The SCFT equations were solved numerically in unit cells with optimized shape and dimensions using advanced algorithms.[4,7,8,9] Given external field configurations, a single chain partition function and volume fractions are evaluated by solving a modified diffusion equation. The external fields are adjusted by means of various numerical convergence schemes.[4,7] Simultaneously, the stress is minimized with regard to the size and the shape of the unit cell by a variable cell shape method.[4] Phase boundaries are

calculated by comparing the calculated free energies of various phases at the same value of fc.

6. References

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