Synthesis, Langmuir and Langmuir–Blodgett film behaviour of new dendritic amphiphiles

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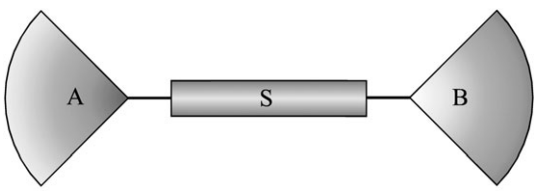
New amphiphilic compounds **1–9** that feature a construction with dendronized hydrophilic and hydrophobic segment groups connected to a specific aromatic or aliphatic spacer unit have been synthesized, following a modular building block strategy. The hydrophilic dendrons are typically branched elements with peripheral carboxylic groups, unlike the hydrophobic dendrons that contain peripheral alkyl chains as part of respective amide functions. The hydrophilic dendrons are in different generations of branching, while the hydrophobic dendrons are all in the first generation of branching (three terminal branching), but differ in the length of the alkyl chains, thus giving rise to designed structure and amphiphilic properties in the new compounds. The resulting surfactants are capable of forming well-defined Langmuir films of remarkable stability when spread from a solution onto an aqueous subphase. Nevertheless, specific packing behaviour and orientation of the amphiphilic molecules were found, depending on the molecular structure, as determined using analysis of the surface pressure–area (π–A) isotherms. Langmuir–Blodgett transfer of the first monolayer from a pure water subphase to a clean silicon wafer proved possible for the amphiphiles of peripheral alkyl chain length C_{12}, while the amphiphiles with the longer alkyl chains failed, possibly due to the more rigid monolayers they form, impeding the transfer.

Introduction

Langmuir and Langmuir–Blodgett (LB) films continue to be topics of current interest,[1] both from theoretical and materials development points of view, involving supramolecular technology and systems relevant to biological processes.[2–4] This has stimulated the design of a great number of new amphiphilic structures, including the bolaamphiphiles and gemini surfactants as two important examples.[5,6] While the former type of amphiphilic molecule contains two water soluble segments attached to the termini of a hydrophobic unit, the latter consists of two amphiphilic components linked through a rigid or flexible spacer. In extension of these principles, a series of oligofunctional amphiphiles that profit from high structural preorganization have recently been described; *i.e.* a geometrically well-defined central building block composed of ethynylene substituted aromatic spacers, with different numbers of amphiphilic segment groups, which are also of rigid geometric design, was used.[7,8] Another topical concept of supramolecular chemistry, which is the strategy of multiple branching, has also been introduced into the design of new surfactant structures, yielding dendritic amphiphiles.[9] The multiple branching results in organic molecules with interesting properties and in highly stable non-crystalline supramolecular architectures. Within this context, arborol-type bolaamphiphiles as well as amphiphilic star dendrimers that combine two hemispheres with different hydrophobic and hydrophilic properties have been prepared.[10] The amphiphilic nature of these molecules disposes them to self-assemble at surfaces and at interfaces or during the generation of gels.[11]

Here, we present a particular type of diepitope dendritic amphiphile that is synthesized so that spacially separate dendronized hydrophilic and hydrophobic segment groups are connected to specific spacer units (Scheme 1). The hydrophilic dendrons are branched structures with peripheral carboxylic groups, while the hydrophobic dendrons contain peripheral alkyl chains as part of respective amide functions. The spacers connecting the dendronized segments feature a rigid aromatic or a flexible alkyl unit. The dendrons are in the same or different generations of branching, including also unilateral branching of the molecular structure, thus giving rise to changes in the hydrophilic and hydrophobic properties of the new dendritic amphiphiles, *i.e.* a gradual increase or



A Hydrophilic dendronized segment
B Hydrophobic dendronized segment
S Spacer unit

Scheme 1 Cartoon of the amphiphilic molecular structure.

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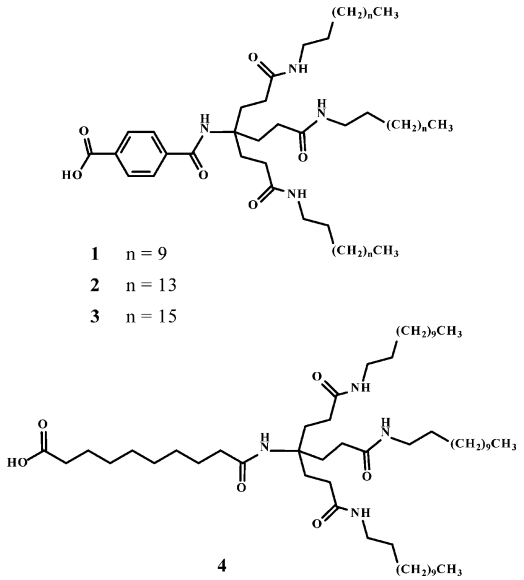
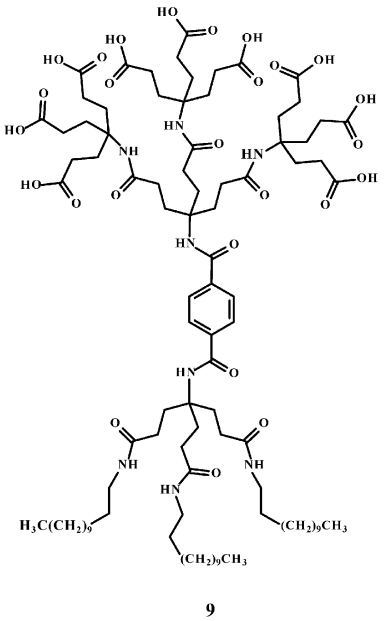


Scheme 2 First generation monodendritic amphiphiles **1–4**.



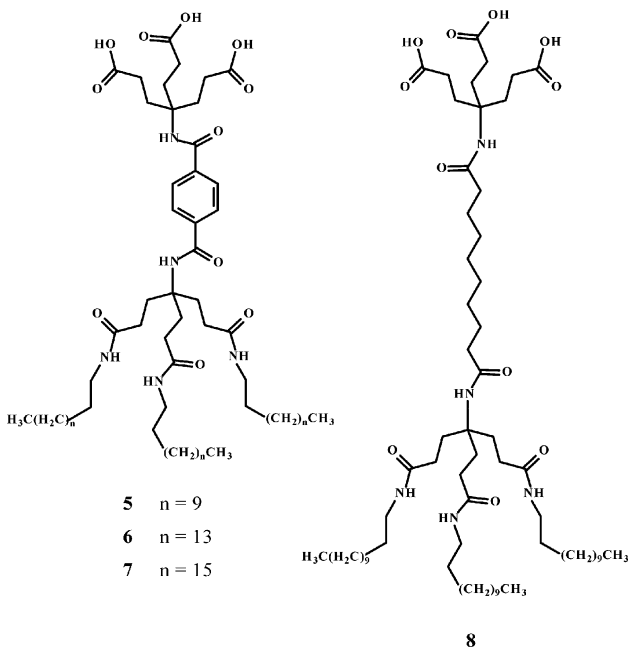
Scheme 4 Second-and-first generation bidendritic amphiphile **9**.

decrease, respectively (Schemes 2–4). We describe their synthesis based on a modular strategy and report on the influence of systematic structure variation on the Langmuir film behaviour and on the Langmuir–Blodgett monolayer transfer.

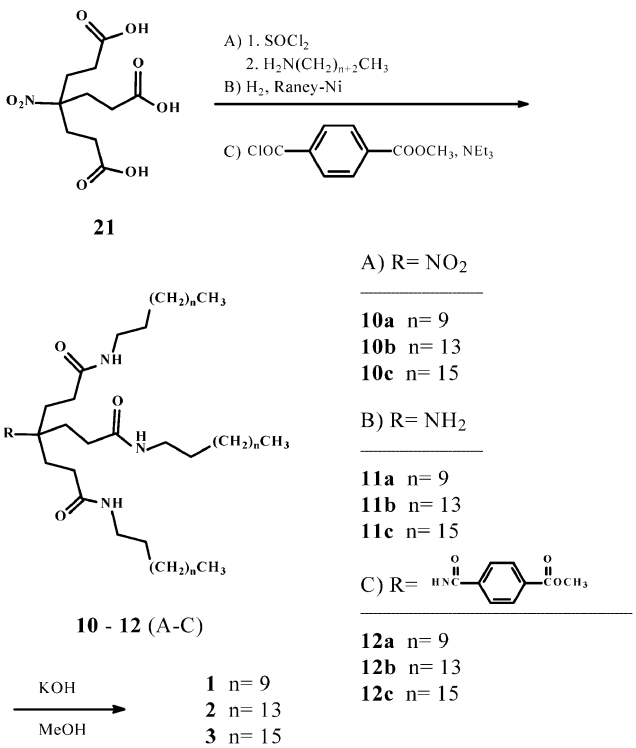
Results and discussion

Synthesis

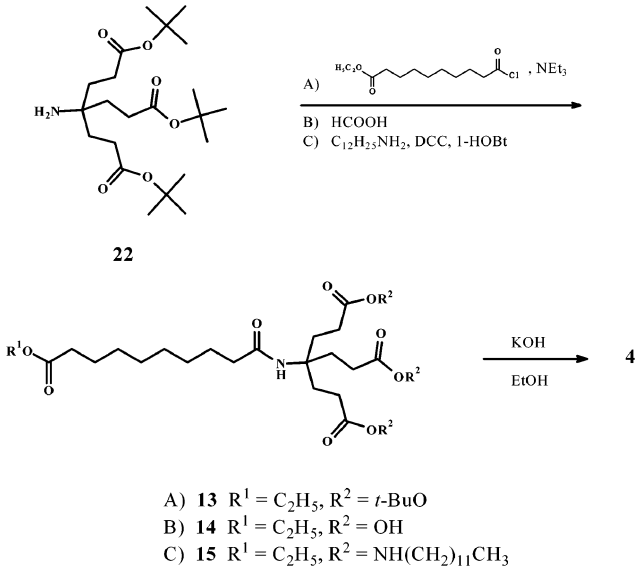
The chosen synthetic pathway for the new amphiphilic compounds follows a known basic strategy of dendrimer synthesis, which is the convergent synthetic approach.[11,12] This involves separate formation of the dendronized hydrophilic and hydrophobic segments, which are linked to the central spacer element one after the other, beginning with attachment of the hydrophobic dendron to produce an intermediate monodendritic amphiphile (Schemes 5–10). In order to connect the dendronized and spacer type building blocks, amide bonds are formed, but using two different methods. In the first coupling step, *i.e.* reaction between the hydrophobic amino-containing dendron and the bifunctional spacer, acid chloride activation



Scheme 3 First-and-first generation bidendritic amphiphiles **5–8**.



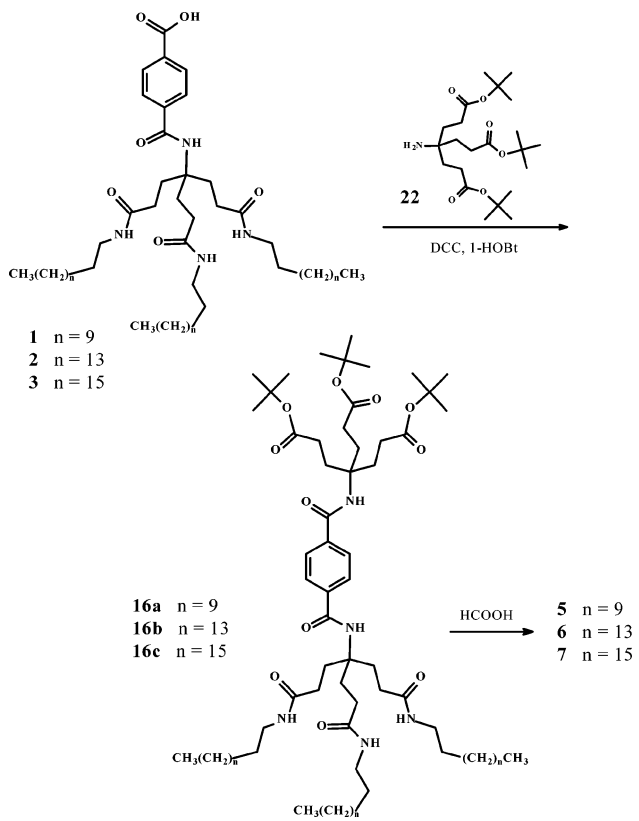
Scheme 5 Synthesis of the first generation monodendritic amphiphiles **1–3**, involving an aromatic spacer unit.



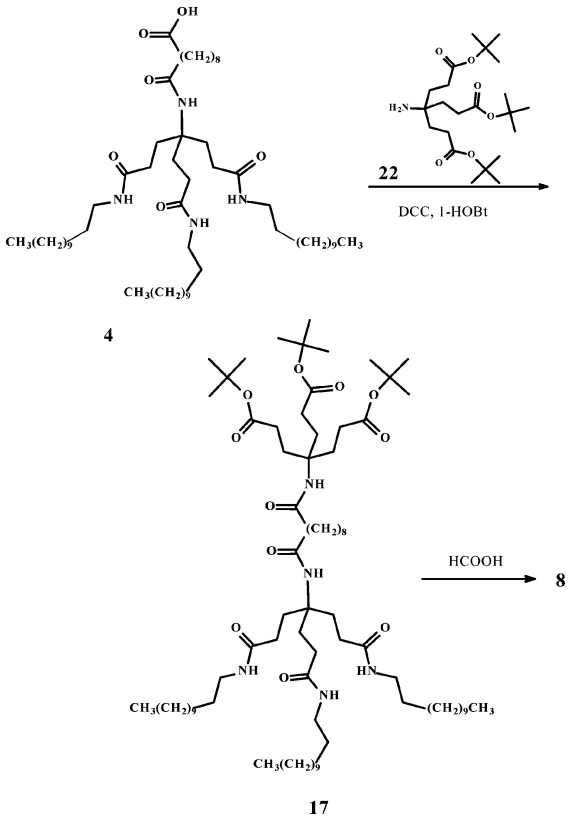
Scheme 6 Synthesis of the first generation monodendritic amphiphile **4**, involving an aliphatic spacer unit.

of the carboxylic spacer element was applied[13] (Schemes 5 and 6). While, in the second step, *i.e.* coupling between the hydrophilic dendron, which is temporarily ester blocked, and the monodendronized intermediate, the carbodiimide (DCC)–1-HOBt activation method[14] was used (Schemes 7, 8 and 10).

The hydrophobic dendrons **11a–c** (Scheme 5) that are capable of coupling were prepared from the nitro group-



Scheme 7 Synthesis of the first-and-first generation bidendritic amphiphiles **5–7**, involving an aromatic spacer unit.



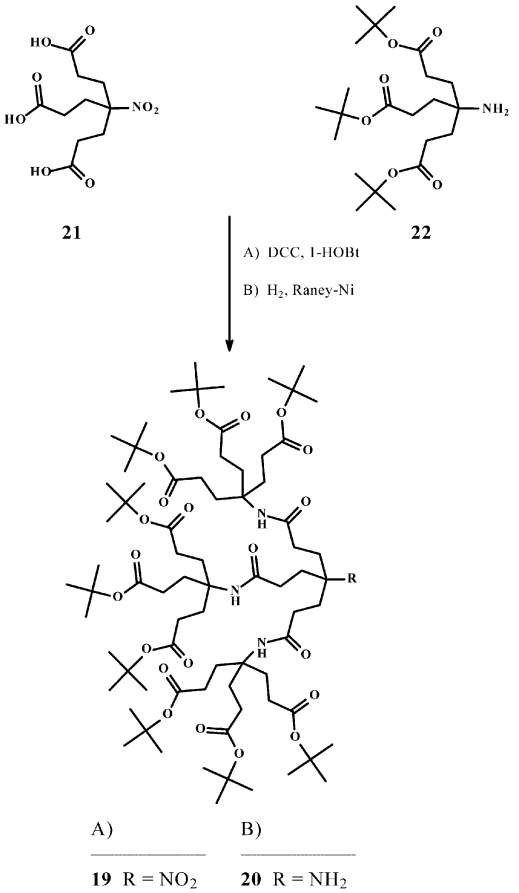
Scheme 8 Synthesis of first-and-first generation bidendritic amphiphile **8**, involving an aliphatic spacer unit.

containing tricarboxylic acid **21** *via* formation of the corresponding trifunctional acid chloride, which was immediately transformed into the respective amides **10a–c**. Their nitro groups were reduced with H_2–Raney-Ni to give the amines **11a–c**. The second generation nonacarboxylic ester dendron **20** (Scheme 9) that is capable of coupling was synthesized from **21** and the amino-containing triester **22**, using DCC–1-HOBt activated triamide formation, followed by H_2–Raney-Ni reduction.

The esters **12a–c** and **15** (Schemes 5 and 6) were hydrolyzed under basic conditions and acidified to yield the monodendritic amphiphiles **1–4**, respectively. The blocking *tert*-butyl groups of the oligoesters **16a–c**, **17** and **18** (Schemes 7, 8 and 10) were removed by treatment with formic acid, leading to the bidendritic amphiphiles **5–9**.

Langmuir monolayers

The Langmuir monolayer technique is an elegant method to prove two-dimensional molecular assembly behaviour of amphiphiles at the air–water interface, including control of molecular orientation and packing.[15] Thus, surface pressure (π) *versus* the area per molecule (A) isotherms (π–A isotherms) of the new dendritic amphiphiles **1–9** were measured. The respective compression isotherms were determined both on water and on 10^{-4} M aqueous $CaCl_2$ subphases, and were recorded on a Langmuir film balance at a defined pH value. The trace characteristics of the isotherms, arising during compression, give information on the phase conditions.[16]

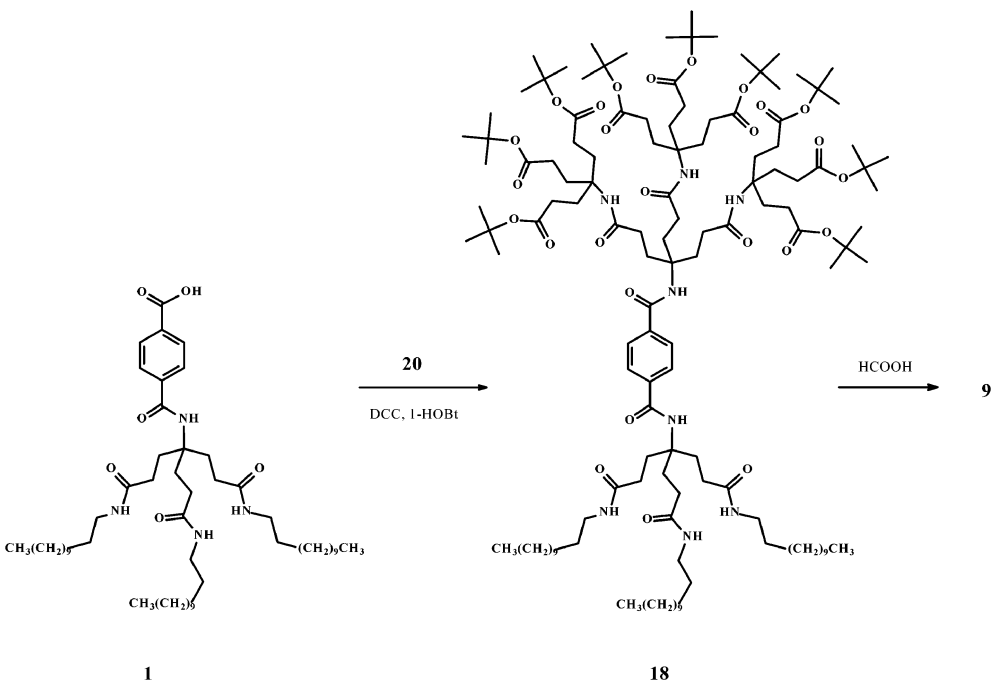


Scheme 9 Synthesis of the second generation dendronized intermediates **19** and **20**.

The π–A isotherms relating to the *monodendritic* amphiphiles **1–3** (Scheme 2) on a water subphase are shown in Fig. 1. Since these monocarboxylic acids differ only in the lengths of the aliphatic chains attached to the dendritic segment (dodecyl, hexadecyl and octadecyl, respectively), the distinctive features of the compression traces are significant.

In the case of compound **1**, which has three short dodecyl chains in the hydrophobic dendronized segment, a first repulsive interaction between the molecules is observed at an area per molecule of 1.36 nm^2, referred to as the lift-off area (Table 1). Both the absolute area per molecule and the amphiphilic structure of the molecule indicate a spontaneous "edge-on" orientation of the molecules after spreading. During further compression, the curve is typical of a rather small ascent, suggesting orientational flexibility of the alkyl substituents in the film. Obviously, the relatively short aliphatic chains result in less stable monolayers compared to the case of hexadecyl or octadecyl alkyl chains. This is also confirmed by the lower collapse pressure (Π) of 34.9 mN m^{-1} and the higher mean molecular collapse area (A_c) of 0.82 nm^2. This mean molecular collapse area, resulting from the steric conditions in the hydrophobic dendronized segment, by far exceeds the corresponding value of three upright standing alkyl chains. The conformational degrees of freedom of the C_{12} alkyl chains in this segment at T = 295 K do not allow for effective close packing of the molecules at the air–water interface. On extrapolation of the linear part of the isotherm to the film pressure π = 0 mN m^{-1}, the average required area per molecule (A_0) can be estimated, which is 1.14 nm^2 for compound **1** (Table 1).

The π–A isotherm of compound **2**, which has three C_{16} alkyl chains, again indicates a spontaneous "edge-on" orientation of the amphiphile after spreading. In contrast with compound **1**, a conformational rearrangement of the three alkyl substituents of the hydrophobic dendronized segment, in the range



Scheme 10 Synthesis of the second-and-first generation bidendritic amphiphile **9**.

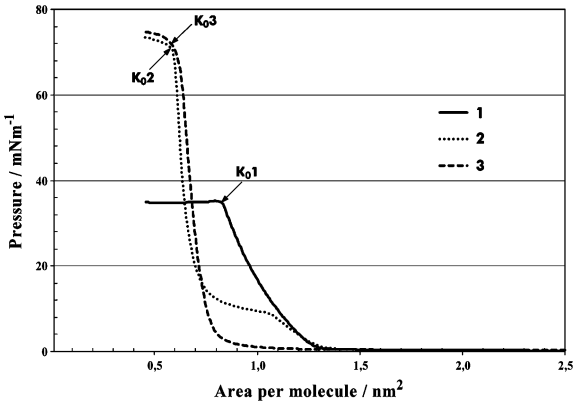


Fig. 1 Isotherms (π–A) of the monodendritic amphiphiles **1–3** on a pure water subphase at 25 °C.

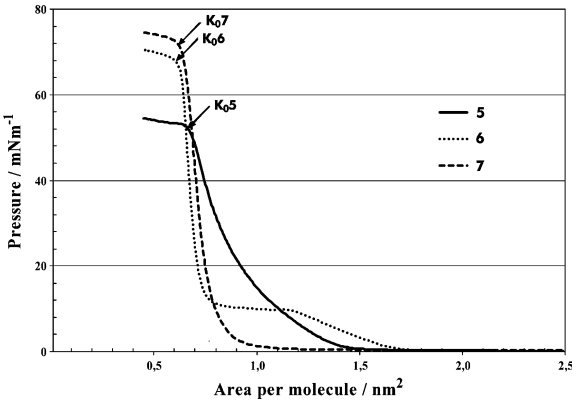


Fig. 2 Isotherms (π–A) of the bidendritic amphiphiles **5–7** on a pure water subphase at 25 °C.

of 1.44–0.75 nm^2 per molecule from a disordered to a—more or less—parallel packing, is indicated by a range of very small ascent. After completion of the pressure-induced conformational transition, further area reduction in the solid analogous phase leads to a steep, almost linear, increase in the surface pressure up to the collapse of the monolayer structure.

The π–A isotherm of the amphiphile **3** reveals only one distinct phase transition, at the lift-off area, which shows that the elongation of the alkyl chains from C_{16} to C_{18} results in a spontaneous aggregation of the three alkyl substituents of the hydrophobic dendronized segments of the "edge-on" oriented molecules without external pressure. These facts are also supported by the required area per molecule (A_c) of **2** and **3** in the respective monolayers, being 0.58 nm^2 in both cases, which is much less than for **1** (0.82 nm^2), but very close to the cross-sectional area of three densely packed alkyl chains (0.19 nm^2 for each chain).[1b] Other indications giving support to the formation of highly dense and remarkably stable two-dimensional packings in the monolayers of **2** and **3** are the extremely high collapse pressures leading to destruction of the monolayers. These are 71.1 and 71.7 mN m^{-1} for **2** and **3**, respectively, which are far higher than the 34.9 mN m^{-1} for compound **1** and resemble the values reported for lung surfactants.[17a]

The π–A isotherms of the analogous *bidendritic* amphiphiles **5–7** (Scheme 3), given in Fig. 2, are roughly similar to those of the monodendritic compounds **1–3** (Fig. 1), as far as the species containing the same length of alkyl chain are concerned. However, the dendritic modifications of the polar head groups, with tripling of the carboxylic acid functions in **5–7** compared to **1–3**, respectively, also show a positive effect on the Langmuir film stability. This is particularly expressed by compound **5**, which forms a much more stable Langmuir monolayer than compound **1**, considering the collapse pressure and the mean molecular collapse area, which are distinctly increased and decreased, respectively. Obviously, the collapse of the Langmuir films of the dendritic amphiphiles can be shifted to higher surface pressure both by improved hydrophilic anchoring (especially when attractive intermolecular hydrophobic interactions are missing) and by the improved intermolecular hydrophobic interactions of the longer alkyl substituents (even in the case of weak hydrophilic anchoring).

Table 1 Data derived from the π–A isotherms of compounds **1–9** on a pure water subphase

Compound	Lift-off area/nm^2	A_0/nm^2	A_c/nm^2	Collapse surface pressure/mN m^{-1}
1	1.36	1.14	0.82	34.9
2	1.44	0.69	0.58	71.1
3	1.19	0.74	0.58	71.7
4	1.97	1.57	0.92	30.9
5	1.59	0.97	0.66	52.3
6	1.75	0.73	0.61	68.1
7	1.23	0.78	0.62	71.8
8	4.71	1.22	0.64	44.2
9	2.02	1.33	0.80	59.3

A comparison of the π–A isotherms of the monodendritic amphiphile **4** (Scheme 2) and the bidendritic compound **8** (Scheme 3), both differing from the analogous amphiphiles **1** and **5** in the nature of the spacer elements, indicates correspondence to the above facts, *i.e.* the bidendritic **8** beats the monodendritic **4** in formation of dense and stable monolayers, as follows from the isotherm data summarized in Table 1. Nevertheless, a comparison between **1** and **4** or **5** and **8** also shows the superiority of the rigid aromatic *versus* the flexible aliphatic spacer group containing amphiphiles, respectively (Table 1). This means that flexibility of the spacer unit leads to destabilization of the Langmuir film. A possible explanation of this observation is the existence of anti-parallel dimers of hydrogen-bonded dendrimers in molecules with a flexible spacer (amphiphiles **4** and **8**). These hypothetic pairs of hydrogen bonds between anti-parallel oriented molecules surely require some flexibility in the spacer in order to meet the steric conditions of bond formation. The resulting aggregate, however, cannot effectively anchor to the subphase because of the lack of amphiphilic properties in these dimers, leading to the observed reduction in the collapse pressure. Another fact, revealed in the compression isotherms, is that the different spacer units, in the case of the bidendritic amphiphiles **5** and **8**, do not affect the mean area per molecule. This observation supports the "edge-on" orientation of the molecules in the Langmuir films.

Compounds **1**, **5** and **9** (Scheme 4) contain both the same hydrophobic segment and spacer unit in their molecular constructions, but feature unbranched and branched

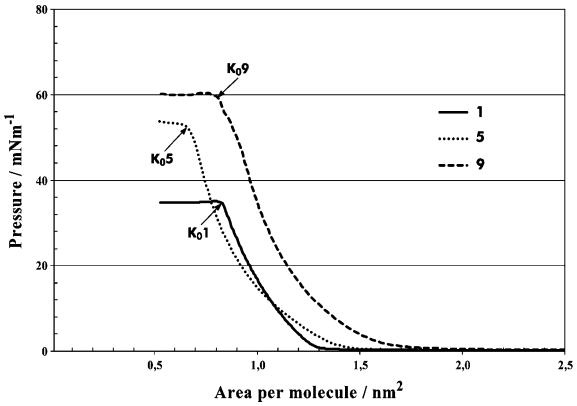


Fig. 3 Isotherms (π–A) of the amphiphiles **1**, **5** and **9**, featuring different degrees of branching of the hydrophilic segment: **1** (unbranched), **5** (first generation branching), **9** (second generation branching).

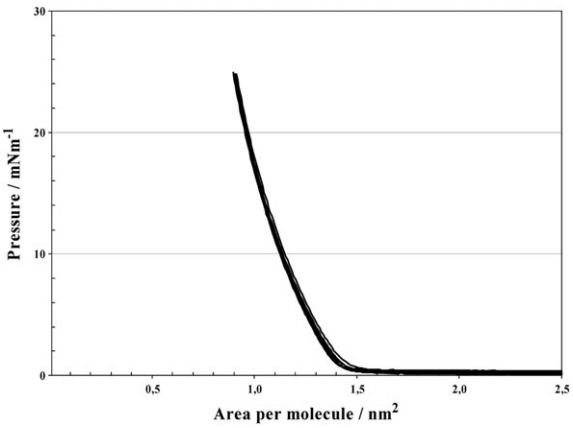


Fig. 4 Hysteresis curves obtained through alternate compression and decompression of the bidendritic amphiphile **5** on a pure water subphase.

hydrophilic segments in different dendritic generations and, thus, different numbers of peripheral carboxylic acid functions. To be precise, there are one, three and nine carboxylic acid groups in **1**, **5** and **9**, respectively. Put another way, this particular series of compounds makes an expressive example, showing the effect on the Langmuir film behaviour of dendritic branching on the carboxylic group side of the amphiphile, while maintaining the hydrophobic segment of the molecules. This also involves a shift in the hydrophilic–hydrophobic balance of the respective amphiphiles. The result, as illustrated by the compression isotherms, is shown in Fig. 3, indicating a distinct increase in the stability of the monolayers formed by compounds **1**, **5** and **9**, in this sequence, which is deduced from the collapse pressure (Table 1). This behaviour nicely meets the expectations for materials with systematically improved anchoring of the molecules to the water surface *via* enhanced hydrophilicity of the amphiphiles ("anchoring effect"). Nevertheless, the mean area per molecule determined for compound **9** is only slightly increased with respect to that of compound **1**, although **9** features extensive second generation dendritic branching of the hydrophilic segment, while **1** is only a monofunctional compound (Table 1). This fact again confirms the "edge-on" orientation of the molecules and it further indicates a slight misfit in the cross-sectional areas of the first generation dendritic branched hydrophobic segment and the second generation dendritic branched hydrophilic segment of compound **9**.

Monolayer hysteresis experiments yield insight into the reversibility of structural transitions in the Langmuir films. In these so-called isotherm cycle studies of selected amphiphiles (**3**, **5** and **9**), compression of the monolayers was advanced up to a surface pressure of about 30 mN m^{-1}, and, after standing for 10 min, the film was allowed to relax by opening of the barriers of the Langmuir trough. Each cycle was run three times. An exemplary hysteresis cycle for compound **5**, which has C_{12} substituents in the hydrophobic dendronized segment, is illustrated in Fig. 4. The highly superimposable traces of the compression and depression curves confirm the high reproducibility and reversibility of the monolayer formation in the case of the dodecyl-substituted compound. The experiment confirms the repulsive inter- and intramolecular interactions of the dodecyl substituents in the hydrophobic dendronized segments of compound **5**.

Bivalent metal ions are well known to interact with carboxylic groups of several amphiphiles, frequently resulting in improved Langmuir or LB film stability.[1a,17b] From a previous report,[8] one may expect that the presence of Ca^{2+} ions in the aqueous subphase, such as with a 10^{-4} M aqueous $CaCl_2$ subphase in comparison with a pure water subphase, will have a bearing on the required area per molecule of carboxylic acid amphiphiles and will stabilize the Langmuir monolayer, through the bivalent cation interaction with two carboxylic groups. However, the amphiphiles discussed here do not adhere strictly to this expectation but behave differently in some cases, *i.e.* some of the compounds (**1**, **4**, **5** and **9**) meet the expectation with a slight increase in the collapse pressure of the Langmuir film in the presence of Ca^{2+}, while in others it is almost unchanged (**6**, **7** and **8**) or even decreased (**2** and **3**). This dependence is probably connected with the structural features of the respective amphiphiles which, however, is difficult to figure out since the contrary effects of the hydrophilic and hydrophobic segment groups, including the spacer unit, seem to play a role. Nevertheless, by considering the monodendritic series of amphiphiles **1–3**, it is shown that the film stability of the short C_{12} chain compound **1** is improved in the presence of Ca^{2+}, while it is decreased in **2** and **3**, with the more extended C_{16} and C_{18} alkyl chains, respectively. On the other hand, the comparative compounds **1**, **5** and **9**, containing an aromatic spacer unit but differing in the degree of dendritic branching of the hydrophilic segments, all showed an increase in the stability of the monolayers, while the respective amphiphiles, **4** and **8**, with alkyl spacers behaved in an opposite manner (Table 2).

Langmuir–Blodgett films

Since the present amphiphiles proved efficient in the formation of stable Langmuir films, and further supported by the hysteresis experiments, transfer of the monolayers to a solid substrate, resulting in Langmuir–Blodgett (LB) films, is promising.[1,15] First, LB deposition experiments were performed

Table 2 Data derived from the π–A isotherms of compounds **1–9** on a 10^{-4} M aqueous $CaCl_2$ subphase

Compound	Lift-off area/nm^2	A_0/nm^2	A_c/nm^2	Collapse surface pressure/mN m^{-1}
1	1.78	1.40	1.03	37.9
2	1.51	0.73	0.60	68.9
3	1.14	0.75	0.61	67.8
4	1.94	1.56	0.92	33.3
5	1.63	1.04	0.68	54.9
6	2.11	0.76	0.61	67.8
7	1.21	0.80	0.60	72.8
8	4.69	1.30	0.68	43.4
9	2.10	1.25	0.88	62.9

using a pure water subphase and freshly cleaned silicon wafers as solid supports at the surface pressures specified in Table 3. Before use, the silicon wafers were treated with a boiling mixture of H_2SO_4–H_2O_2 (1 : 2), rinsed with pure water, dried and sputtered with argon ions in a plasma cleaner to ensure a clean, but highly hydrophilic surface, on the wafer, with a high ratio of free hydroxyl groups.

Unexpectedly, the transfer of the monolayers to the hydrophilic silicon wafer by vertical lifting of the substrate from the Langmuir films to produce a hydrophobic coating on the support was only successful in the cases of the amphiphiles **1**, **4**, **5**, **8** and **9**, while compounds **2**, **3**, **6** and **7** failed. The transfer ratio, defined as the ratio of the decrease in the surface area covered by the Langmuir film to the area of the dipped substrate, gives quantitative information about the coating process. The transfer ratios of the first monolayer of amphiphiles **1**, **5**, **8** and **9** are very close to 1 (range between 1.0 and 1.1), indicating the effectiveness of the transfer with complete coating of the substrate, except compound **4** shows a lower transfer ratio of only 0.7 (Table 3).

The different behaviour of the amphiphiles **1–9** in forming a first Langmuir–Blodgett monolayer on a silicon wafer may be connected with the structural features of the molecules. Obviously, the long C_{16} and C_{18} alkyl chains of both the mono- and bidendritic amphiphiles **2**, **3**, **6** and **7** give rise to the formation of rather rigid Langmuir layers on the water subphase (*cf.* Table 1), impeding the transfer. Thus, in spite of using different experimental conditions, these compounds did not yield either a complete or reproducible film transfer. This is a known property of strongly associated stiff monolayers. Actually, the formation of Langmuir–Blodgett films requires a reversibly compressible monolayer, with alkyl chains capable of reorientation during the transfer. However, in the case of a rigid monolayer, the process of transfer is problematic, due to the mechanical stress experienced by the film in the meniscus region, leading to cracks and disruptions. This opposes the transfer of an ordered film. On the other hand, low stability of the Langmuir monolayer (*cf.* Table 1) is another parameter hindering the transfer of the film, which seems to be the case for compound **4**, which shows only an incomplete coating of the support, while the amphiphiles **1**, **5**, **8** and **9** enable the efficient transfer of the first monolayer to the silicon wafers. For all our compounds, the deposition of a second LB monolayer failed, in that the previously transferred monolayer came off upon vertical dipping into the Langmuir trough, even in the case of compound **5** which features a balanced amphiphilic structure.

Table 3 LB transfer ratios of selected amphiphiles from a pure water subphase to a single crystalline silicon wafer (rendered hydrophilic)

Compound	Transfer surface pressure/mN m^{-1}	Transfer ratio of first monolayer
1	15	1.10
4	15	0.72
5	25	1.09
8	30	1.04
9	25	1.00

Conclusion

New amphiphilic compounds **1–9**, composed of dendronized hydrophilic and hydrophobic segment groups featuring peripheral carboxylic functions and alkyl chains, respectively, and involving different generations of branching, connected to specific aromatic or aliphatic spacer units, have been synthesized, following a modular building block strategy. This particular design of amphiphile proved useful in the formation of well-defined Langmuir monolayers when spread from a solution at the air–water interface or when a 10^{-4} M aqueous $CaCl_2$ solution was used. However, analysis of the π–A isotherms of the different compounds shows the following trends. Among the compounds with a peripheral alkyl chain length of C_{12} (**1**, **4**, **5**, **8** and **9**), increase in the number of carboxylic groups gives rise to increasing stability in the Langmuir monolayers. Moreover, within this series of compounds, the flexible alkyl spacer type amphiphiles (**4** and **8**) compare unfavorably with the corresponding rigid aromatic spacer-containing amphiphiles (**1** and **5**). The formation of antiparallel, hydrogen-bonded dimers of amphiphiles **4** and **8** after spreading, resulting in a distortion of the amphiphilic self-organization potential of the isolated molecule, might account for this observation. In contrast, the π–A isotherms of the amphiphiles, which have varied polar head groups but uniform alkyl chain length, either C_{16} (**2** and **6**) or C_{18} (**3** and **7**), show no significant differences in the solid analogous state, indicating the minor role of the polar segment in the compression behaviour of the monofilms. Obviously, with reference to the longer alkyl chain amphiphiles, the hydrophobic dendrons determine the traces of the π–A isotherms. Also, an extension in the alkyl chains of the hydrophobic dendron helps with stabilization of the monofilm *via* enhanced hydrophobic interactions, as derived from the remarkably high collapse pressure values.

Compared to the pure water subphase, the π–A isotherms determined on a 10^{-4} M aqueous $CaCl_2$ subphase behave, in part, inconsistently, in that the expected stabilization of the monolayer is not always found and even destabilization is encountered (**2** and **3**).

Langmuir–Blodgett transfer of the first monolayer from a pure water subphase to a clean silicon wafer proved possible for the amphiphiles with a peripheral alkyl chain length of C_{12}, while the amphiphiles with the longer alkyl chains failed, possibly due to their formation of more rigid monolayers, impeding the transfer. For all our compounds, the deposition

of a second LB monolayer failed; coating of surfaces with multilayers of this particular type of diepitope dendritic amphiphile requires a further search for both improved chemical structures and efficient deposition strategies and parameters, involving horizontal dipping (Langmuir–Schaefer technique) and appropriate substrate surface pre-treatment.[1] Thus, the present modular design of dendritic compounds has the potential to provide two-dimensional surface arrangements of amphiphiles that may cause particular properties, involving promising aspects for surfactant application.[1,4] The combination of different self-organization principles in shape-anisotropic dendritic amphiphiles, resulting in supramolecular liquid crystals, is also an obvious target.[26]

Experimental

Methods and materials

Melting points (uncorrected): Kofler melting point microscope (VEB Dresden Analytik). IR: Perkin Elmer FT-IR 1600 (ν in cm^{-1}). NMR: Bruker Avance DPX 400; ^1H NMR (400.1 MHz) and ^{13}C NMR spectra (100.6 MHz) were recorded at room temperature in $CDCl_3$, d_4-MeOH or d_4-MeOH–$CDCl_3$, with TMS as the internal standard (δ in ppm, J in Hz). ESI-mass spectra: HP 59987A; ESI-TOF-mass spectra: Mariner ESI-TOF-MS (Applied Biosystems, Weiterstadt, Germany) and Bruker Bio TOF III; DEI-mass spectra and FAB^+ (LSIMS)-mass spectra: Finnigan MAT SSQ 710 (NBA matrix). EA: Heraeus CHN rapid analyzer. The course of the reactions was monitored using TLC (Merck silica gel 60-F_{254} coated plates). Column chromatography was performed with Merck silica gel 60 (0.063–0.100 mm) and Sephadex LH-20 (0.025–0.100 mm, Fluka).

Reagents and chemicals, including *n*-dodecylamine, *n*-hexadecylamine, *n*-octadecylamine, 4-(methoxycarbonyl)benzoyl chloride, decanedioyl dichloride, *N*,*N*′-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole, were obtained from commercial sources and used without further purification. The solvents used were purified or dried according to common literature procedures.[18]

Synthesis

Ethyl 9-chlorocarbonylnonanoate,[19] tri-*tert*-butyl 3,3′,3″-(1-nitromethanetriyl)tripropanoate[20] and 3,3′,3″-(1-nitromethanetriyl)tripropionic acid[21] were prepared according to published procedures.

Tri-*tert*-butyl 3,3′,3″-(1-aminomethanetriyl)tripropanoate (22). This compound was prepared from tri-*tert*-butyl 3,3′,3″-(1-nitromethanetriyl)tripropanoate, using a modification of the literature procedure,[20,22] which results in, under easy work up conditions, a product of higher purity and yield. This modification involves the use of *n*-heptane instead of EtOH as the solvent for the hydrogenation. Thus, a stirred suspension of freshly prepared Raney-nickel (5.0 g) and the nitro compound (6.0 g, 13.5 mmol) in *n*-heptane (200 mL) was purged with H_2 for 0.5 h, and then hydrogenated with H_2 at 0.35 MPa pressure for 24 h at 48 °C. The catalyst was removed by filtration through Celite and the solvent evaporated to yield 5.5 g (98%) of a white powder; mp 62–64 °C (lit.[20,22] 51–52 °C). $C_{22}H_{41}NO_6$ (415.57): calcd C 63.59, H 9.94, N 3.37; found C 63.58, H 9.84, N 3.36%.

General procedure[13] for preparation of the dendritic nitro compounds 10a–c. Under dry conditions, a stirred mixture of the tricarboxylic acid **21** and freshly distilled thionyl chloride, containing a few drops of DMF, was heated to reflux until a clear solution had formed. The excess thionyl chloride was carefully distilled off and the residue, without further purification, was dissolved in dry THF or $CHCl_3$. This solution was added dropwise, at room temperature and under dry conditions, to a stirred solution of the corresponding alkylamine and triethylamine in the respective solvent as before. After 4 d stirring at 40 °C, the mixture was quenched with 10% aqueous HCl. The organic phase was separated, washed with water, saturated aqueous NaOAc and brine, and dried (Na_2SO_4). Evaporation of the solvent, washing with ether, and subsequent recrystallization from EtOH and *n*-heptane yielded the pure compounds. Details and data are given for each compound.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-(1-nitromethanetriyl)tripropanamide (10a).** Reaction mixture: **21** (10.0 g, 36.0 mmol), thionyl chloride (80 mL), dodecylamine (20.0 g, 108.0 mmol), triethylamine (15 mL), THF (300 mL). Yield: 20.3 g (72%) of a white powder; mp 97–99 °C. IR (KBr): ν = 3302 cm^{-1} (s, NH), 2960 (s), 2924 (s), 2877 (m), 2857 (s), 1648 (s, C═O), 1539 (s, NO_2), 1467 (m), 1377 (w), 720 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26 (s, 54 H, CH_2), 1.48 (m, 6 H, CH_2), 2.15 (m, 6 H, CH_2), 2.25 (m, 6 H, CH_2), 3.19 (m, 6 H, CH_2), 6.11 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.05 (CH_3), 22.6, 27.0, 29.3, 29.5, 29.55, 29.6, 29.7, 30.8, 31.9 (CH_2), 39.8 (CH_2NH), 93.6 (CNO_2), 171.1 (CO) ppm. MS (ESI-TOF, pos.): m/z = 801.7 $[M + Na]^+$. $C_{46}H_{90}N_4O_5$ (779.24): calcd C 70.90, H 11.64, N 7.19; found C 70.94, H 11.78, N 7.26%.

***N*,*N*′,*N*″-Trihexadecyl-3,3′,3″-(1-nitromethanetriyl)tripropanamide (10b).** Reaction mixture: **21** (10.0 g, 36.0 mmol), thionyl chloride (80 mL), hexadecylamine (26.1 g, 108.0 mmol), triethylamine (15 mL), $CHCl_3$ (300 mL). Yield: 22.5 g (66%) of a white powder; mp 103–105 °C. IR (KBr): ν = 3306 cm^{-1} (m, NH), 2960 (m), 2918 (s), 2874 (m), 2851 (s), 1645 (s, C═O), 1538 (s, NO_2), 1468 (m), 1376 (w), 721 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 78 H, CH_2), 1.48 (m, 6 H, CH_2), 2.14 (m, 6 H, CH_2), 2.25 (m, 6 H, CH_2), 3.20 (m, 6 H, CH_2), 5.87 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.4, 29.5, 29.55, 29.6, 29.7, 30.8, 30.9, 31.9 (CH_2), 39.8 (CH_2NH), 93.6 (CNO_2), 171.1 (CO) ppm. MS (ESI-TOF, pos.): m/z = 969.9 $[M + Na]^+$. $C_{58}H_{114}N_4O_5$ (947.57): calcd C 73.52, H 12.13, N 5.91; found C 73.47, H 12.09, N 5.93%.

***N*,*N*′,*N*″-Trioctadecyl-3,3′,3″-(1-nitromethanetriyl)tripropanamide (10c).** Reaction mixture: **21** (10.0 g, 36.0 mmol), thionyl chloride (80 mL), octadecylamine (29.1 g, 108.0 mmol), triethylamine (15 mL), $CHCl_3$ (300 mL). Yield: 18.7 g (50%) of a white powder; mp 105–108 °C. IR (KBr): ν = 3308 cm^{-1} (m, NH), 2961 (m), 2919 (s), 2875 (m), 2851 (s), 1643 (s, C═O), 1538 (NO_2), 1467 (m), 1376 (w), 723 (w). ^1H

NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 90 H, CH_2), 1.48 (m, 6 H, CH_2), 2.14 (m, 6 H, CH_2), 2.25 (m, 6 H, CH_2), 3.19 (m, 6 H, CH_2), 6.03 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.4, 29.5, 29.6, 29.7, 30.8, 30.9, 31.9 (CH_2), 39.8 (CH_2NH), 93.6 (CNO_2), 171.2 (CO) ppm. MS (ESI-TOF, pos.): m/z = 1053.9 $[M + Na]^+$. $C_{64}H_{126}N_4O_5$ (1031.73): calcd C 74.51, H 12.13, N 5.43; found C 74.35, H 12.20, N 5.52%.

General procedure[20,22] for preparation of the dendritic amino compounds 11a–c and 20. A stirred suspension of freshly prepared Raney-nickel[23] and the respective nitro compound in dry EtOH or toluene in an autoclave was purged with H_2 for 0.5 h, and then hydrogenated with H_2 at 0.35 MPa pressure for 24 h at 60 °C. The catalyst was removed by filtration through Celite (washing with warm EtOH) and the solvent evaporated. Details, including the purification method and data, are given for each compound.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-(1-aminomethanetriyl)tripropanamide (11a).** Reaction mixture: **10a** (3.90 g, 5.0 mmol) in EtOH (200 mL), Raney-Ni alloy (5.0 g). Recrystallization from EtOH yielded 3.4 g (88%) of a white powder; mp 102–103 °C. IR (KBr): ν = 3302 cm^{-1} (br, NH), 2960 (s), 2929 (s), 2857 (s), 1647 (C═O), 1553 (s), 1466 (m), 1372 (w), 726 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26 (s, 54 H, CH_2), 1.48 (m, 6 H, CH_2), 1.64 (t, 6 H, CH_2), 2.21 (t, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 6.11 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6, 27.0, 29.3, 29.6, 31.1, 31.9, 35.0 (CH_2), 39.7 (CH_2NH), 53.1 (CNH_2), 173.2 (CO) ppm. MS (ESI-TOF, pos.): m/z = 750 $[M + H]^+$. $C_{46}H_{92}N_4O_3$ (749.26): calcd C 73.74, H 12.38, N 7.48; found C 73.79, H 12.50, N 7.47%.

***N*,*N*′,*N*″-Trihexadecyl-3,3′,3″-(1-aminomethanetriyl)tripropanamide (11b).** Reaction mixture: **10b** (4.70 g, 5.0 mmol) in EtOH (200 mL), Raney-Ni alloy (5.0 g). Recrystallization from EtOH yielded 3.75 g (83%) of a white powder; mp 105–106 °C. IR (KBr): ν = 3296 cm^{-1} (br, NH), 2955 (m), 2919 (s), 2872 (m), 2851 (s), 1642 (s, C═O), 1555 (m), 1467 (m), 1377 (w), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26 (s, 78 H, CH_2), 1.48 (m, 6 H, CH_2), 1.64 (t, 6 H, CH_2), 2.21 (t, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 6.05 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.6, 29.7, 31.1, 31.9, 34.9 (CH_2), 39.7 (CH_2NH), 53.2 (CNH_2), 173.2 (CO) ppm. MS (ESI-TOF, pos.): m/z = 918 $[M + H]^+$. $C_{58}H_{116}N_4O_3$ (917.58): calcd C 75.92, H 12.74, N 6.11; found C 75.82, H 12.88, N 6.25%.

***N*,*N*′,*N*″-Trioctadecyl-3,3′,3″-(1-aminomethanetriyl)tripropanamide (11c).** Reaction mixture: **10c** (5.25 g, 5.0 mmol) in EtOH (200 mL), Raney-Ni alloy (5.0 g). Recrystallization from EtOH yielded 3.9 g (77%) of a white powder; mp 108–109 °C. IR (KBr): ν = 3301 cm^{-1} (br, NH), 2955 (m), 2919 (s), 2851 (s), 1643 (s, C═O), 1552 (m), 1469 (m), 1377 (w), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26 (s, 90 H, CH_2), 1.47 (m, 6 H, CH_2), 1.65 (t, 6 H, CH_2), 2.22 (t, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 6.02 (t, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.4, 29.6, 29.7, 31.1, 31.9, 34.9 (CH_2), 39.7 (CH_2NH), 53.3 (CNH_2), 173.1 (CO) ppm. MS (ESI-TOF, pos.): m/z = 1003 $[M + 2H]^+$. $C_{64}H_{128}N_4O_3$ (1001.75): calcd C 76.74, H 12.88, N 5.59; found C 76.75, H 12.82, N 5.41%.

***N*,*N*′,*N*″-Tris[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]-3,3′,3″-(1-aminomethanetriyl)tripropanamide (20).** Reaction mixture: **19** (2.95 g, 2.0 mmol) in toluene (200 mL), Raney-Ni alloy (5.0 g). Treatment with pentane yielded 2.0 g (17%) of a white powder; mp 186–190 °C. IR (KBr): ν = 3374 cm^{-1} (br, NH), 2975 (s), 2934 (m), 2882 (w), 1729 (s, C═O, ester), 1680 (s, C═O, amide), 1536 (s), 1456 (m), 1390 (m), 1367 (s), 1155 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 81 H, CH_3), 1.95, 2.12, 2.21 (m, 48 H, CH_2), 6.10 (s, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.0 (CH_3), 29.7, 29.9, 31.2, 31.3 (CH_2), 53.2 (CNH_2), 57.6 (C–NH), 80.6 [$C(CH_3)_3$], 170.2 (CO, amide), 172.7 (CO, ester) ppm. MS (ESI-TOF, pos.): m/z = 1461.9 $[M + Na]^+$. $C_{76}H_{134}N_4O_{21}$ (1439.91): calcd C 63.40, H 9.38, N 3.89; found C 63.59, H 9.17, N 3.98%.

General procedure[13] for preparation of the dendritic esters 12a–c. A procedure analogous to the preparation of compounds **10a–c** applies, excepting the method of purification, which was performed as follows: the crude products were purified using consecutive column chromatography on SiO_2, with CH_2Cl_2–ethyl acetate (1 : 1) then CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1) as eluents, in this sequence. Treatment with *n*-pentane and storage in the fridge yielded white powders which were further purified by recrystallization. Details and data are given for each compound.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-[(4-methoxycarbonylphenyl-carbonylamino)methanetriyl]tripropanamide (12a).** Reaction mixture: mono-methyl terephthalate (2.71 g, 15.0 mmol), thionyl chloride (50 mL), **11a** (11.23 g, 15.0 mmol), triethylamine (5 mL), $CHCl_3$ (300 mL). Recrystallization from acetone yielded 10.9 g (80%) of a white powder; mp 102–107 °C. IR (KBr): ν = 3301 cm^{-1} (br, NH), 2960 (s), 2924 (s), 2874 (m), 2851 (s), 1730 (s, C═O, ester), 1647 (s, C═O, amide), 1547 (s), 1466 (m), 1379 (w), 1277 (s), 723 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 54 H, CH_2), 1.45 (m, 6 H, CH_2), 2.20 (m, 6 H, CH_2), 2.30 (m, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 3.94 (s, 3 H, OCH_3), 5.83 (t, 3 H, N*H*CH_2), 7.96 (d, 2 H, Ar–H), 8.09 (d, 2 H, Ar–H), 8.36 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 31.1, 31.7, 31.9 (CH_2), 39.7 (CH_2NH), 52.3 (OCH_3), 58.6 (C–NH), 127.3, 129.6, 132.4, 138.8 (C–Ar), 166.3, 166.4 (Ar–*C*O, amide, ester), 173.1 (CH_2*C*ONH) ppm. MS (FAB, NBA): m/z = 912 $[M + H]^+$. $C_{55}H_{98}N_4O_6$ (911.41): calcd C 72.48, H 10.84, N 6.15; found C 72.23, H 10.83, N 6.10%.

***N*,*N*′,*N*″-Trihexadecyl-3,3′,3″-[(4-methoxycarbonylphenyl-carbonylamino)methanetriyl]tripropanamide (12b).** Reaction mixture: mono-methyl terephthalate (2.71 g, 15.0 mmol), thionyl chloride (50 mL), **11b** (13.91 g, 15.0 mmol), triethylamine (5 mL), $CHCl_3$ (300 mL). Recrystallization from acetone–EtOH (2 : 1) yielded 10.4 g (76%) of a white powder; mp 100–104 °C. IR (KBr): ν = 3302 cm^{-1} (br, NH), 2960 (m), 2924 (s), 2851 (m), 1727 (s, C═O, ester), 1643 (s, C═O, amide), 1548 (s), 1467 (m), 1376 (w), 1278 (s), 722 (w). ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 78 H, CH_2), 1.45 (m, 6 H, CH_2), 2.19 (m, 6 H, CH_2), 2.30 (m, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 3.94 (s, 3 H, OCH_3), 5.87 (t, 3 H, N*H*CH_2), 7.95 (d, 2 H, Ar–H), 8.09 (d, 2 H, Ar–H), 8.38 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.4, 29.6, 29.7, 31.3, 31.9, 32.0, 39.8 (CH_2), 52.3 (OCH_3), 58.6 (C–NH), 127.3, 129.7, 132.4, 138.9 (C–Ar), 166.3, 166.4 (Ar–*C*O, amide, ester), 173.1 (CH_2*C*ONH) ppm. MS (ESI-TOF, pos.): m/z = 1101.9 [M + Na]$^+$. $C_{67}H_{122}N_4O_6$ (1079.73): calcd C 74.53, H 11.39, N 5.19; found C 74.51, H 11.40, N 5.36%.

***N*,*N*′,*N*″-Trioctadecyl-3,3′,3″-[(4-methoxycarbonylphenylcarbonylamino)methanetriyl]tripropanamide (12c).** Reaction mixture: mono-methyl terephthalate (2.71 g, 15.0 mmol), thionyl chloride (50 mL), **11c** (15.02 g, 15.0 mmol), triethylamine (5 mL), $CHCl_3$ (300 mL). Recrystallization from acetone–EtOH (1 : 1) yielded 13.0 g (75%) of a white powder; mp 103–109 °C. IR (KBr): ν = 3301 cm^{-1} (br, NH), 2960 (m), 2918 (s), 2851 (s), 1728 (s, C=O, ester), 1640 (s, C=O, amide), 1545 (s), 1466 (m), 1376 (w), 1277 (s), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 90 H, CH_2), 1.45 (m, 6 H, CH_2), 2.19 (m, 6 H, CH_2), 2.30 (m, 6 H, CH_2), 3.19 (q, 6 H, CH_2), 3.94 (s, 3 H, OCH_3), 5.86 (t, 3 H, N*H*CH_2), 7.96 (d, 2 H, Ar–H), 8.09 (d, 2 H, Ar–H), 8.37 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.4, 29.6, 29.7, 31.3, 31.9, 39.8 (CH_2), 52.3 (OCH_3), 58.7 (C–NH), 127.3, 129.7, 132.5, 138.9 (C–Ar), 166.3, 166.4 (Ar–*C*O, amide, ester), 173.1 (CH_2*C*ONH) ppm. MS (ESI-TOF, pos.): m/z = 1186.0 [M + Na]$^+$. $C_{73}H_{134}N_4O_6$ (1163.89): calcd C 75.33, H 11.60, N 4.81; found C 75.42, H 11.70, N 4.51%.

Tri-*tert*-butyl 3,3′,3″-[9-(ethoxycarbonyl-nonanoylamino)-methanetriyl]tripropanoate (13). To a solution of **22** (7.48 g, 18.0 mmol) and triethylamine (3 mL) in dry Et_2O (100 mL), cooled to 0 °C, was added ethyl 9-chlorocarbonylnonanoate (4.48 g, 18.0 mmol) dropwise under dry conditions. After 24 h stirring at room temperature, the mixture was quenched with 10% aqueous HCl. The organic phase was washed with 10% aqueous NaOAc and brine, and dried (Na_2SO_4). Evaporation of the solvent and subsequent purifications by column chromatography on SiO_2 using CH_2Cl_2, ethyl acetate, and ethyl acetate–toluene (1 : 2) as the eluents, in this sequence, followed by treatment with *n*-pentane and storage in the fridge, yielded 6.5 g (58%) of a white powder; mp 49–50 °C. IR (KBr): ν = 3300 cm^{-1} (br, NH), 2981 (s), 2934 (s), 2857 (m), 1732 (s, C=O, ester), 1649 (s, C=O, amide), 1540 (s), 1456 (m), 1391 (m), 1368 (s), 1155 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, 3 H, CH_3), 1.30 (m, 8 H, CH_2), 1.44 (s, 27 H, *t*-Bu), 1.61 (m, 4 H, CH_2), 1.97 (t, 6 H, CH_2), 2.09 (t, 4 H, CH_2), 2.22 (t, 6 H, CH_2), 2.28 (t, 4 H, CH_2), 4.12 (q, 2 H, OCH_2), 5.83 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 24.9, 25.7 (CH_2), 28.0 [C(CH_3)$_3$], 29.0, 29.1, 29.2, 29.8, 30.1 (CH_2), 34.3, 37.5 (CH_2CO), 57.3 (C–NH), 60.0 (OCH_2), 80.5 [*C*(CH_3)$_3$], 172.4, 172.8 (CO, ester), 173.7 (CO, amide) ppm. MS (ESI-TOF, pos.): m/z = 650.4 [M + Na]$^+$. $C_{34}H_{61}NO_9$ (627.86): calcd C 65.04, H 9.79, N 2.23; found C 65.07, H 9.98, N 2.21%.

3,3′,3″-[9-(Ethoxycarbonyl-nonanoylamino)methanetriyl]-tripropionic acid (14). A solution of **13** (5.00 g, 7.96 mmol) in formic acid (30 mL) was stirred at room temperature for 3 d. The formic acid was evaporated at reduced pressure. The residue was extracted into toluene and the solvent evaporated. In order to get complete removal of the formic acid, this procedure of extraction into toluene and evaporation was repeated five times. The crude oily product was dissolved in ethyl acetate. On addition of petroleum ether (40–60 °C) and storage in the fridge, the compound crystallized to yield 3.3 g (90%) of a white powder; mp 89–93 °C. IR (KBr): ν = 3100 cm^{-1} (br, OH), 2981 (m), 2929 (s), 2857 (m), 1730 (s, C=O, ester), 1699 (s, C=O, acid), 1629 (m, C=O, amide), 1458 (m), 1375 (m), 1307 (m), 1177 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, 3 H, CH_3), 1.33 (m, 8 H, CH_2), 1.60 (m, 4 H, CH_2), 2.02 (t, 6 H, CH_2), 2.19, 2.29 (m, 10 H, CH_2CO), 4.10 (q, 2 H, OCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (CH_3), 26.0, 27.1, 29.3, 30.1, 30.2, 30.5, 35.1, 37.7 (CH_2), 58.6 (C–NH), 61.4 (OCH_2), 175.7, 176.0 (CO, ester, amide), 177.1 (CO, acid) ppm. MS (ESI, pos.): m/z = 460.2 [M + H]$^+$. $C_{22}H_{37}NO_9$ (459.54): calcd C 57.50, H 8.12, N 3.05; found C 57.53, H 8.34, N 3.05%.

General procedure for preparation of the dendritic amides 15, 16a–c and 17–19 using carbodiimide–1-HOBt activation.[14,24]. To a cooled (0 °C) solution of the respective carboxylic acid in a dry solvent (THF, CH_2Cl_2 or $CHCl_3$) and under an atmosphere of N_2, was added *N*,*N*′-dicyclohexylcarbodiimide (DCC). After stirring for 10 min, 1-hydroxybenzotriazole (1-HOBt), and then the corresponding amine were added slowly. Stirring of the mixture was continued for 1 h at 0 °C, and then for 4 d at room temperature. The precipitate that formed was separated by filtration. The filtrate was washed with water and brine, dried (Na_2SO_4), and evaporated. The residue was extracted into CH_2Cl_2. The extract was washed with 10% aqueous $NaHCO_3$, water and brine, in this sequence, and evaporated. Purification of the crude products was performed by consecutive column chromatography on SiO_2, using different elution protocols. Treatment of the eluates with *n*-pentane and storage in the fridge yielded the pure compounds. Details and data are given for each compound.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-[9-ethoxycarbonyl-nonanoylamino)methanetriyl]tripropanamide (15).** Reaction mixture: **14** (2.80 g, 6.10 mmol), DCC (3.78 g, 18.30 mmol), 1-HOBt (2.47 g, 18.3 mmol), dodecylamine (3.40 g, 18.30 mmol), THF (130 mL). Elution protocol: CH_2Cl_2, ethyl acetate, and CH_2Cl_2–ethyl acetate–MeOH (5 : 2 : 1), in this sequence. Yield: 1.6 g (27%) of a white solid; mp 62–65 °C. IR (KBr): ν = 3296 cm^{-1} (br, NH), 2955 (m), 2924 (s), 2851 (s), 1737 (s, C=O, ester), 1645 (s, C=O, amide), 1550 (s), 1466 (m), 1376 (w), 1168 (m), 721 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26, 1.29 (m, 65 H, CH_2, CH_3CH_2O), 1.48 (m, 6 H, CH_2), 1.60 (m, 4 H, CH_2), 2.01 (m, 6 H, CH_2), 2.12 (t, 2 H, CH_2), 2.19 (m, 6 H, CH_2), 2.28 (t, 2 H, CH_2), 3.19 (q, 6 H, CH_2), 4.12 (q, 2 H, OCH_2), 5.99 (t, 3 H, N*H*CH_2), 7.15 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.2 (*C*H_3CH_2O), 22.6, 24.9, 25.8, 27.0, 29.05, 29.1, 29.2,

29.25, 29.3, 29.5, 29.6, 29.7, 31.2, 31.8, 31.9, 34.3, 37.6, 39.7 (CH_2), 57.9 (C–NH), 60.1 (OCH_2), 173.2, 173.5 (CO, amide), 173.8 (CO, ester) ppm. MS (ESI-TOF, pos.): m/z = 983.9 [M + Na]$^+$. $C_{58}H_{112}N_4O_6$ (961.55): calcd C 72.45, H 11.74, N 5.83; found C 72.54, H 11.70, N 5.91%.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N*′-[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]terephthaldiamide (16a).** Reaction mixture: **1** (3.24 g, 3.61 mmol), DCC (0.75 g, 3.61 mmol), 1-HOBt (0.49 g, 3.61 mmol), **22** (1.50 g, 3.61 mmol), CH_2Cl_2 (100 mL). Elution protocol: CH_2Cl_2–ethyl acetate (1 : 1), CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1), in this sequence. Yield: 2.8 g (60%) of white plates; mp 115–117 °C. IR (KBr): ν = 3301 cm^{-1} (br, NH), 2957 (s), 2929 (s), 2856 (s), 1730 (s, C=O, ester), 1643 (s, C=O, amide), 1541 (s), 1466 (m), 1396 (m), 1367 (s), 1154 (s), 848 (w), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 54 H, CH_2), 1.44 (s, 33 H, *t*-Bu, CH_2), 2.15, 2.29 (m, 24 H, CH_2), 3.19 (q, 6 H, CH_2), 5.93 (t, 3 H, CH_2NH), 7.13 (s, 1 H, C–NH), 7.84 (d, 2 H, Ar–H), 7.92 (d, 2 H, Ar–H), 8.25 (s, 1 H, C–NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.07 (CH_3), 22.6, 26.9 (CH_2), 28.1 [C(CH_3)$_3$], 29.3, 29.5, 29.6, 29.9, 30.2, 31.2, 31.8, 31.9 (CH_2), 39.8, 58.0 (CH_2), 58.5 (C–NH), 80.8 [C(CH_3)$_3$], 127.1, 127.3, 137.3, 137.5 (C–Ar), 165.9, 166.4, 173.05, 173.1 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 670.0 [M + Na]$^{2+}$. $C_{76}H_{135}N_5O_{11}$ (1294.94): calcd C 70.49, H 10.51, N 5.41; found C 70.39, H 10.56, N 5.47%.

***N*-[Tris(2-hexadecylaminocarbonyl-ethyl)methyl]-*N*′-[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]terephthaldiamide (16b).** Reaction mixture: **2** (5.73 g, 5.38 mmol), DCC (1.11 g, 5.38 mmol), 1-HOBt (0.73 g, 5.38 mmol), **22** (2.23 g, 5.38 mmol), CH_2Cl_2 (200 mL). Elution protocol: CH_2Cl_2–ethyl acetate (1 : 1), CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1), in this sequence. Yield: 2.95 g (56%) of a white powder; mp 92–94 °C. IR (KBr): ν = 3303 cm^{-1} (br, NH), 2958 (s), 2924 (s), 2851 (s), 1729 (s, C=O, ester), 1645 (s, C=O, amide), 1542 (s), 1466 (m), 1391 (m), 1365 (s), 1155 (s), 847 (w), 721 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 78 H, CH_2), 1.44 (s, 33 H, *t*-Bu, CH_2), 2.15, 2.29 (m, 24 H, CH_2), 3.19 (q, 6 H, CH_2), 5.92 (t, 3 H, $NHCH_2$), 7.12 (s, 1 H, CONH), 7.84 (d, 2 H, Ar–H), 7.92 (d, 2 H, Ar–H), 8.24 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0 (CH_2), 28.1 [C(CH_3)$_3$], 29.3, 29.35, 29.5, 29.6, 29.65, 29.7, 30.0, 30.2, 31.2, 31.8, 31.9 (CH_2), 39.8, 58.0 (CH_2), 58.5 (C–NH), 80.8 [C(CH_3)$_3$], 127.1, 127.3, 137.3, 137.5 (C–Ar), 165.9, 166.4, 173.05, 173.1 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 754.6 [M + Na]$^{2+}$. $C_{88}H_{159}N_5O_{11}$ (1463.26): calcd C 72.23, H 10.95, N 4.79; found C 72.15, H 10.96, N 4.75%.

***N*-[Tris(2-octadecylaminocarbonyl-ethyl)methyl]-*N*′-[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]terephthaldiamide (16c).** Reaction mixture: **3** (2.00 g, 1.74 mmol), DCC (0.38 g, 1.83 mmol), 1-HOBt (0.25 g, 1.83 mmol), **22** (0.76 g, 1.83 mmol), CH_2Cl_2 (80 mL). Elution protocol: CH_2Cl_2–ethyl acetate (1 : 1), CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1), CH_2Cl_2–ethyl acetate–MeOH (20 : 2 : 1), in this sequence. Yield: 1.35 g (50%) of a white powder; mp 93–95 °C. IR (KBr): ν = 3302 cm^{-1} (br, NH), 2957 (s), 2924 (s), 2851 (s), 1730 (s, C=O, ester), 1641 (s, C=O, amide), 1540 (s), 1467 (m), 1391 (m), 1366 (s), 1155 (s), 850 (w), 724 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 90 H, CH_2), 1.44 (m, 33 H, *t*-Bu, CH_2), 2.15, 2.29 (m, 24 H, CH_2), 3.20 (q, 6 H, CH_2), 5.81 (t, 3 H, $NHCH_2$), 7.10 (s, 1 H, CONH), 7.85 (d, 2 H, Ar–H), 7.92 (d, 2 H, Ar–H), 8.24 (s, 1 H, CONH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.9 (CH_2), 28.0 [C(CH_3)$_3$], 29.5, 29.6, 29.7, 29.9, 30.2, 31.1, 31.6, 31.9, 39.7, 58.0 (CH_2), 58.5 (C–NH), 80.7 [C(CH_3)$_3$], 127.1, 127.3, 137.4, 137.5 (C–Ar), 166.0, 166.5, 173.0, 173.1 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 1569.4 [M + Na]$^+$. $C_{94}H_{171}N_5O_{11}$ (1547.42): calcd C 72.96, H 11.14, N 4.53; found C 73.06, H 11.18, N 4.65%.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N*′-[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]decanediamide (17).** Reaction mixture: **4** (1.71 g, 1.83 mmol), DCC (0.38 g, 1.83 mmol), 1-HOBt (0.25 g, 1.83 mmol), **22** (0.76 g, 1.83 mmol), THF (75 mL). Elution protocol: CH_2Cl_2–ethyl acetate (1 : 1), CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1), in this sequence. Yield: 1.85 g (76%) of a white powder; mp 59–62 °C. IR (KBr): ν = 3296 cm^{-1} (br, NH), 2958 (s), 2924 (s), 2851 (s), 1732 (s, C=O, ester), 1641 (s, C=O, amide), 1547 (s), 1466 (m), 1391 (m), 1365 (s), 1154 (s), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 9 H, CH_3), 1.19 (s, 62 H, CH_2), 1.36 (m, 33 H, *t*-Bu, CH_2), 1.49 (m, 4 H, CH_2), 1.91, 2.04, 2.14 (m, 28 H, CH_2), 3.09 (m, 6 H, CH_2), 6.24 (s, 1 H, C–NH), 6.83 (t, br, 3 H, CH_2NH), 7.37 (s, 1 H, C–NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.7, 25.7, 25.9, 27.1 (CH_2), 28.1 [C(CH_3)$_3$], 29.0, 29.1, 29.4, 29.5, 29.7, 29.9, 30.0, 30.9, 31.5, 31.9, 37.3, 37.4, 39.8 (CH_2), 57.2, 57.9 (C–NH), 80.5 [C(CH_3)$_3$], 172.9, 173.0, 173.5, 173.6 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 1353.1 [M + Na]$^+$. $C_{78}H_{147}N_5O_{11}$ (1331.05): calcd C 70.39, H 11.13, N 5.26; found C 70.22, H 11.10, N 4.96%.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N*′-{[*N*,*N*′,*N*″-tris[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]aminocarbonyl-ethyl]methyl}terephthaldiamide (18).** Reaction mixture: **1** (0.75 g, 0.84 mmol), DCC (0.17 g, 0.84 mmol), 1-HOBt (0.11 g, 0.84 mmol), **20** (1.21 g, 0.84 mmol), $CHCl_3$ (100 mL). Elution protocol: CH_2Cl_2–ethyl acetate (1 : 1), CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1), in this sequence. Yield: 1.43 g (73%) of a white powder; mp 55–58 °C. IR (KBr): ν = 2975 cm^{-1} (m), 2929 (s), 2856 (m), 1734 (s, C=O, ester), 1648 (s, C=O, amide), 1539 (s), 1458 (m), 1393 (m), 1368 (s), 1154 (s), 721 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 54 H, CH_2), 1.44 (m, 87 H, *t*-Bu, CH_2), 1.95, 2.06, 2.19, 2.28 (m, 60 H, CH_2), 3.20 (q, 6 H, CH_2), 6.00 (t, 3 H, CH_2NH), 6.10 (s, 3 H, C–NH), 7.41 (s, 1 H, C–NH), 7.86 (d, 2 H, Ar–H), 7.98 (d, 2 H, Ar–H), 8.72 (s, 1 H, C–NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6, 27.0 (CH_2), 28.1 [C(CH_3)$_3$], 29.3, 29.5, 29.6, 29.8, 29.9, 31.2, 31.5, 31.7, 31.9, 39.8 (CH_2), 57.6, 58.1, 58.7 (C–NH), 80.6 [C(CH_3)$_3$], 127.2, 127.5, 137.2, 137.4 (C–Ar), 166.2, 166.5, 172.6, 172.8, 172.9 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 2340.9 [M + Na]$^+$. $C_{130}H_{228}N_8O_{26}$ (2319.28): calcd C 67.32, H 9.91, N 4.83; found C 67.10, H 9.71, N 4.85%.

***N*, *N*′, *N*″-Tris[tris(2-*tert*-butoxycarbonyl-ethyl)methyl]-3,3′,3″-(1-nitromethanetriyl)tripropanamide (19).** Reaction mixture: **21** (2.50 g, 9.00 mmol), DCC (5.60 g, 27.10 mmol), 1-HOBt (1.20 g, 9.10 mmol), **22** (11.20 g, 27.00 mmol), THF (100 mL). Elution protocol: CH_2Cl_2–ethyl acetate (4 : 1). Yield: 6.8 g (51%) of a white powder; mp 176–181 °C. IR (KBr): ν = 2976 cm^{-1} (s), 2929 (m), 1729 (s, C=O, ester), 1680 (s, C=O, amide), 1538 (s, NO_2), 1455 (m), 1392 (m), 1366 (s), 1156 (s). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 81 H, CH_3), 1.96, 2.12, 2.20 (m, 48 H, CH_2), 6.08 (s, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.1 (CH_3), 29.8, 30.0, 31.2, 31.3 (CH_2), 57.6 (C–NH), 80.6 [$C(CH_3)_3$], 92.6 (C–NO_2), 170.3, 172.7 (CO, amide, ester) ppm. MS (ESI-TOF, pos.): m/z = 1491.9 $[M + Na]^+$. $C_{76}H_{132}N_4O_{23}$ (1469.89): calcd C 62.10, H 9.05, N 3.81; found C 61.83, H 8.96, N 3.77%.

General procedure[25] for preparation of the monodendritic amphiphiles 1–4. A mixture of the corresponding monodendritic ester and aqueous 1 N KOH in MeOH or EtOH was refluxed for 5 h. After cooling down to room temperature, the precipitate that formed was filtered off and the filtrate acidified with diluted hydrochloric acid to give a precipitate of the crude compound, which was washed with water and dried. Alternatively, for separation of the compound, the reaction mixture can also be extracted with $CHCl_3$, acidified with diluted hydrochloric acid, washed with water, and evaporated. Details, including methods of purification and data, are given for each compound.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-[(4-carboxyphenyl-carbonylamino)methanetriyl]tripropanamide (1).** Reaction mixture: **12a** (5.54 g, 6.10 mmol), KOH (60 mL), MeOH (100 mL). Recrystallization from acetone (activated carbon as clarifier) and intensive drying of the formed solid (P_4O_{10}, 40–50 °C, 2 d) yielded 4.7 g (86%) of a white powder; mp 156–158 °C. IR (KBr): ν = 3296 cm^{-1} (br, NH), 2955 (m), 2918 (s), 2851 (s), 1695 (s, C=O, acid), 1641 (s, C=O, amide), 1550 (s), 1467 (m), 1376 (w), 1269 (s), 721 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 9 H, CH_3), 1.24 (m, 54 H, CH_2), 1.47 (m, 6 H, CH_2), 2.25 (m, 6 H, CH_2), 2.37 (m, 6 H, CH_2), 3.20 (q, 6 H, CH_2), 6.24 (s, 3 H, CH_2NH), 7.61 (s, 1 H, C–NH), 7.71 (d, 2 H, Ar–H), 7.81 (d, 2 H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.4, 29.5, 29.6, 29.7, 31.4, 31.9, 39.9 (CH_2), 59.0 (C–NH), 127.1, 130.2, 132.5, 139.5 (C–Ar), 167.4, 168.4, 173.8 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 920.6 $[M + Na]^+$. $C_{54}H_{96}N_4O_6$ (897.38): calcd C 72.28, H 10.78, N 6.24; found C 72.17, H 10.66, N 6.29%.

***N*,*N*′,*N*″-Trihexadecyl-3,3′,3″-[(4-carboxyphenyl-carbonylamino)methanetriyl]tripropanamide (2).** Reaction mixture: **12b** (7.60 g, 7.00 mmol), KOH (100 mL), MeOH (150 mL). Recrystallization from acetone–EtOH (2 : 1, activated carbon as clarifier) and intensive drying of the formed solid (P_4O_{10}, 40–50 °C, 2 d) yielded 5.9 g (79%) of a white powder; mp 108-135 °C. IR (KBr): ν = 3312 cm^{-1} (br, NH), 2955 (s), 2924 (s), 2851 (s), 1701 (s, C=O, acid), 1648 (s, C=O, amide), 1547 (m), 1467 (m), 1378 (w), 1269 (s), 723 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 78 H, CH_2), 1.46 (m, 6 H, CH_2), 2.20 (m, 6 H, CH_2), 2.36 (m, 6 H, CH_2), 3.19 (m, 6 H, CH_2), 6.43 (s, 3 H, CH_2NH), 7.67 (s, 1 H, C–NH), 7.71 (d, 2 H, Ar–H), 7.81 (d, 2 H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.3, 29.5, 29.6, 29.65, 29.7, 31.2, 31.8, 31.9, 39.9 (CH_2), 59.0 (C–NH), 127.0, 130.0, 132.8, 139.5 (C–Ar), 167.4, 168.5, 173.8 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1087.9 $[M + Na]^+$. $C_{66}H_{120}N_4O_6$ (1065.70): calcd C 74.39, H 11.35, N 5.26; found C 74.30, H 11.38, N 5.17%.

***N*,*N*′,*N*″-Trioctadecyl-3,3′,3″-[(4-carboxyphenyl-carbonylamino)methanetriyl]tripropanamide (3).** Reaction mixture: **12c** (6.00 g, 5.20 mmol), KOH (80 mL), MeOH (100 mL). Recrystallization from acetone–EtOH (1 : 1, activated carbon as clarifier), followed by column chromatography on SiO_2 (eluent: CH_2Cl_2–ethyl acetate–MeOH, 7 : 2 : 1) and intensive drying of the formed solid (P_4O_{10}, 40–50 °C, 2 d) yielded 2.7 g (46%) of a white powder; mp 110–130 °C. IR (KBr): ν = 3299 cm^{-1} (br, NH), 2960 (s), 2918 (s), 2851 (s), 1695 (s, C=O, acid), 1647 (s, C=O, amide), 1550 (s), 1466 (m), 1378 (w), 1269 (s), 722 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.25 (s, 78 H, CH_2), 1.46 (m, 6 H, CH_2), 2.23 (m, 6 H, CH_2), 2.36 (m, 6 H, CH_2), 3.19 (m, 6 H, CH_2), 6.30 (s, 3 H, CH_2NH), 7.62 (s, 1 H, C–NH), 7.71 (d, 2 H, Ar–H), 7.81 (d, 2 H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.0, 29.4, 29.5, 29.7, 31.3, 31.9, 39.9 (CH_2), 59.0 (C–NH), 127.0, 130.1, 132.6, 139.4 (C–Ar), 167.4, 168.5, 173.8 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1172.0 $[M + Na]^+$. $C_{72}H_{132}N_4O_6$ (1149.86): calcd C 75.21, H 11.57, N 4.87; found C 74.98, H 11.90, N 5.04%.

***N*,*N*′,*N*″-Tridodecyl-3,3′,3″-[(carboxynonanoylamino)methanetriyl]tripropanamide (4).** Reaction mixture: **15** (3.40 g, 3.50 mmol), KOH (30 mL), EtOH (100 mL). Purification by consecutive column chromatography on SiO_2 with CH_2Cl_2–ethyl acetate (1 : 1) and CH_2Cl_2–ethyl acetate–MeOH (7 : 2 : 1) as the eluents, in this sequence. On treatment with *n*-pentane and storage in the fridge, a solid was obtained, which was intensively dried (P_4O_{10}, 30 °C, 2 d) to yield 2.2 g (67%) of a white powder; mp 60–80 °C. IR (KBr): ν = 3296 cm^{-1} (br, NH), 2955 (m), 2924 (s), 2857 (s), 1713 (s, C=O, acid), 1646 (s, C=O, amide), 1553 (s), 1460 (m), 1377 (w), 720 (w). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.26 (s, 62 H, CH_2), 1.48 (m, 6 H, CH_2), 1.58 (m, 4 H, CH_2), 2.01 (m, 6 H, CH_2), 2.14, 2.30 (m, 4 H, CH_2), 2.24 (m, 6 H, CH_2), 3.16 (m, 6 H, CH_2), 6.89 (s, 3 H, CH_2NH), 7.31 (s, 1 H, C–NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 24.9, 25.8, 26.9, 28.7, 28.8, 29.3, 29.4, 29.6, 30.8, 31.5, 31.8, 34.4, 37.2, 39.7 (CH_2), 58.1 (C–NH), 173.7, 174.0, 176.7 (CO, amide, acid) ppm. MS (DEI, pos.): m/z = 934 $[M + H]^+$. $C_{56}H_{108}N_4O_6$ (933.50): calcd C 72.05, H 11.66, N 6.00; found C 72.03, H 11.48, N 5.95%.

General procedure[21] for preparation of the bidendritic amphiphiles 5–9. A solution of the corresponding ester in formic acid was stirred at room temperature for 4 d. The precipitate that formed was separated and thoroughly washed with water. Details, including methods of purification and data, are given for each compound.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N′*-[tris(2-carboxyethyl)methyl]terephthaldiamide (5).** Reaction mixture: **16a** (2.20 g, 1.70 mmol), HCOOH (30 mL). Purification by column chromatography on Sephadex LH-20 (eluent: MeOH) and recrystallization from acetone yielded 1.6 g (84%) of a white powder; mp 162–196 °C. IR (KBr): ν = 3312 cm^{-1} (br, NH), 2960 (s), 2924 (s), 2855 (s), 1710 (s, C═O, acid), 1648 (s, C═O, amide), 1545 (s), 1466 (m), 1379 (w), 1296 (s), 868 (w), 724 (w). ^{1}H NMR (400 MHz, d_4-MeOH–$CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.27 (s, 54 H, CH_2), 1.49 (m, 6 H, CH_2), 2.15, 2.21, 2.22, 2.33 (m, 24 H, CH_2), 3.15 (t, 6 H, CH_2), 7.85 (m, 4 H, Ar–H) ppm. ^{13}C NMR (100 MHz, d_4-MeOH–$CDCl_3$): δ = 14.2 (CH_3), 23.0, 27.4, 29.6, 29.7, 30.0, 30.5, 30.9, 31.5, 32.3, 40.1 (CH_2), 58.7, 59.1 (C–NH), 127.6, 127.7, 138.2 (C–Ar), 168.8, 174.6, 176.2 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1126.9 $[M + H]^+$. $C_{64}H_{111}N_5O_{11} \cdot 2H_2O$ (1162.63): calcd C 66.12, H 9.97, N 6.02; found C 66.08, H 9.63, N 6.03%.

***N*-[Tris(2-hexadecylaminocarbonyl-ethyl)methyl]-*N′*-[tris(2-carboxyethyl)methyl]terephthaldiamide (6).** Reaction mixture: **16b** (2.50 g, 1.70 mmol), HCOOH (35 mL). Purification by column chromatography on Sephadex LH-20 (eluent: MeOH) and recrystallization from acetone yielded 1.7 g (77%) of a white powder; mp 105–115 °C. IR (KBr): ν = 3306 cm^{-1} (br, NH), 2957 (m), 2924 (s), 2851 (s), 1712 (s, C═O, acid), 1643 (s, C═O, amide), 1541 (s), 1467 (m), 1367 (w), 1290 (s), 868 (w), 722 (w). ^{1}H NMR (400 MHz, d_4-MeOH): δ = 0.90 (t, 9 H, CH_3), 1.29 (s, 78 H, CH_2), 1.48 (m, 6 H, CH_2), 2.15, 2.21, 2.25, 2.35 (m, 24 H, CH_2), 3.14 (t, 6 H, CH_2), 7.84 (m, 4 H, Ar–H) ppm. ^{13}C NMR (100 MHz, d_4-MeOH–$CDCl_3$): δ = 14.4 (CH_3), 23.5, 27.9, 29.2, 30.2, 30.3, 30.6, 31.3, 31.9, 32.9, 40.5 (CH_2), 59.3, 59.8 (C–NH), 128.3, 128.4, 138.9 (C–Ar), 169.0, 175.4, 176.8 (CO, amide, acid) ppm. MS (ESI-TOF, neg.): m/z = 645.9 $[M - 2H]^{2-}$, 430.2 $[M - 3H]^{3-}$. $C_{76}H_{135}N_5O_{11} \cdot H_2O$ (1312.94): calcd C 69.53, H 10.52, N 5.33; found C 69.52, H 10.43, N 5.38%.

***N*-[Tris(2-octadecylaminocarbonyl-ethyl)methyl]-*N′*-[tris(2-carboxyethyl)methyl]terephthaldiamide (7).** Reaction mixture: **16c** (1.00 g, 0.65 mmol), HCOOH (25 mL). Recrystallization from acetone yielded 0.70 g (79%) of a white powder; mp 105–135 °C. IR (KBr): ν = 3307 cm^{-1} (br, NH), 2957 (m), 2924 (s), 2851 (s), 1710 (s, C═O, acid), 1641 (s, C═O, amide), 1540 (s), 1466 (m), 1376 (w), 1261 (s), 866 (w), 721 (w). ^{1}H NMR (400 MHz, d_4-MeOH–$CDCl_3$): δ = 0.89 (t, 9 H, CH_3), 1.28 (s, 90 H, CH_2), 1.48 (m, 6 H, CH_2), 2.16, 2.20, 2.24, 2.36 (m, 24 H, CH_2), 3.15 (t, 6 H, CH_2), 7.84 (m, 4 H, Ar–H) ppm. ^{13}C NMR (100 MHz, d_4-MeOH–$CDCl_3$): δ = 14.4 (CH_3), 23.4, 27.7, 30.0, 30.1, 30.3, 30.4, 31.2, 31.7, 32.7, 40.4 (CH_2), 59.1, 59.5 (C–NH), 128.1, 128.2, 138.5, 138.6 (C–Ar), 168.8, 168.7, 175.2, 176.8 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1401.2 $[M + Na]^+$. $C_{82}H_{147}N_5O_{11}$ (1379.10): calcd C 71.42, H 10.74, N 5.08; found C 71.33, H 10.83, N 5.19%.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N′*-[tris(2-carboxyethyl)methyl]decanediamide (8).** Reaction mixture: **17** (1.40 g, 1.05 mmol), HCOOH (20 mL). Purification by consecutive column chromatography on SiO_2 (eluent: CH_2Cl_2–ethyl acetate–MeOH, 7 : 2 : 1) and Sephadex LH-20 (eluent: MeOH), in this sequence. Treatment with *n*-pentane and storage in the fridge yielded 0.85 g (70%) of a white powder; mp 103–115 °C. IR (KBr): ν = 3312 cm^{-1} (br, NH), 2957 (m), 2924 (s), 2851 (s), 1711 (s, C═O, acid), 1648 (s, C═O, amide), 1548 (s), 1458 (m), 1374 (w), 1301 (s), 722 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 9 H, CH_3), 1.25 (s, 62 H, CH_2), 1.44 (m, 6 H, CH_2), 1.52 (m, 4 H, CH_2), 2.05, 2.13, 2.43 (m, 28 H, CH_2), 3.19 (m, 6 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.0, 27.1, 28.7, 29.2, 29.4, 29.7, 31.4, 31.9, 36.7, 40.4 (CH_2), 58.1, 58.5 (C–NH), 174.9, 175.7, 176.5 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1184.9 $[M + Na]^+$. $C_{66}H_{123}N_5O_{11} \cdot 1.5H_2O$ (1189.74): calcd C 66.63, H 10.67, N 5.89; found C 66.75, H 10.46, N 5.87%.

***N*-[Tris(2-dodecylaminocarbonyl-ethyl)methyl]-*N′*-{[*N*,*N′*,*N″*-tris[tris(2-carboxyethyl)methyl]aminocarbonyl-ethyl]methyl}terephthaldiamide (9).** Reaction mixture: **18** (0.95 g, 0.41 mmol), HCOOH (10 mL). Recrystallization from acetone and treatment with *n*-pentane yielded 0.62 g (84%) of an off-white powder; mp 100–118 °C. IR (KBr): ν = 3350 cm^{-1} (br, NH), 2957 (m), 2929 (s), 2856 (s), 1713 (s, C═O, acid), 1637 (s, C═O, amide), 1542 (s), 1457 (m), 1383 (w), 1193 (s), 724 (w). ^{1}H NMR (400 MHz, d_4-MeOH): δ = 0.89 (t, 9 H, CH_3), 1.28 (s, 54 H, CH_2), 1.49 (m, 6 H, CH_2), 2.02, 2.14, 2.25 (m, 60 H, CH_2), 3.14 (t, 6 H, CH_2), 7.85 (d, 2 H, Ar–H), 7.92 (d, 2 H, Ar–H) ppm. ^{13}C NMR (100 MHz, d_4-MeOH): δ = 14.4 (CH_3), 23.7, 28.0, 29.3, 30.4, 30.5, 30.6, 30.7, 31.4, 31.9, 32.1, 33.1, 40.6 (CH_2), 58.7, 59.8, 60.0 (C–NH), 128.6, 139.0, 139.2 (C–Ar), 169.1, 169.5, 175.6, 175.7, 177.1 (CO, amide, acid) ppm. MS (ESI-TOF, pos.): m/z = 1836.2 $[M + Na]^+$. $C_{94}H_{156}N_8O_{26} \cdot 2H_2O$ (1850.33): calcd C 61.02, H 8.72, N 6.06; found C 61.13, H 8.69, N 6.24%.

Langmuir and Langmuir–Blodgett films

A computer-controlled Langmuir film balance system Lauda FW2, equipped with a platinum Wilhelmy plate and a Teflon coated trough, was applied. As subphases, pure water, obtained using a Milli-Q-Gradient apparatus (18.2 MΩ cm), as well as a 10^{-4} M aqueous $CaCl_2$ solution were used. The dendritic amphiphiles, all prepared in high purity, were first dissolved in a few drops of DMSO followed by the addition of $CHCl_3$, to prepare solutions of a concentration of 1 mg mL^{-1}. These solutions were spread on the water surface with a 100 μL micro syringe and by waiting 15 min for solvent evaporation. The monolayers were compressed with a barrier speed of 10 mm min^{-1}. To confirm their reproducibility, all isotherms were run at least three times in the direction of increasing surface pressure, with freshly prepared Langmuir films. The measurements were performed at the constant temperature of 25 °C under clean room conditions.

The Langmuir–Blodgett film transfers onto hydrophilic silicon wafers were performed by vertical upward dipping of the substrate through the compressed Langmuir monolayers generated on a pure water subphase of a LB 5000 Langmuir–Blodgett trough (KSV Instruments, Helsinki). The transfers to the silicon wafers were carried out at given surface pressures (Table 3) with a dipper speed of 0.5 mm min^{-1}.

Before use, the single crystalline silicon wafers, polished on both sides, were treated with a boiling mixture of H_2SO_4–H_2O_2 (1 : 2) for 30 min, then rinsed with pure water, dried and sputtered with argon ions in a plasma cleaner.

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