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The straightforward one-pot approach to five- and six-membered saturated heterocyclic cationic gemini-surfactants

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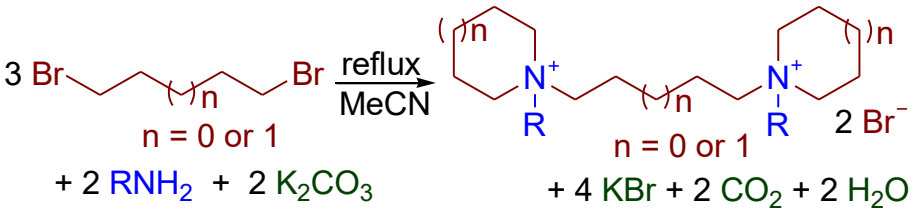
Abstract

Gemini-surfactants bearing pyrrolidine and piperidine moieties were prepared by a one-pot procedure consisting in the series of subsequent alkylation reactions between a primary amine and 1,4-dibromobutane or 1,5-dibromopentane in the presence of potassium carbonate. The pyrrolidinium salts (n = 0) were isolated in yields of 37-89% and the piperidinium salts (n = 1) in yields of 20-64%. The procedure is suitable for functionally substituted primary amines, such as those bearing double bounds, hydroxyl groups, and fluorine atoms, however the highly fluorinated amines fail to react.



Keywords: Amines, Annulation, Gemini-Surfactants, Synthetic Methods

Introduction

Cationic gemini-surfactants are members of a large bisquaternary ammonium salt family;[1] Figure 1 provides a selection of illustrative examples. Typically, gemini-surfactants share the following features: both the quaternary nitrogen atoms bearing long alkyl chains are at the same time connected by a smaller carbon chain, a linker.[1-4] The physicochemical properties of gemini-surfactants in aqueous solutions dramatically differ from the properties of the parent "monomeric" cationic surfactants; a gemini-surfactant in comparison with a "monomeric" surfactant demonstrates lower values of the critical micelle concentration and of the surface tension at the critical micelle concentration, and a sharp increase in the solution viscosity.[1-4] Either a change in the linker length, as well as an alteration of its flexibility/rigidity (the presence of unsaturation/aromatic ring), or the substitution of the other functional groups (ester/amide) or a heteroatom for methylene units affects the named properties.[1-4] The partial fluorination of the long alkyl chains also affects the microscopic behavior of gemini-surfactants in solutions.[5] Due to their remarkable properties, cationic gemini-surfactants find application as antimicrobial agents,[6,7] special detergents in tertiary oil recovery,[5,8,9] and corrosion inhibitors.[10] The numerous concerns over ecology and environmental safety have induced the search for biodegradable gemini-surfactants from renewable sources.[11]

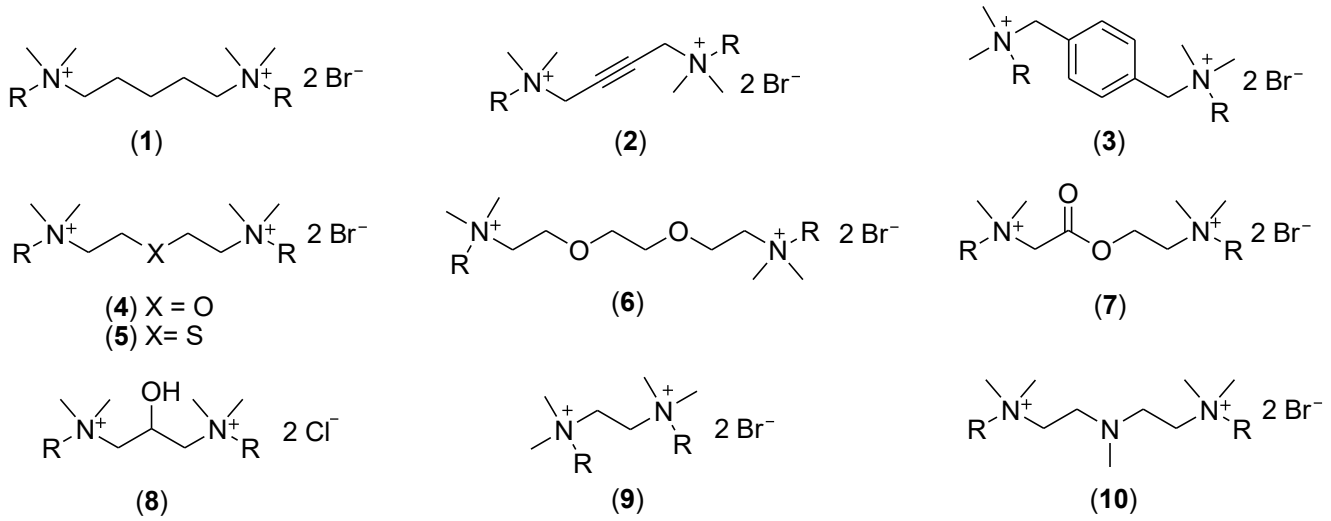


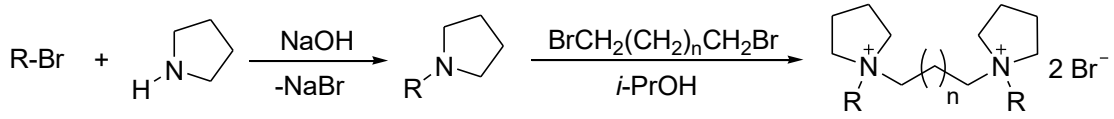
Figure 1. A variety of gemini-surfactants types which have been reported in the literature, where R = $C_{18}H_{37}$ for (**3**), R = $C_{16}H_{33}$ for (**6**), and R = $C_{12}H_{25}$ for the rest of the depicted compounds.

A general synthetic approach to cationic gemini-surfactants consists in a quaternization reaction between a twofold excess of a corresponding tertiary amine and an α,ω-dihaloalkane, usually an α,ω-dibromoalkane, for instance (**1**) was prepared by heating 1,5-dibromopentane with a slight excess (5-10%) of *N*,*N*-dodecyldimethylamine in dry ethyl alcohol.[12] A variety of α,ω-dibromoalkanes possessing either short or long methylene chains were successively employed for this bisquaternization reaction.[12,13] Many bifunctional electrophiles can be successfully utilized in gemini-surfactants syntheses, thus 1,4-dibromobutyne-2 was employed for the synthesis of (**2**),[14] *p*-xylylene dibromide for (**3**),[15] 2,2′-dibromodiethyl ether, along with bis(2-bromoethyl)sulfide, for (**4**) and (**5**), respectively,[16] 1,2-bis(2-bromoethoxy)ethane for (**6**)[17] and 2-bromoethyl bromoacetate for (**7**).[18] Compound (**8**) was synthesized by heating together *N*,*N*-dimethyldodecylamine, its hydrochloride, and epichlorohydrin, an example of somewhat lesser obvious bifunctional electrophile, in ethyl

alcohol;[19] this remarkable transformation proceeds via the formation of the ring opening product and the subsequent quaternization reaction. Heterocyclic and functionally substituited tertiary amines[5,8,10] can also be subjected to a bisquaternization reaction with α,ω-dihaloalkanes, for example acylation of *N*,*N*-dimethylaminopropylamine with fatty acids gave the corresponding acylamides, the latter on treatment with 1,3-dibromopropane afforded a series of amidoamine gemini-surfactants.[20]

Because elimination reactions may accompany or even predominate over a quaternization reaction,[21] some gemini-surfactants cannot be synthesized by treating an α,ω-dihaloalkane with an excess of a tertiary amine, for example 1,2-dibromoethane with fatty tertiary amines instead of producing the desired gemini-surfactants suffers an elimination reaction.[1,3,12] To access gemini-surfactants bearing an ethylenic linker, *N*,*N*′-tetramethylethylenediamine (TMEDA) was treated with a twofold excess of a fatty alkyl bromide[12] or a fatty alkylchloroacetate,[22] thus (**9**) was prepared from TMEDA and dodecyl bromide.[12] Carefully controlling the reaction conditions, such a trifunctional tertiary amine as *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDTA) was converted into a gemini-surfactant (**10**) by allowing PMDTA to react with a twofold excess of dodecyl bromide,[16] this transformation was also successively conducted not only with fatty alkyl bromides but also with a variety of 2-bromoethylesters of fatty acids.[23] These transformations are possible because the total alkylation (trisquaternization) of all the three nitrogen atoms of PMDTA requires more harsh conditions (100-140 ˚C) or more reactive alkylating agents.[24] The incomplete bisquaternization reaction of an α,ω-dihaloalkane or a bifunctional tertiary amine results in the formation of a monosubstitution product.[12] In either case the purification of the synthesized gemini-surfactant is achieved either by a number of successive recrystallizations or by a variety of chromatographic techniques.[1] The following publications survey the recent advances in the synthesis and application of gemini-surfactants[25-28] and related compounds, for instance bolaform surfactants.[29,30]

Gemini-surfactants bearing the cyclic structural motif on each quaternary nitrogen atom, as depicted in Scheme 1, are somewhat superior to the related noncyclic gemini-surfactants in the macroscopic properties of their solutions.[31] A typical approach to pyrrolidinium gemini-surfactants (**14**) is a two-step procedure which consists in the following reaction sequence. The synthesis of an *N*-alkyl pyrrolidine (**13**) by alkylation of pyrrolidine (**12**) with a selected fatty alkyl bromide (**11**), for instance dodecyl bromide, in the presence of sodium hydroxide and a catalytic amount of potassium iodide in acetonitrile, isolation of the prepared *N*-alkyl pyrrolidine (**13**), its further purification by flash chromatography, and the subsequent bisquaternization of the prepared pyrrolidine (**13**) with an α,ω-dibromoalkane in isopropyl alcohol.[31] The present paper describes a straightforward approach to both pyrrolidinium and piperidinium gemini-surfactants.

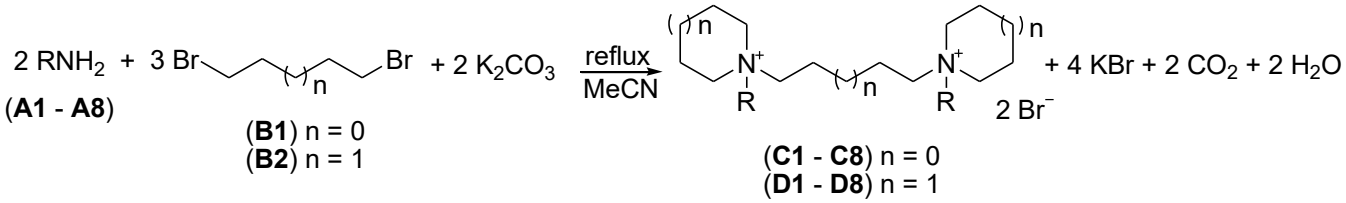


(**11**) (**12**) (**13**) (**14**)

Scheme 1. The typical synthesis of pyrrolidinium gemini-surfactants, where R = $C_{12}H_{25}$, and the linker length is determined by the number n = 1, 2, 4, 6, 8, 10, 12, 14.

Results and Discussion

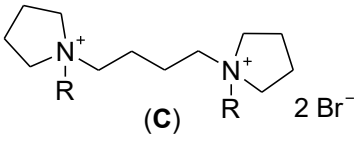
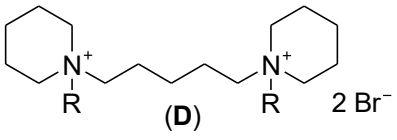
At first thought, it was speculated that if two equivalents of a primary amine were allowed to react with three equivalents of an α,ω-dibromoalkane in the presence of an inorganic base, a cyclisation product, a tertiary cyclic amine, should be formed at first, and if the latter participated in the further quaternization reaction with the remaining α,ω-dibromoalkane, the corresponding cycle-bearing bisquaternary ammonium salt, a gemini-surfactant, should be the end product. Since it is known that ω-haloamines in base mediated cyclization reactions form five- and six-membered rings more readily than three- of four-membered rings,[32] the number of α,ω-dibromoalkanes was limited to 1,4-dibromobutane and 1,5-dibromopentane, respectively. Indeed, the primary amines (**A1**-**A8**) depicted in Table 1 react with 1,4-dibromobutane (**B1**) and 1,5-dibromopentane (**B2**) in the presence of potassium carbonate (K_2CO_3) producing the cycle-bearing bisquaternary ammonium salts (**C1**-**C8**, **D1**-**D8**) in accordance with the overall reaction equation depicted in Scheme 2.



Scheme 2. The overall reaction equation.

From all the solvents acetonitrile (MeCN) was chosen as the reaction medium because the highest rates of Menschutkin reactions were reported for this solvent as well as for nitromethane, dimethylsulfoxide, and propylene carbonate.[33] K_2CO_3 perfectly fills the role of an inorganic base: it is a mild base, it does not react with the solvent nor with the bisquaternary ammonium salts; it, along with potassium bromide (KBr), is hardly soluble in MeCN, a property which facilitates the separation of the products.

Table 1. The isolation yields of cyclo-gemini-surfactants, a dash sign "–" indicates that the reaction was not conducted.

RNH_2 (**A**)	 (**C**)	 (**D**)
(**A1**) -CH_2CH_2OH	(**C1**) 37%	(**D1**) –
(**A2**) -$CH_2CH_2CH_2CH_3$	(**C2**) 72%	(**D2**) 61%
(**A3**) -$CH_2CH_2CH_2CF_3$	(**C3**) 60%	(**D3**) Not isolated
(**A4**) -$CH_2CH_2CH_2CH_2CH_2CH_3$	(**C4**) 51%	(**D4**) Not isolated
(**A5**) -$CH_2CF_2CF_2CF_2CF_2CF_3$	(**C5**) No product	(**D5**) No product
(**A6**) -$CH_2(CH_2)_{14}CH_3$	(**C6**) 75%	(**D6**) 64%
(**A7**) -$CH_2(CH_2)_{16}CH_3$	(**C7**) 89%	(**D7**) 27%
(**A8**) -*cis*-$CH_2(CH_2)_7CH{=}CH(CH_2)_7CH_3$	(**C8**) 77%	(**D8**) 20%

The reaction produces carbon dioxide (CO_2). Probably, K_2CO_3 consuming hydrogen bromide, which originated during alkylation of the primary amines (**A1**-**A8**) with the α,ω-dibromoalkanes (**B1** and **B2**), produces KBr and potassium hydrogencarbonate ($KHCO_3$), the latter under the employed reaction conditions decomposes to the starting K_2CO_3, H_2O, and CO_2.

Both β-ethanolamine (**A1**) and oleylamine (**A8**) react with CO_2 forming the corresponding carbamates,[34] a complication which significantly lowers the yields of the salts (**C1**, **C8**, and **D8**). This complication may be avoided by changing the addition order of the starting compounds so that at first two equivalents of the amine on the reaction with three equivalents of the α,ω-dibromoalkane (**B1** or **B2**) form the monoalkylation product [$BrCH_2CH_2(CH_2)_nCH_2CH_2NH_2^+R\ Br^-$, n = 0 or 1] that on further treatment with K_2CO_3 via the cyclic amine converts into the salt (**C1**, **C8**, and **D8**).

It was demonstrated that both the aliphatic primary amines (**A2**, **A4**, **A6** and **A7**) and the other substituted amines, which bear a double bound (**A8**) or a hydroxyl group (**A1**) or fluorine atoms (**A3**), were successfully converted into the salts (**C8**, **D8**, **C1** and **C3**), although the highly fluorinated amine (**A5**) failed to produce the expected salts (**C5** and **D5**) probably due to its low nucleophilicity.

Probably, the steric effect explains the low isolation yields of the piperidinium gemini-surfactants (**D2**-**D8**): the intermediate *N*-alkyl piperidines are more sterically hindered than the related *N*-alky pyrrolidines, and as a result the intermediate piperidines are less susceptible to quaternization with 1,5-dibromopentane.

Conclusions

The one-pot approach to cycle-bearing gemini-surfactants was developed. The presented procedure suffers only from the three major disadvantages. The first disadvantage is: the procedure gives the surfactants with constant linker lengths (only four or five atoms long); the second, the procedure is sensitive to the nucleophilicity of the amines employed; and the third, the steric hindrance at the nitrogen atom of the intermediate cyclic amine impedes the quaternization reaction, therefore the bulky amines afford the products in lower yields or do not react at all. Despite all the disadvantages enumerated above, this method has one fortunate advantage: it is free from the difficulties associated with rather tiring isolation and purification, ether by distillation or by chromatography, of the intermediate *N*-alky pyrrolidines and piperidines.

Experimental Section

General. 1,4-Dibromobutane (**B1**), 1,5-dibromopentane (**B2**), β-aminoethanol (**A1**), *n*-butylamine (**A2**), *n*-hexylamine (**A4**), *n*-hexadecylamine (**A6**), *n*-octadecylamine (**A7**) and oleylamine [(9Z)-octadec-9-en-1-amine] (**A8**) were purchased from Sigma-Aldrich and were utilized without further purification. 4,4,4-Trifuorobutan-1-amine (**A3**) and 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexan-1-amine (**A5**) were a gift from Dr. A. A. Tutunov. Potassium carbonate (K_2CO_3) was dried by heating above +200°C prior use. All the solvents used in the study as methanol (MeOH), ethanol (EtOH; 96%), isopropyl alcohol (*i*-PrOH), *n*-buthyl alcohol (*n*-BuOH), acetone (Me_2CO), acetonitrile (MeCN), ethyl acetate (AcOEt) and *tert*-butyl methyl ether (*t*-BuOMe) were of commercial origin and were used without receiving further purification.

All the melting points, in degrees Centigrade, of the prepared compounds were determined using a Boetius apparatus and were uncorrected. Elemental analysis was performed using a CHN combustion analyzer CarloErba model 1106; the halogens were determined by combustion-ion chromatography using an Anton Paar microwave oxygen combustion apparatus in conjunction with a Dionex ion chromatography system. All the ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 machine with the working frequency 400 MHz. Both the ^{1}H and ^{13}C NMR spectra are reported utilizing the δ-scale and are in ppm; a multiplication sign "×" denotes the number of functional groups whose nuclei possess the same resonance frequencies; the abbreviation "dist" indicates a distorted NMR signal. The traces of protonated solvents ($CHCl_3$; DMSO) in deuterated solvents ($CDCl_3$; DMSO-d_6) were used as internal standards during ^{1}H spectra acquisition, and the deuterated solvents themselves were serving as internal standards during ^{13}C spectra acquisition. All the NMR spectra of the prepared quaternary ammonium salts in deuterium oxide (D_2O) solutions were recorded using capillary tubes filled with HMDS [$(Me_3Si)_2O$] serving as an external standard, neat HMDS chemical shifts were assumed as ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.06 ppm and ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 1.94 ppm, respectively,[35,36] and they were corrected: the correction value is +0.68.[37]

A few preparations presented down below exemplify the method, the rest of the cognate preparations can be found in the Supporting Information within the "Supplementary Material" section.

1,1′-(Butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (C1). A solution of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole) and β-aminoethanol (**A1**, 1.5 ml, 1.46 g, 24 mmole) in MeCN (20 ml) was refluxed at stirring under an argon (Ar) flow for 3 h. Then the resulting clear solution was cooled to rt. Thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) was introduced to the resulting mass, and the mixture was brought to reflux at stirring, the refluxing was continued for 12 h. After the specified time had passed, *n*-BuOH (20-30 ml) was added to the warm (+50-60 °C) mixture to dissolve the deposited crystals of the product. Then the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot *n*-BuOH (20 ml), and the resulting solution was concentrated *in vacuo*. The concentrated solution was diluted with Me_2CO (100 ml), and the cloudy solution was left to stand at rt overnight. The formed precipitate was filtered off, and the crude product (**C1**) left on a filter was immediately recrystallised from a mixture of MeOH/*i*-PrOH (approximately 1:10 v/v); this sequence of procedures afforded pure (**C1**) in 1.66 g (37%) yield as white very hygroscopic crystals, mp was not determined. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 4.75 (2H, s, OH × 2), 4.02 (4H, br s, CH_2 × 2), 3.63 (8H, br s, CH_2 × 4), 3.52 (4H, dist t, CH_2 × 2), 3.46 (4H, br s, CH_2 × 2), 2.20 (8H, br s, CH_2 × 4), 1.88 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 64.3 (CH_2 × 4), 61.0 (CH_2 × 2), 59.7 (CH_2 × 2), 56.5 (CH_2 × 2), 21.9 (CH_2 × 4), 20.7 (CH_2 × 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 5.25 (2H, t, $^{3}J_{HH}$ 5.3 Hz, OH × 2), 3.79 (4H, br s, CH_2 × 2), 3.61 (4H, br s, CH_2 × 2), 3.57 (4H, br s, CH_2 × 2), 3.41 (8H, br s, CH_2 × 4), 2.06 (8H, br s, CH_2 × 4), 1.76 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 62.7 (CH_2 × 4), 60.0 (CH_2 × 2), 58.2 (CH_2 × 2), 55.2 (CH_2 × 2), 21.0 (CH_2 × 4), 19.7 (CH_2 × 2). Anal. calcd for $C_{16}H_{34}N_2O_2Br_2$ (446.26): C, 43.06; H, 7.68; N, 6.28; Br, 35.81. Found: C, 43.04; H, 7.70; N, 6.25; Br, 35.83.

1,1′-(Butane-1,4-diyl)bis(1-(4,4,4-trifluorobutyl)-pyrrolidinium) dibromide (C3). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), 4,4,4-trifuorobutan-1-amine (**A3**, 2.8 ml, 3.05 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 15 h. After the specified time had passed, *n*-BuOH (20-30 ml) was added to the warm (+50-60 °C) mixture to dissolve the deposited crystals of the product. Then the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot *n*-BuOH (20 ml), and the resulting solution was

concentrated *in vacuo*. The concentrated solution was diluted with Me_2CO (200 ml), and the cloudy solution was left to stand at rt overnight. The precipitated crystals were filtered off, they were washed on a filter with Me_2CO (20 ml) and dried in the air; this sequence of procedures afforded (**C3**) in 3.49 g (60%) yield as white nonhygroscopic crystals. Further recrystallisation from a mixture of MeCN/Me_2CO (approximately 1:10 v/v) afforded the pure product (**C3**) in 3.20 g (92%) yield, mp 260-261 °C, it decomposes at 262 °C. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 3.66 (8H, br s, CH_2 × 4), 3.46 (8H, br s, CH_2 × 4), 2.40 (4H, sext, $^3J_{HH}$ 9.4 Hz, CH_2 × 2), 2.27 (8H, br s, CH_2 × 4), 2.13 (4H, dist quint, CH_2 × 2), 1.92 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 127.3 (q, $^1J_{CF}$ 275.9 Hz; CF_3 × 2), 63.9 (CH_2 × 4), 59.3 (CH_2 × 2), 58.6 (CH_2 × 2), 30.4 (q, $^2J_{CF}$ 29.6 Hz; CH_2 × 2), 20.2 (CH_2 × 4), 20.6 (CH_2 × 2), 16.8 (q appears as d, $^3J_{CF}$ 2.7 Hz; CH_2 × 2). Anal. calcd for $C_{20}H_{36}N_2F_6Br_2$ (578.31): C, 41.54; H, 6.27; N, 4.84; F, 19.71; Br, 27.63. Found: C, 41.56; H, 6.29; N, 4.80; F 19.69; Br, 27.60.

(Z)-1,1′-(Butane-1,4-diyl)bis(1-((Z)-octadec-9-enyl)pyrrolidinium) dibromide (C8). A solution of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole) and oleylamine (**A8**, 8.0 ml, 6.4 g, 24 mmole) in MeCN (20 ml) was refluxed at stirring under an Ar flow for 3 h. Then the resulting clear solution was cooled to rt. Thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) was introduced to the resulting mass, and the mixture was brought to reflux at stirring, the refluxing was continued for 20 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (50 ml), and the resulting filtrate was diluted with *t*-BuOMe (200 ml), and the resulting cloudy solution was left to stand at +5 °C overnight. The formed wax-like material was filtered off, it was washed on a filter with *t*-BuOMe (20 ml), at first it was dried in the air and later in a vacuum desiccator over P_2O_5; this sequence of procedures afforded pure (**C8**) in 6.60 g (77%) yield as a white nonhygroscopic wax-like material, mp 185-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.29 (4H, app q, CH=CH × 2), 3.95 (4H, dist quint, CH_2 × 2), 3.77 (4H, br s, CH_2 × 2), 3.50 (4H, dist quint, CH_2 × 2), 3.25 (4H, dist t, CH_2 × 2), 2.35 (4H, br s, CH_2 × 2), 2.12 (8H, br s, CH_2 × 4), 1.96 (8H, dist q, CH_2 × 4), 1.75 (4H, br s, CH_2 × 2), 1.21-1.32 (44H, br m, CH_2 × 22), 0.83 (6H, t, $^3J_{HH}$ 6.7 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 129.9 (CH × 2), 129.5 (CH × 2), 63.0 (CH_2 × 4), 60.9 (CH_2 × 2), 59.7 (CH_2 x 2), 31.8 (CH_2 × 2), 29.6 (CH_2 × 2), 29.5 (CH_2 × 2), 29.4 (CH_2 × 2), 29.3 (CH_2 × 2), 29.2 (CH_2 × 4), 29.0 (CH_2 × 4), 27.1 (CH_2 × 2), 27.0 (CH_2 × 2), 26.4 (CH_2 × 2), 23.5 (CH_2 × 2), 22.5 (CH_2 × 2), 22.4 (CH_2 × 4), 20.8 (CH_2 × 2), 14.0 (CH_3 × 2). Anal. calcd for $C_{48}H_{94}N_2Br_2$ (859.08): C, 67.11; H, 11.03; N, 3.26; Br, 18.60. Found: C, 66.86; H, 11.23; N, 3.20; Br, 18.57.

1,1′-(Pentane-1,5-diyl)bis(1-hexadecylpiperidinium) dibromide (D6). A mixture of 1,5-dibromopentane (**B2**, 4.7 ml, 7.82 g, 34 mmole), *n*-hexadecylamine (**A6**, 5.78 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 24 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (50 ml), and the resulting filtrate was evaporated to dryness *in vacuo*. The resulting oily residue was dissolved in hot AcOEt (50-70 ml), and the resulting clear solution was left to stand at rt for several days (1-2 days). The formed precipitate was filtered off, it was washed with AcOEt (20 ml) on a filter and dried in the air; this sequence of procedures afforded pure (**D6**) in 5.40 g (64%) yield as a white nonhygroscopic powder, mp 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.79 (4H, dist t, CH_2 × 2), 3.67 (4H, dist t, CH_2 × 2), 3.50 (4H, dist d, CH_2 × 2), 3.36 (4H, dist t, CH_2 × 2), 2.02 (4H, dist t, CH_2 × 2), 1.92 (4H, br s, CH_2 × 2), 1.76 (4H, br s, CH_2 × 2), 1.68 (4H, br s, CH_2 × 2), 1.58 (6H, dist d, CH_2 × 3), 1.19-1.30 (52H, br m, CH_2 × 26), 0.81 (6H, t, $^3J_{HH}$ 6.6 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 60.3 (CH_2 × 2), 58.8 (CH_2 × 4), 56.5 (CH_2 × 2), 31.8 (CH_2 × 2), 29.5 (CH_2 × 16), 29.3 (CH_2 × 2), 29.2 (CH_2 × 2), 29.1 (CH_2 × 2), 26.4 (CH_2 × 2), 22.7 (CH_2), 22.5 (CH_2 × 2), 21.7 (CH_2 × 2), 20.7 (CH_2

× 2), 19.8 (CH_2 × 4), 14.0 (CH_3 × 2). Anal. calcd for $C_{47}H_{96}N_2Br_2$ (849.09): C, 66.48; H, 11.40; N, 3.30; Br, 18.82. Found: C, 66.52; H, 11.58; N, 2.27; Br, 18.90.

Supplementary Material

The Supporting Information is available and contains the synthesis of oleylaminium oleyl carbamate, the rest of the cognate preparations, and the physical properties of the prepared compounds as their NMR spectra and their melting points.

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