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Gemini Pyridinium Surfactants: Synthesis and Conductometric Study of a Novel Class of Amphiphiles[1]

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A new series of pyridinium cationic gemini surfactants was prepared by quaternization of the 2,2′-(α,ω-alkanediyl)bispyridines with N-alkylating agents, whose reactivity is briefly discussed. Particularly useful was the use of long-chain alkyl triflates (trifluoromethanesulfonates) for both overcoming the sterical hindrance in the pyridines and obtaining higher synthetic yields. Well-known 4,4′-(α,ω-alkanediyl)bis(1-alkylpyridinium) structures showed narrow temperature ranges for practical applications, due to their high Krafft points, while the new 2,2′-(α,ω-alkanediyl)bis-(1-alkylpyridinium) series, accounted for good surface active properties. Due to the Krafft points below 0 °C, they could be exploited as solutions in water at any temperature. The characterization of the behavior of the series was performed by conductivity measurements. Some of the proposed structures exhibited unusual surface active behavior, which was interpreted in terms of particular conformational arrangements.

Introduction

The application of cationic surfactants in high technology fields has become very important. Among these applications, the use of surfactant aggregates, mainly vesicles, to form complexes with DNA has impressively grown. Starting from 1987 with the experiments of Felgner and co-workers,[2] these complexes, normally known as lipoplexes, were used to introduce genetic material into cells followed by DNA expression, showing that the use of nonviral carriers was a possible alternative to normally used modified viruses.[2−4] The study of this application allowed for the use of commercially available formulated cationic surfactants for the in vitro transfection of cells. However, the more important in vivo application, namely gene therapy, was the final aim of this research topic.[4] Even if several problems connected with the complexity of the whole transfecting and therapeutic process were dealt with, a few results were obtained. As an example, a first solution to the problem of the rapid elimination of complexes from the bloodstream was achieved, thus permitting a longer circulation time for lipoplexes.[5,6] However, a clear structure−activity relationship about the transfecting performances of cationic surfactants is not available. In fact, a deeper study about the aggregation behavior of these surfactants and their DNA complexation ability, joined to a better characterization of the surfactant/DNA complex, could give important information on the different steps involved in the transfection process.

Due to our experience in the synthesis and characterization of cationic surfactants,[7−12] we envisaged the

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(1) Presented in part at the 5th World Surfactants Congress, Florence, Italy, May 29−June 2, 2000. Barni, E.; Barolo, C.; Compari, C.; Fisicaro, E.; Quagliotto, P.; Viscardi, G. *World Surfactants Congress, 5th* **2000**, 1044−1048.

(2) Felgner, P. L.; Gadek, T. R.; Holm, M.; Roman, R.; Chan, H. W.; Wenz, M.; Northrop, J. P.; Ringold, G. M.; Danielsen, M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 7413−7417.

(3) (a) Meekel, A. A. P.; Wagenaar, A.; Kroeze, J. E.; Haadsma, P.; Bosgraaf, B.; Stuart, M. C. A.; Brisson, A.; Ruiters, M. H. J.; Hoekstra, D.; Engberts, J. B. F. N. *Eur. J. Org. Chem.* **2000**, 665−673. (b) for an extensive recent review, see: Kirby, A. J.; Camilleri, P.; Engberts, J. B. F: N.; Feiters, M.; Nolte, R. J. M.; Soderman, O.; Bergsma, M.; Bell, P. C.; Fielden, M. L.; Garcia Rodriguez, C.; Guédat, P.; Kremer, A.; McGregor, C.; Perrin, C.; Ronsin, G.; van Eijk, M. C. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 1448−1457.

(4) Miller, A. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1768−1785.

(5) Litzinger, D. C.; Brown, J. M.; Wala, I.; Kaufman, S. A.; Van, G. Y.; Farrell, C. L.; Collins, D. *Biochim. Biophys. Acta* **1996**, *1281*, 139−149.

(6) Hong, K.; Zheng, W.; Baker, A.; Papahadjopoulos, D. *FEBS Lett.* **1997**, *400*, 233−237.

(7) Fisicaro, E.; Compari, C.; Róøycka-Roszak, B.; Viscardi, G.; Quagliotto, P. *Curr. Top. Colloid Interface Sci.* **1997**, *2*, 54−68.

(8) Viscardi, G.; Quagliotto, P.; Barolo, C.; Savarino, P.; Barni, E.; Fisicaro, E. *J. Org. Chem.* **2000**, *65*, 8197−8203.

(9) Fisicaro, E.; Pelizzetti, E.; Viscardi, G.; Quagliotto, P.; Trossarelli, L. *Colloids Surf. A: Physicochem. Eng. Aspects* **1994**, *84*, 59−70.

(10) Fisicaro, E.; Ghiozzi, A.; Pelizzetti, E.; Viscardi, G.; Quagliotto, P. *J. Colloid Interface Sci.* **1996**, *182*, 549−557.

(11) Fisicaro, E.; Ghiozzi, A.; Pelizzetti, E.; Viscardi, G.; Quagliotto, P. *J. Colloid Interface Sci.* **1996**, *184*, 147−154.

(12) Ardizzone, S.; Bianchi, C. L.; Drago, P.; Mozzanica, D.; Quagliotto, P.; Savarino, P.; Viscardi, G. *Colloids Surf. A: Physicochem. Eng. Aspects* **1996**, *113*, 135−144.

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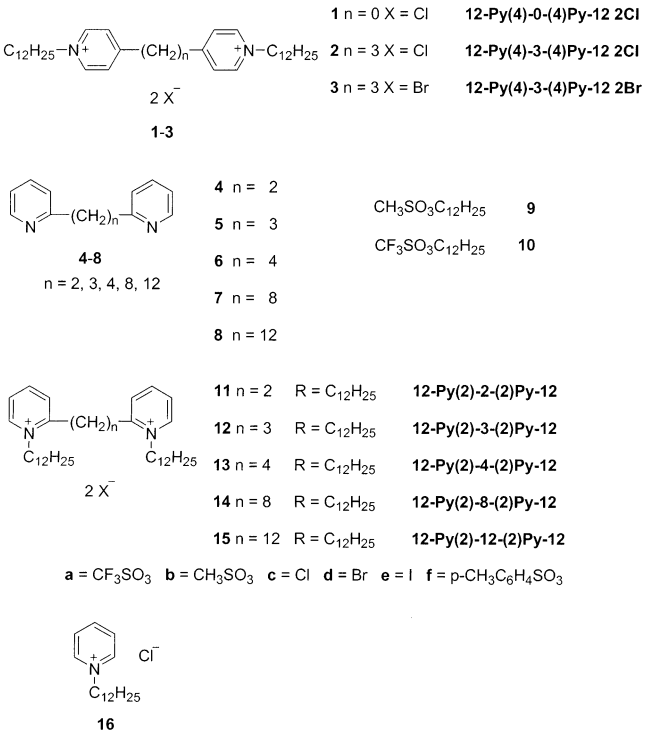
possibility of both in vitro and in vivo applications of our already prepared structures. With this goal in mind, we started a wide investigation involving organic synthesis, physicochemical characterization, biological evaluations, and molecular modeling. This article is the first report on the organic synthesis and the early physicochemical characterization of novel pyridinium gemini cationic surfactants. Their unusual amphiphilic properties and the tunability of structure, by variation of chain hydrophobicity, spacer length, and counterion, makes them attractive for transfection purposes.

In the past decade, a growing interest was devoted to new structures called gemini surfactants. The challenge, at first, was mainly directed to the synthesis and fundamental surface activity characterization of these structures, made up of two typical surfactant molecules connected by a spacer at the headgroup level. Recently, many studies concerning the practical use of gemini molecules appeared in the literature, showing that the first speculative interests were followed by practical applications, due to their unusual properties:[7,13,14] (i) the lower critical micellar concentration (cmc) and C_{20} (the concentration at which a reduction of the surface tension of 20 mN/m is attained) values, (ii) the better adsorption behavior at both the air/water and the solid/water interfaces with respect to their *monomers*, and (iii) the tendency to form micelles of different shapes and dimensions (i.e., spherical, rodlike, threadlike, vesicles), even at low concentration, when compared with similar *normal* surfactants.

In the field of cationic surfactants, the structures bearing an ammonium headgroup were more widely studied because of their fast and simple synthetic pathway.[13,15−19] However, different and more tailored structures were prepared in recent years, showing the great interest connected with these kinds of molecules.[20] Due to our activity in the field of cationic surfactants and, in particular, of pyridinium ones,[8−12] we started a synthetic project about the gemini pyridinium surfactants, reported in the present paper. Many papers are present in the literature that refer to viologen-type structures,[21,22] similar to **1**−**3** (Chart 1). Their positional isomers differing for the connection site of the spacer on the pyridine ring are lacking.

The information about the behavior of these surfactant molecules[3,21] is scarce. Thus, the study was focused on the preparation and preliminary characterization of a few

CHART 1. Products Prepared in the Present Work



terms belonging to the 1,1′-dialkyl-4,4′-bispyridinium or 4,4′-(α,ω-alkanediyl)bis(1-alkylpyridinium) series. The results showed low surface activity and a low tendency to form micelles at room temperature or below, thus reducing the range of applicability. In view of these preliminary results, the preparation of a 2,2′-(α,ω-alkanediyl)bis(1-alkylpyridinium) series (structures **11**−**15**), differing for the positional isomerism of the spacer on the pyridinium rings, came out. However, their synthesis was not easy, as for former structures, owing to steric hindrance of the pyridines in the 2-position, which opposes the quaternization reaction that was studied using different alkylating agents: iodide, methanesulfonate, and trifluoromethansulfonate esters. The triflates appeared the best for both the lower reaction temperatures and the higher yields attainable. The amphiphilic characterization of the products showed peculiar behavior of some structures which, in our opinion, is due to a particular conformational arrangement.

Experimental Section

General Procedures and Materials. See the Supporting Information.

Synthesis. 1,1′-Didodecyl-4,4′-dipyridinium chloride (1). In a three-necked round-bottom flask, purged with argon, were introduced 4,4′-dipyridyl (15.6 g, 0.1 mol), dodecyl chloride (204.57 g, 1.0 mol), and DMF (100 mL). The solution was refluxed for 8 h and cooled at 0 °C with formation of a beige solid, which was crystallized from acetone/methanol: yield 34.55 g (62%); mp undetermined, dec above 280 °C; R_f 0.1 on silica (eluent methanol/acetic acid/chloroform, MAC 20:10:70); UV (ethanol) λ_{max} 266 nm, logϵ 4.10; ^{1}H NMR (DMSO-d_6) δ 0.87 (t, 6H, $2CH_3$), 1.26 (m, 36H, $18CH_2$), 1.99 (m, 4H, $N^+CH_2CH_2$), 4.71 (t, 4H, N^+CH_2), 8.82 (d, 2H, H″), 9.42 (d, 2H, H′); FT-IR (KBr) 3048, 2916, 2848, 1636, 1570, 1512, 1468,

(13) Zana, R. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 566−571 and references therein.
(14) (a) Rosen, M. J.; Tracy, D. J. *J. Surfactants Deterg.* **1998**, *1*, 547−554 and references therein. (b) For a more recent review, see: Menger, F. M.; Keiper, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1906−1920.
(15) Zana, R.; Benrraou, M.; Rueff, R. *Langmuir* **1991**, *7*, 1072−1075.
(16) Alami, E.; Levy, H.; Zana, R. *Langmuir* **1993**, *9*, 940−944.
(17) Alami, E.; Beinert, G.; Marie, P.; Zana, R. *Langmuir* **1993**, *9*, 1465−1467.
(18) Frindi, M.; Michels, B.; Levy, H.; Zana, R. *Langmuir* **1994**, *10*, 1140−1145.
(19) Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, *11*, 1448−1456.
(20) Pérez, L.; Torres, J. L.; Manresa, A.; Solans, C.; Infante, M. R. *Langmuir* **1996**, *12*, 5296−5301.
(21) Lee, D. K.; Kim, Y. I.; Kwon, Y. S.; Kang, Y. S.; Kevan, L. *J. Phys. Chem. B.* **1997**, *101*, 5319−5323.
(22) Vassiltsova, O. V.; Chuvilin, A. L.; Parmon, V. N. *J. Photochem. Photobiol. A* **1999**, *125*, 127−134.

1174, 842, 786 cm^{-1}. Anal. Calcd for $C_{34}H_{58}Cl_2N_2$: C, 72.18; H, 10.33; N, 4.95. Found: C, 72.09; H,10.37; N, 4.93.

1,1′-Didodecyl-4,4′-trimethylenebispyridinium Chloride (2).

The 1,3-bis(4-pyridyl)propane (25.00 g, 0.126 mol) was dissolved in DMF (10 mL) in a three-necked round-bottom flask. The temperature was raised to 150−155 °C, and the dodecyl chloride (258.04 g, 297 mL, 1.26 mol) was slowly dropped into the solution. The reaction was stopped after 12 h, and the DMF was evaporated under vacuum. The residue was filtered, suspended in ethyl ether under stirring, obtaining a brown solid, which was crystallized two times from hot acetonitrile/toluene to give white-beige crystals: yield 63.0 g (82%); mp 65−66 °C; R_f 0.1 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 230, 257 nm, log ϵ 4.21, 3.88; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.23 (m, 36H, $18CH_2$), 1.89 (m, 4H, $N^+CH_2CH_2$), 2.12 (m, 2H, $PyCH_2CH_2CH_2Py$), 2.96 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.54 (t, 4H, N^+CH_2), 8.04 (d, 2H, H″), 8.97 (d, 2H, H′); FT-IR (KBr) 2954, 2918, 2848, 1640, 1570, 1516, 1468, 1176, 842, 726, cm^{-1}. Anal. Calcd for $C_{37}H_{64}Cl_2N_2$: C, 73.11; H, 10.61; N, 4.61. Found: C, 73.01; H, 10.57; N, 4.63.

1,1′-Didodecyl-4,4′-trimethylenebispyridinium Bromide (3). The 1,3-bis(4-pyridyl)propane (10.0 g, 0.05 mol) was dissolved in DMF (15 mL) in a three-necked round-bottom flask. The temperature was raised to 150−155 °C, and the dodecyl bromide (125.61 g, 120 mL, 0.5 mol) was slowly dropped into the solution. The reaction was stopped after 6 h, and the DMF was evaporated under vacuum. The residue was filtered, suspended in ethyl ether, and crystallized two times from acetonitrile/toluene giving white-gray crystals: yield 25.80 g (73.5%); mp 65 °C; R_f 0.1 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 229, 257 nm, log ϵ 4.28, 3.88; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.26 (m, 36H, $18CH_2$), 1.92 (m, 4H, $N^+CH_2CH_2$), 2.12 (m, 2H, $PyCH_2CH_2CH_2Py$), 2.96 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.57 (t, 4H, N^+CH_2), 8.07 (d, 2H, H″), 9.01 (d, 2H, H′); FT-IR (KBr) 2954, 2911, 2847, 1636, 1570, 1514, 1468, 1174, 844, 786 cm^{-1}. Anal. Calcd for $C_{37}H_{64}Br_2N_2$: C, 63.78; H, 9.26; N, 4.02. Found: C, 63.86; H, 9.22; N, 4.00.

General Procedure for the Synthesis of Bases 4, 7, and 8. In a three-necked round-bottom flask equipped with gas insertion adapter were introduced under argon anhydrous ethyl ether (300 mL) and a 2.5 M solution of butyllithium in hexane (100 mL, 0.25 mol). The temperature was lowered to −20 °C with a dry ice−acetone bath, and the 2-methylpyridine was added dropwise under stirring, giving a red orange solution. The proper α,ω-dibromoalkane was then added dropwise, under stirring. The solution was allowed to react for 50 min at −20 °C and allowed to return to room temperature, reacting for further 2 h. The reaction was quenched by the dropwise addition of water (30 mL). The ethereal solution was extracted with 1:2 hydrogen chloride solution. The aqueous layer was separated and treated with a sodium hydroxide aqueous solution, until basic reaction, when an orange-reddish oil separated. The oil was extracted three times with ethyl ether. The ether solution of the base was dried with anhydrous sodium sulfate, filtered, and evaporated, leaving a crude product which was purified by distillation or column flash chromatography (FC).[23]

1,2-Bis(2-pyridyl)ethane (4). The crude product obtained following the general procedure, using 1,2-dibromoethane as the dibromoalkane reactant, was distilled under vacuum, obtaining a pale oil: yield 25.78 g (56%); bp 73 °C/8 × 10^{-5} Torr; R_f 0.6 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 263 nm, log ϵ 3.81; ^{1}H NMR (DMSO-d_6) δ 3.13 (s, 4H, $2CH_2$), 7.20 (dt, 2H, H_{meta}), 7.25 (d, 2H, H'_{meta}), 7.67 (dt, 2H, H_{para}), 8.50 (dd, 2H, H_{orto}); FT-IR (KBr) 3062, 2928, 2856, 1581, 1567, 1472, 1450, 787 cm^{-1}; GC−MS (*m*/*z*) 184 (M^+). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.16; H, 6.60; N, 15.17.

(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923−2925.

1,3-Bis(2-pyridyl)propane (5).[24] In a three-necked flask, previously purged with argon, was introduced 2-methylpyridine (431 g; 458 mL; 4.64 mol), followed by the addition of sodium (2.4 g; 0.104 mol) in small portions under magnetic stirring. After the sodium dissolution (which took about 1 h), the temperature was raised to 120 °C and 2-vinylpyridine (97.5 g; 100 mL; 0.93 mol) was added dropwise to the brown solution. After 4 h, the reaction was stopped and cooled at 0 °C. Methanol (50 mL) was added to quench the reaction giving a red solution which was distilled to remove the excess of methanol and 2-methylpyridine. Distillation of the resulting oil gave a pale yellow oil: yield 85.05 g (46%); bp 97 °C/3 × 10^{-5} Torr (lit.[25] bp 135 °C/25 Torr); R_f 0.36 on silica (eluent: butanol/acetic acid/water BAW 4:1:5, organic phase); UV (ethanol) λ_{max} 206, 263, 331 nm, log ϵ 4.14, 3.90, 2.82; ^{1}H NMR (DMSO-d_6) δ 2.07 (m, 2H, CH_2), 2.76 (t, 4H, $2CH_2$), 7.19 (d, 2H, H_{meta}), 7.26 (d, 2H, H'_{meta}), 7.62(dt, 2H, H_{para}), 8.47 (d, 2H, H_{orto}); FT-IR (KBr) 3008, 2924, 2858, 1590, 1568, 1474, 1434, 766 cm^{-1}; GC−MS (*m*/*z*) 198 (M^+). Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.70; H, 7.14; N, 14.11.

1,4-Bis(2-pyridyl)butane (6). The procedure of Richards et al.[26] was followed. The addition of lithium metal was accomplished under argon in a glovebag to ensure the best anhydrous conditions: yield 35.5 g (46%); bp 109−110 °C/1.5 × 10^{-4} Torr (lit.[26] bp 140 °C/1 Torr, lit.[25] bp 125 °C/0.2 Torr); R_f 0.28 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 257, 262, 269 nm, log ϵ 3.76, 3.83, 3.69; ^{1}H NMR (DMSO-d_6) δ 1.70 (m, 4H, $PyCH_2CH_2CH_2CH_2Py$), 2.75 (t, 4H, $PyCH_2CH_2CH_2CH_2$-Py), 7.18 (dd, 2H, H_{meta}), 7.23 (d, 2H, H'_{meta}), 7.67 (dt, 2H, H_{para}), 8.47 (d, 2H, H_{orto}); FT-IR (film) 2945, 2920, 2852, 1582, 1564, 1475, 1458, 1429, 1147, 1049, 771, 750, 734 cm^{-1}; GC−MS (*m*/*z*) 212 (M^+). Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.22; H, 7.57; N, 13.15.

1,8-Bis(2-pyridyl)octane (7). The crude product obtained following the general procedure was purified by flash chromatography on alumina with petroleum ether/ethyl acetate 95:5, obtaining a pale oil: yield 15.02 g (70%); R_f 0.41 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 257, 262, 269 nm, log ϵ 3.81, 3.87, 3.73; ^{1}H NMR (DMSO-d_6) δ 1.28 (bs, 8H, 4 CH2), 1.65 (m, 4H, $PyCH_2CH_2$), 2.70 (t, 4H, $PyCH_2$), 7.18 (td, 2H, H_{meta}), 7.23 (d, 2H, H'_{meta}), 7.68 (td, 2H, H_{para}), 8.46 (d, 2H, H_{orto}); FT-IR (film) 2928, 2854, 1591, 1475, 1435, 1265, 1150, 1051, 897, 742, 704, 626 cm^{-1}; GC−MS (*m*/*z*) 268 (M^+). Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 80.32; H, 8.97; N, 10.41.

1,12-Bis(2-pyridyl)dodecane (8). The crude product obtained following the general procedure was purified by flash chromatography on alumina with petroleum ether/ethyl acetate 90:10, obtaining a pale oil: yield 22.33 g (55%); mp 39−42; R_f 0.44 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 257, 262, 269 nm, log ϵ 3.76, 3.81, 3.68; ^{1}H NMR (DMSO-d_6) δ 1.25 (m 16H, $8CH_2$), 1.65 (m, 4H, $PyCH_2CH_2$), 2.70 (t, 4H, $PyCH_2$), 7.17 (dd, 2H, H_{meta}), 7.22(d, 2H, H'_{meta}), 7.67 (td, 2H, H_{para}), 8.46 (dd, 2H, H_{orto}); FT-IR (film) 2935, 2850, 1587, 1561, 1471, 1436, 1276, 1259, 1145, 1051, 99, 750 cm^{-1}; GC−MS (*m*/*z*) 324 (M^+). Anal. Calcd for $C_{22}H_{32}N_2$: C, 81.43; H, 9.94; N, 8.63. Found: C, 81.34; H, 9.98; N, 8.59.

Dodecylmethansulfonate (9). A general procedure[27] was applied for the synthesis of the dodecylmethanesulfonate. All characterization data (mp, FT-IR, and NMR) agreed with literature data.

Dodecyl Trifluoromethansulfonate (10).[28,29] To a solution of trifluoromethanesulfonic anhydride in dry dichlo-

(24) Sartoris, N. E.; Pines, H. *J. Org. Chem.* **1969**, *34*, 2119−2122.
(25) Bönnemann, H.; Brinkmann, R. *Synthesis* **1975**, 600−602.
(26) Richards, D. H.; Scilly, N. F.; Williams, F. J. *Chem. Ind.* **1970**, 1298−1299.
(27) Marvel, C. S. and Sekera, V. C. *Organic Syntheses*; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. III, pp 366−369.
(28) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *21*, 3673−3677.
(29) Fife, W. K.; Ranganathan, P.; Zeldin, M. *J. Org. Chem.* **1990**, *55*, 5610−5613.

romethane, at 0 °C under argon, was added dropwise an equimolar solution of dodecyl alcohol and pyridine in dichloromethane. The reaction was continued for 15 min and successively the solution was quenched with water, extracted repeatedly with water and separated. The organic phase was then dried with Na_2SO_4 and evaporated. The resulting oil was used immediately for the quaternization reactions. The product was obtained in 85% yield: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, CH_3), 1.26 (m, 16H, $8CH_2$), 1.41 (m, 2H, $CF_3SO_3CH_2CH_2CH_2$), 1.82 (m, 2H, $CF_3SO_3CH_2CH_2$), 4.53 (t, 2H, $CF_3SO_3CH_2$).

General Procedure for the Quaternization of Bases 4−8 with the Dodecyl Trifluoromethanesulfonate.[29,30] A solution of an excess of the dodecyl trifluoromethanesulfonic ester (1.25 mol per mol of nitrogen to be quaternized) in anhydrous chloroform, kept under argon, was stirred at reflux, and a solution of the proper base in chloroform was added dropwise. The reaction was continued for 1.5 h. The reaction was worked up as described in each of the following entries.

Ionic Exchange General Procedure for Obtaining Products 11−15 with Different Counterions. The ionic exchange was performed using a strong anionic exchange resin, conditioned by suspension in water for a few hours, packing in a glass column, and treating in the order with a solution of NaOH 4%, water until neutral reaction of the effluent, aqueous 10% solution of sodium salt of proper counterion, and water to eliminate the residual salt.

Before use, the resin was unpacked, filtered on a funnel, and twice suspended in methanol for 0.5 h. Finally, the methanolic suspension was packed in the column and washed with 3 volumes of methanol. A methanolic solution of the product to be subjected to the ionic exchange was put onto the column and eluted with methanol. After evaporation of methanol, the product with desired counterion was recovered and purified by crystallization from acetonitrile/ethyl acetate mixture.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Ditrifluoromethanesulfonate (12a). A white solid, which separated from the solution, was filtered off, giving the pure product as a white powder: yield 2.73 g (80%); mp 200−202 °C; R_f 0.31 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269, log ϵ 4.10; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.24 (m, 36H, $18CH_2$), 1.86 (m, 4H, $N^+CH_2CH_2$), 2.19 (m, 2H, $PyCH_2CH_2CH_2Py$), 3.28 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.57 (t, 4H, N^+CH_2), 8.02 (t, 2H, H_{meta}), 8.10 (d, 2H, H'_{meta}), 8.54 (t, 2H, H_{para}), 9.03 (d, 2H, H_{orto}); FT-IR (KBr) 3088, 2922, 2852, 1634, 1576, 1514, 1482, 1468, 1256, 1226, 1166, 1032, 786, 644 cm^{-1}. Anal. Calcd for $C_{39}H_{64}F_6N_2O_6S_2$: C, 56.10; H, 7.72; N, 3.35. Found: C, 55.98; H, 7.70; N, 3.38.

1,1′-Didodecyl-2,2′-tetramethylenebispyridinium Ditrifluoromethanesulfonate (13a). The reaction mixture was evaporated, and the resulting oil was treated with ethyl acetate obtaining a white solid, which was filtered off, giving the pure product as a white powder: yield 2.10 g (70%); mp 129−131 °C; R_f 0.20 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.15; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.23 (m, 36H, $18CH_2$), 1.87 (m, 8H, $N^+CH_2CH_2$ + $PyCH_2CH_2$), 3.18 (t, 4H, $PyCH_2$), 4.56 (t, 4H, N^+CH_2), 8.00 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.50 (t, 2H, H_{para}), 9.01 (d, 2H, H_{orto}); FT-IR (KBr) 3086, 2920, 2851, 1629, 1578, 1513, 1469, 1260, 1226, 1159, 1034, 642 cm^{-1}. Anal. Calcd for $C_{40}H_{66}F_6N_2O_6S_2$: C, 56.58; H, 7.83; N, 3.30. Found: C, 56.50; H, 7.81; N, 3.33.

1,1′-Didodecyl-2,2′-octamethylenebispyridinium Ditrifluoromethanesulfonate (14a). The solvent was evaporated under vacuum and the resulting oil was purified by FC on alumina with ethyl acetate/methanol 95:5 and 80:20. The product was an oil, which crystallized on standing: yield 11.76 g (83%); mp 50−52 °C; R_f 0.20 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.13; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.23 (m, 44H, $22CH_2$), 1.73 (m, 4H, $PyCH_2CH_2$), 1.85 (m, 4H, $N^+CH_2CH_2$), 3.08 (t, 4H, $PyCH_2$), 4.54 (t, 4H, N^+CH_2), 7.98 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.48 (t, 2H, H_{para}), 9.00 (d, 2H, H_{orto}); FT-IR (KBr)3088, 2926, 2854, 1630, 1580, 1514, 1466, 1260, 1224, 1160, 1032, 782, 640 cm^{-1}. Anal. Calcd for $C_{44}H_{74}F_6N_2O_6S_2$: C, 58.38; H, 8.24; N, 3.09. Found: C, 58.42; H, 8.27; N, 3.06.

1,1′-Didodecyl-2,2′-dodecamethylenebispyridinium Ditrifluoromethanesulfonate (15a). The solvent was evaporated under vacuum and the resulting oil was washed several times with petroleum ether. A white crystalline solid was obtained: yield 2.30 g (94%); mp 93−96 °C; R_f 0.31 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.09; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, $2CH_3$), 1.24 (m, 52H, $26CH_2$), 1.70 (m, 4H, $PyCH_2CH_2$), 1.84 (m, 4H, $N^+CH_2CH_2$), 3.08 (t, 4H, $PyCH_2$), 4.54 (t, 4H, N^+CH_2), 7.98 (t, 2H, H_{meta}), 8.04 (d, 2H, H'_{meta}), 8.49 (t, 2H, H_{para}), 8.98 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2912, 2852, 1627, 1576, 1516, 1468, 1266, 1225, 1157, 1034, 640 cm^{-1}. Anal. Calcd for $C_{48}H_{82}F_6N_2O_6S_2$: C, 59.97; H, 8.60; N, 2.91. Found: C, 56.01; H, 8.57; N, 2.94.

1,1′-Didodecyl-2,2′-dimethylenebispyridinium Dimethanesulfonate (11b). An excess of dodecylmethanesulfonate (28.7 g; 0.18 mol) was heated at 140 °C under magnetic stirring, and the base **1a** (5 g; $2.7\cdot10^{-2}$ mol) was slowly added in small portions. After the additions were completed, the mixture was reacted for 10 h. The resulting dark mixture was suspended a few times in ethyl acetate, until a brown powder separated. The powder was purified by column chromatography on alumina (eluent: ethyl acetate/ethanol) and finally by crystallization from acetonitrile/ethyl acetate. The crystallization seemed to suffer from the possible partial instability of the compound in that solvent system: yield 12.95 g. (67%); mp 189−190 °C. R_f 0.13 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269, 316 nm, logϵ 4.09, 2.49; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 6H, $2CH_3$), 1.25 (m, 36H, $18CH_2$), 1.89 (m, 4H, $N^+CH_2CH_2$), 2.30 (s, 6H, CH_3SO_3), 3.64 (t, 4H, $PyCH_2$), 4.65 (t, 4H, N^+CH_2), 8.09 (t, 2H, H_{meta}), 8.21 (d, 2H, H'_{meta}), 8.60 (t, 2H, H_{para}), 9.11 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2918, 2850, 1620, 1580, 1208, 1192, 786, 718 cm^{-1}. Anal. Calcd for $C_{38}H_{68}N_2O_6S_2$: C, 64.01; H, 9.61; N, 3.93. Found: C, 63.97; H, 9.65; N, 3.95.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Dimethanesulfonate (12b). In a three necked round-bottom flask was introduced the dodecylmethanesulfonate **9** (26.99 g; 0.102 mol), and the mixture was warmed at 140 °C under magnetic stirring. The base **5** (5 g; 0.0252 mol) was introduced by adding small quantities every 10 min. The viscosity of the mixture became greater as the reaction proceeded, preventing the ease of stirring. After 6 h, the reaction was stopped. The dark crude solid mixture was suspended with ethyl acetate under vigorous stirring. The procedure was repeated a few times, giving a gray-brownish powder. The product was finally purified by crystallization with acetonitrile/ethyl acetate. Alternatively, the product was obtained by anionic exchange from **12a**, giving a white product with the same analytical data: yield 15.39 g (84%); mp 225−227 °C; R_f 0.19 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 3.97; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 6H, $2CH_3$), 1.25 (m, 36H, $18CH_2$), 1.87 (m, 4H, $N^+CH_2CH_2$), 2.21 (m, 2H, $PyCH_2CH_2CH_2Py$), 2.34 (s, 6H, CH_3SO_3), 3.29 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.59 (t, 4H, N^+CH_2), 8.01 (t, 2H, H_{meta}), 8.12 (d, 2H, H'_{meta}), 8.54 (t, 2H, H_{para}), 9.02 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2920, 2852, 1630, 1516, 1472, 1208, 1192, 786, 722 cm^{-1}. Anal. Calcd for $C_{39}H_{70}N_2O_6S_2$: C, 64.42; H, 9.70; N, 3.85. Found: C, 64.40; H, 9.66; N, 3.87.

1,1′-Didodecyl-2,2′-tetramethylenebispyridinium Dimethanesulfonate (13b). A procedure similar to that for **12b** was applied. The suspension of the crude product in ethyl acetate gave a gray-beige solid, which was crystallized from acetonitrile/ethyl acetate. The product was also obtained by anionic exchange from **13a**, giving a white product with the same analytical data: yield 69%; mp 72−73 °C; R_f 0.22 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 268 nm, log ϵ 4.15; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 6H, $2CH_3$), 1.25 (m, 36H,

(30) Ranganathan, P.; Fife, W. K.; Zeldin, M. *J. Polym. Sci. A* **1990**, *28*, 2711−2717.

18CH_2), 1.87 (m, 4H, $N^+CH_2CH_2$), 1.91 (m, 4H, $PyCH_2CH_2$), 2.32 (s, 6H, CH_3SO_3), 3.22 (t, 4H, $PyCH_2CH_2$), 4.60 (t, 4H, N^+CH_2), 8.02 (t, 2H, H_{meta}), 8.11 (d, 2H, H'_{meta}), 8.55 (t, 2H, H_{para}), 9.07 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2920, 2852, 1630, 1516, 1472, 1208, 1192, 786, 722 cm^{-1}. Anal. Calcd for $C_{40}H_{72}N_2O_6S_2$: C, 64.82; H, 9.79; N, 3.78. Found: C, 64.76; H, 9.74; N, 3.80.

1,1′-Didodecyl-2,2′-octamethylenebispyridinium Dimethanesulfonate (14b). The ionic exchange from **14a** gave a white powder, crystallized from acetonitrile/ethyl acetate: yield 88%; mp 108−110 °C; R_f 0.27 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, logϵ 4.20. ^{1}H NMR (DMSO-d_6) δ 0.84 (t, 6H, 2CH_3), 1.23 (m, 44H, 22CH_2), 1. 70 (m, 4H, $N^+CH_2CH_2$), 1.82 (m, 4H, $PyCH_2CH_2$), 2.30 (s, 6H, CH_3SO_3), 3.09 (t, 4H, $PyCH_2$), 4.56 (t, 4H, N^+CH_2), 7.99 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.51 (t, 2H, H_{para}), 9.02 (d, 2H, H_{orto}); FT-IR (KBr) 2926, 2854, 1629, 1465, 1210, 1191, 1059, 784 cm^{-1}. Anal. Calcd for $C_{44}H_{80}N_2O_6S_2$: C, 66.29; H, 10.11; N, 3.51. Found: C, 66.21; H, 10.08; N, 3.49.

1,1′-Didodecyl-2,2′-dodecamethylenebispyridinium Dimethanesulfonate (15b). The ionic exchange from **15a** gave a white powder, crystallized from ethanol/ethyl acetate: yield 94%; mp 119−120 °C; R_f 0.33 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.10; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, 2CH_3), 1.25 (m, 52H, 26CH_2), 1.70 (m, 4H, $N^+CH_2CH_2$), 1.82 (m, 4H, $PyCH_2CH_2$), 2.30 (s, 6H, CH_3SO_3), 3.08 (t, 4H, $PyCH_2CH_2$), 4.55 (t, 4H, N^+CH_2), 7.98 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.50 (t, 2H, H_{para}), 9.01 (d, 2H, H_{orto}); FT-IR (KBr) 2926, 2854, 1629, 1465, 1210, 1191, 1059, 784 cm^{-1}. Anal. Calcd for $C_{48}H_{88}N_2O_6S_2$: C, 67.56; H, 10.39; N, 3.28. Found: C, 67.51; H, 10.43; N, 3.31.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Dichloride (12c). The product obtained by ionic exchange of **12a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 92%; mp 162−164 °C; R_f 0.15 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.17; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 6H, 2CH_3), 1.25 (m, 36H, 18CH_2), 1.86 (m, 4H, $N^+CH_2CH_2$), 2.21 (m, 2H, $PyCH_2CH_2CH_2Py$), 3.40 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.70 (t, 4H, N^+CH_2), 8.04 (t, 2H, H_{meta}), 8.26 (d, 2H, H'_{meta}), 8.57 (t, 2H, H_{para}), 9.19 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2920, 2852, 1630, 1516, 1472, 786, 722 cm^{-1}. Anal. Calcd for $C_{37}H_{64}Cl_2N_2$: C, 73.11; H, 10.61; N, 4.61. Found: C, 73.05; H, 10.58; N, 4.58.

1,1′-Didodecyl-2,2′-tetramethylenebispyridinium Dichloride (13c). The product obtained from the ionic exchange of **13a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 98%; mp 69−71 °C; R_f 0.18 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 268 nm, log ϵ 4.16; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, 2CH_3), 1.24 (m, 36H, 18CH_2), 1.86 (m, 4H, $N^+CH_2CH_2$), 1.90 (m, 4H, $PyCH_2CH_2$), 3.20 (t, 4H, $PyCH_2CH_2$), 4.59 (t, 4H, N^+CH_2), 7.99 (t, 2H, H_{meta}), 8.08 (d, 2H, H'_{meta}), 8.52 (t, 2H, H_{para}), 9.02 (d, 2H, H_{orto}); FT-IR (KBr) 3046, 2922, 2852, 1628, 1512, 1464, 784, 722 cm^{-1}. Anal. Calcd for $C_{38}H_{66}Cl_2N_2$: C, 73.40; H, 10.70; N, 4.50. Found: C, 73.45; H, 10.67; N, 4.49.

1,1′-Didodecyl-2,2′-octamethylenebispyridinium Dichloride (14c). The product obtained from the ionic exchange of **14a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 91%; mp 88−90 °C; R_f 0.22 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.07; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, 2CH_3), 1.24 (m, 44H, 22CH_2), 1.70 (m, 4H, $N^+CH_2CH_2$), 1.82 (m, 4H, $PyCH_2CH_2$), 3.10 (t, 4H, $PyCH_2CH_2$), 4.56 (t, 4H, N^+CH_2), 7.98 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.51 (t, 2H, H_{para}), 9.04 (d, 2H, H_{orto}); FT-IR (KBr) 2920, 2850, 1629, 1576, 1520, 1474, 793, 723 cm^{-1}. Anal. Calcd for $C_{42}H_{74}Cl_2N_2$: C, 74.41; H, 11.00; N, 4.13. Found: C, 74.39; H, 10.94; N, 4.16.

1,1′-Didodecyl-2,2′-dodecamethylenebispyridinium Dichloride (15c). The product obtained by ionic exchange of **15a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 92%; mp 87−90 °C; R_f 0.31 on silica (eluent BAW 4:1:5); UV (ethanol) λ_{max} 269 nm, log ϵ 4.04. ^{1}H NMR (DMSO-d_6) δ 0.85 (t, 6H, 2CH_3), 1.24 (m, 52H, 26CH_2), 1.69 (m, 4H, $N^+CH_2CH_2$), 1.81 (m, 2H, $PyCH_2CH_2$), 3.08 (t, 4H, $PyCH_2CH_2$), 4.55 (t, 4H, N^+CH_2), 7.98 (t, 2H, H_{meta}), 8.05 (d, 2H, H'_{meta}), 8.48 (t, 2H, H_{para}), 9.04 (d, 2H, H_{orto}); FT-IR (KBr) 3030, 2917, 2851, 1628, 1511, 1474, 800, 719 cm^{-1}. Anal. Calcd for $C_{46}H_{82}Cl_2N_2$: C, 75.27; H, 11.26; N, 3.82. Found: C, 75.29; H, 11.21; N, 3.79.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Dibromide (12d). The product obtained by ionic exchange of **12a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 88%; mp 153−155 °C; R_f 0.04 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 208, 272 nm, log ϵ 4.06, 4.08; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, 6H, 2CH_3), 1.25 (m, 36H, 18CH_2), 1.88 (m, 4H, $N^+CH_2CH_2$), 2.21 (m, 2H, $PyCH_2CH_2CH_2Py$), 3.40 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.68 (t, 4H, N^+CH_2), 8.04 (t, 2H, H_{meta}), 8.23 (d, 2H, H'_{meta}), 8.57 (t, 2H, H_{para}), 9.14 (d, 2H, H_{orto}); FT-IR (KBr) 3040, 2920, 2852, 1628, 1574, 1514 1466, 790, 722 cm^{-1}. Anal. Calcd for $C_{37}H_{64}Br_2N_2$: C, 63.78; H, 9.26; N, 4.02. Found: C, 63.70; H, 9.29; N, 3.99.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Diiodide (12e). The product obtained by ionic exchange of **12a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 93%; mp 190−192 °C; R_f 0.04 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 218, 269 nm, log ϵ 4.52, 4.21; ^{1}H NMR (DMSO-d_6) δ 0.87 (t, 6H, 2CH_3), 1.26 (m, 36H, 18CH_2), 1.89 (m, 4H, $N^+CH_2CH_2$), 2.22 (m, 2H, $PyCH_2CH_2CH_2Py$), 3.36 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.63 (t, 4H, N^+CH_2), 8.04 (t, 2H, H_{meta}), 8.18 (d, 2H, H'_{meta}), 8.57 (t, 2H, H_{para}), 9.09 (d, 2H, H_{orto}); FT-IR (KBr) 3034, 2920, 2852, 1628, 1572, 1512, 1468, 784, 721 cm^{-1}. Anal. Calcd for $C_{37}H_{64}I_2N_2$: C,56.20; H, 8.16; N, 3.54. Found: C, 56.23; H, 8.12; N, 3.51.

1,1′-Didodecyl-2,2′-trimethylenebispyridinium Di-*p*-toluenesulfonate (12f). The product obtained by ionic exchange of **12a** was freeze-dried from which a white powder was obtained. Crystallization from acetonitrile/ethyl acetate gave white crystals: yield 91%; mp 245−248 °C; R_f 0.04 on silica (eluent MAC 20:10:70); UV (ethanol) λ_{max} 218, 269 nm, log ϵ 4.52, 4.21; ^{1}H NMR (DMSO-d_6) δ 0.87 (t, 6H, 2CH_3), 1.26 (m, 36H, 18CH_2), 1.90 (m, 4H, $N^+CH_2CH_2$), 2.20 (m, 2H, $PyCH_2CH_2CH_2Py$), 2.31 (s, 6H, $CH_3C_6H_5SO_3$), 3.30 (t, 4H, $PyCH_2CH_2CH_2Py$), 4.59 (t, 4H, N^+CH_2), 7.12 (d, 4H, H″), 7.48 (d, 4H, H′), 8.03 (t, 2H, H_{meta}), 8.13 (d, 2H, H'_{meta}), 8.55 (t, 2H, H_{para}), 9.06 (d, 2H, H_{orto}); FT-IR (KBr) 3060, 2922, 2852, 1630, 1574, 1514, 1458, 1200, 786 cm^{-1}. Anal. Calcd for $C_{51}H_{78}N_2O_6S_2$: C, 69.66; H, 8.94; N, 3.19. Found: C, 69.59; H, 8.97; N, 3.22.

Conductivity Measurements. Conductivity measurements were performed on a conductivity meter equipped with a conductivity cell having cell constant of 0.943 cm^{-1}, as already reported.[8] The addition of concentrated surfactant solutions by a titrator and the collection of the conductivity data were performed by using a computer controlled automated system, working with a homemade program, written in Quick Basic, available from the author.

Krafft Point Measurements. The Krafft points were first estimated by visual inspection of the clearing point of surfactant suspensions (50 mg in 2 mL of water). When values different from 0 °C were evidenced, a careful procedure was applied using conductivity measurements.[31,32]

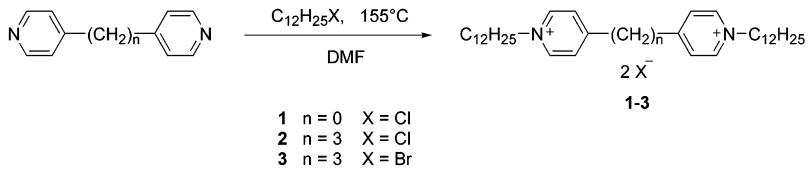
Results and Discussion

Synthesis. The synthesis of some gemini structures, 4,4′-(1,1′-dialkyl)bispyridinium salts with and without

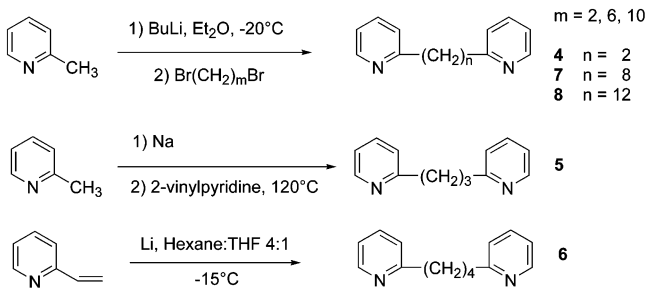
(31) Kamenka, N.; Burgaud, I.; Treiner, C.; Zana, R. *Langmuir* **1994**, *10*, 3455−3460.

(32) Zana, R. *J. Colloid Interface Sci.* **2002**, *252*, 259−261.

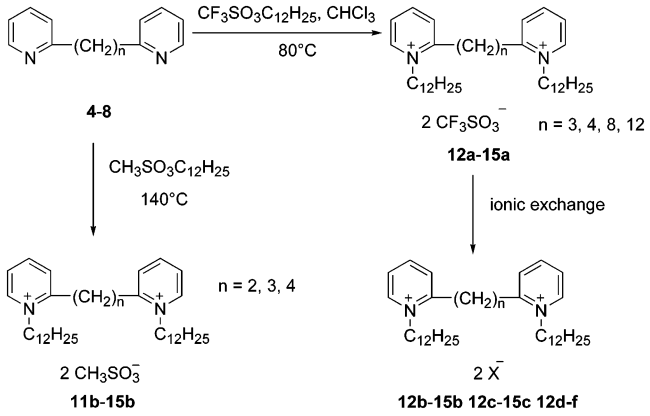
SCHEME 1. Preparation of Compounds 1−3



SCHEME 2. Preparation of Bases 4−8



SCHEME 3. Preparation of the Gemini Pyridinium Surfactants 11−15



spacer, was reported previously,[21,22] but no surface activity data are available. In the first step of the present study, we prepared some compounds of the above family to evaluate their amphiphilic properties. Structures **1**−**3** were obtained by reacting the proper halide and base in DMF at reflux (Scheme 1). The relative Krafft points were determined obtaining values of 50 °C or higher. This parameter means the minimum temperature at which micellization occurs; below that temperature, a surfactant is poorly soluble and it only adsorbs at the surfaces. The values obtained for surfactants **1**−**3** suggest that they are scarcely utilizable for usual purposes. Moreover, as Jampolsky et al.[33] previously stated, the preparation of starting α,ω-bis(4-pyridyl)alkane bases appeared particularly difficult. Low yields characterize the preparation of bases having a spacer equal to eight methylene groups or longer.

The previous considerations induced us to modify the spacer linking point on the pyridine ring, and 2,2′-(α,ω-alkanediyl)bispyridines (structures **4**−**8**) were prepared on a 50 g minimum scale, following easy and well-stated methods. The bases having 2, 8, and 12 methylene groups as spacer were prepared by using *n*-BuLi, 2-methylpyridine, and an α,ω-dibromoalkane (Scheme 2).[34] 1,3-Bis(2-pyridyl)propane[25,35−41] and 1,4-bis(2-pyridyl)butane[25,26] were prepared according to the literature, reacting the sodium salt of 2-methylpyridine with 2-vinylpyridine at 120 °C, and by head−head dimerization of 2-vinylpyridine with lithium metal in THF/hexane 1:4 respectively (Scheme 2).

The quaternization reaction with alkyl halides, as used for obtaining surfactants **1**−**3**, was unsuccessful. Only monoquaternized product was obtained using alkyl iodide as alkylating reagent. Analogously, few examples of quaternization of 2-hindered pyridines with long chain alkyl halides are reported in the literature.[41] In particular, if the substituent in position 2 is branched, only methyl was inserted on the nitrogen atom,[42,43] and for longer alkyl moiety more active reactants[44] (e.g., fluorosulfates or triflates) or higher pressures were applied.[44−46] The polymethylene chain, bearing a pyridine at its end, has a higher steric hindering than methyl and a reasonable high degree of conformational freedom, especially when the number of methylene groups is raised. Probably, the side chain in the 2-position of each pyridine ring makes the nitrogen atom hindered to the S_N2 Menschutkin reaction. Besides, the rate of the reaction is severely affected by the sterical hindrance exerted by the alkyl chain of the quaternizing reagent on the pentacoordinate center which is normally postulated for the S_N2 reaction.[46,47]

Alkyl mesylates and triflates were considered whose reactivity is higher than halides.[48] The alkyl mesylates (Scheme 3) were adopted successfully to quaternize the shorter spacer bases **4**−**6** ($n = 2-4$) with dodecyl chain in solvent-free reactions at 140 °C, while they failed, in the same conditions, for bases having longer spacers and hexadecyl chain of alkylating agent. An accurate temperature control and the addition of proper base to alkylating agent were decisive factors for good yields. When dodecyl methanesulfonate was added to base or both reactants were added and warmed, the yield de-

(33) Jampolsky, L. M.; Baum, M.; Kaiser, S.; Sternbach, L. H.; Goldberg, M. W. *J. Am. Chem. Soc.* **1952**, *74*, 5222−5224.
(34) Bianchetti, G. *Il Farmaco* **1956**, *11*, 346−356.
(35) Magnus, G.; Levine, R. *J. Am. Chem. Soc.* **1956**, *78*, 4127−4130.
(36) Magnus, G.; Levine, R. *J. Org. Chem.* **1957**, *22*, 270−273.
(37) Michalski, J.; Zajac, H. *J. Chem. Soc.* **1963**, 593−597.
(38) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53−66.
(39) Ames, D. E.; Archibald, J. L. *J. Chem. Soc.* **1962**, 1475−1481.
(40) Anderson, J. D.; Baizer, M.; Prill, E. J. *J. Org. Chem.* **1965**, *30*, 1645−1647.
(41) Edwards, P. N. Pyridine derivatives. US 3,875,175, 1975.
(42) Harris, G. H.; Shelton, R. S.; Van Campen, M. G.; Andrews, E. R.; Schumann, E. L. *J. Am. Chem. Soc.* **1951**, *73*, 3959−3963.
(43) Kosower, E. M.; Skorcz, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 2195−2203.
(44) Okamoto, Y.; Lee, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 4015−4018.
(45) Le Noble, W. J.; Asano, T. *J. Am. Chem. Soc.* **1975**, *97*, 1778−1782.
(46) Le Noble, W. J.; Ogo, Y. *Tetrahedron* **1970**, *26*, 4119−4124.
(47) Gallo, R.; Roussel, C.; Berg, U. *Adv. Heterocycl. Chem.* **1988**, *43*, 173−299.
(48) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85−126.

creased to about 15% and tars were produced. Nitrobenzene was used for the reaction of dodecyl mesylate with the 1,8-bis(2-pyridyl)octane **7** at 140 °C, but the yields were low and the quantity of tars was substantial. Probably, in these conditions the elimination reaction on the alkylating reagent, promoted by the presence of the bispyridine base, is competitive and gives the corresponding alkene product. The polymerization of such alkene could be the source of the observed tars.

The use of triflates appeared more general as an approach. All the bases **4**−**8** were quaternized using dodecyl triflate and the preliminary test with the hexadecyl one appeared successful.[49] It is noticeable that in the literature the use of long alkyl triflates is limited to unhindered systems.[28,29,48,50,51] This is the first time that the sterical hindrance at the α-position of the pyridine is overcome with long alkyl triflates.

The dodecyl triflate (**10**) was prepared by modifying the method used for the preparation of alkyl triflates, obtaining very good yields (80−94%).[29] The literature procedure appeared to be quite tedious and time wasting. The product was recovered by simply washing the organic solution with water to eliminate pyridinium triflate, giving a straightforward and efficient protocol. The quaternization step (Scheme 3) was performed by adding a solution of the base to the alkyl triflate in chloroform at 60 °C for about 1.5 h. The separation step was easier, and the products were all solid white crystals except for the compound **14a**, which crystallized only after prolonged standing (a few months).

A particular comment has to be devoted to compound **11b**, obtained by synthesis with dodecyl methanesulfonate. It appeared particularly unstable during the purification step, by either flash chromatography and crystallization, with substantial loss of yield. However, by crystallization a small sample useful for amphiphilic characterization was obtained. Its instability prevented the exchange of counterion by usual resin, in either water or methanol. Due to this problem, the other products of the series **11** were not prepared. The instability could be due to the short spacer. The inductive effect of the two positive charges of the pyridinium rings, increasing the acidity of the methylene protons, could promote the relative deprotonation by reaction with residual amine centers of the ionic exchanger resin. Analogously, Kosower et al.[43] invoked the acidity of these protons to explain the formation of 4-ethylidene-1-methyl-1,4-dihydropyridine as a byproduct during the preparation and crystallization of 4-ethyl-1-methylpyridinium iodide.

Attempts to protonate these centers with a proper acid (HCl for exchange to chloride anion) did not give successful results.

The ionic exchange step in methanol was performed to obtain the surfactants **12**−**15** having different counterions. The experimental procedure here described proved them pure enough to be characterized even by surface tension,[49] which is commonly known as a technique severely affected by very small amounts of impurities.[52−55]

Amphiphilic Characterization. The gemini surfactants **1**−**3** and **11**−**15** from now on will be referred to by an acronym, like the simple "n-s−n" recently used by Zana et al.[13,15] for the ammonium gemini surfactants. As an example, the compound **3** should be named 12-Py(4)-3-(4)Py-12 2Br, where the first number describes the number of carbon atoms of alkyl chain to pyridinium nitrogen, Py stands for the pyridinium ring, (4) indicates the spacer connection position on the pyridinium ring, 3 is the number of methylenes in the polymethylenic spacer, and 2Br stands for the two bromide counterions. In the same way, compounds **11**−**15** should be identified by the general name: n-Py(m)-s-(m)Py-n 2X, where n, m, s and X have the already specified general meaning.

Krafft Points. The Krafft points of all of the products were determined, showing that the insertion of spacer moiety in position 2 of piridinium ring increases the solubility of gemini surfactant in water. An exception was observed for surfactants **12a**−**15a** having trifluoromethanesulfonate anion as counterion, for which the Krafft point ranged between 80 and 95 °C. Different counterions were considered in the series **12**, having three methylenes as spacer. An increase of halide polarizability determines a raising of the Krafft point, while in the presence of *p*-toluenesulfonate the value of this parameter raised to 79 °C. The last effect could be due to both hydrophobic character and easier stacking of benzene moiety between two pyridinium headgroups. This preliminary study showed that when it is advisable to work at low temperature and in the presence of micelles, the chloride or the methanesulfonate counterions are needed, while for different applications other counterions can be suitable, e.g. bromide, starting just above room temperature.

CMC Measurements. The cmc and the degree of counterion binding of the compounds under exam were determined by conductivity (see Table 1) by using a computer-controlled automated system to improve both the data collection and the data analysis steps. In fact, by the use of this system, it was possible to control when the conductivity reached the equilibrium value for any surfactant addition. Besides, when working with gemini surfactants, it was common to obtain very smooth conductivity vs *C* plots, where the transition between the pre- and post-micellar regimes, was occurring on a wide concentration range (see examples in the Supporting Information) and difficult to be precisely determined. In such a case, the classical method,[56] in which the cmc is determined by the intersection of the lines fitted in the diluted and concentrated regions before and after the cmc, is sometimes difficult to apply, since the transition between the two linear regimes occurs gradually. In fact, when trying to find the linear regimes in the classical method, one assume that some points can be used or not

(49) Quagliotto, P. et al. Manuscript in preparation.
(50) Ross, S. A.; Pitié, M.; Meunier, B. *J. Chem. Soc., Perkin Trans. 1* **2000**, 571−574.
(51) Howells, R. D.; Mc, C. *Chem. Rev.* **1977**, *77*, 69−92.
(52) Rosen, M. J. *J. Colloid Interface Sci.* **1981**, *79*, 587−588.
(53) Rosen, M. J.; Dahanayake, M.; Cohen, A. W. *Colloids Surf.* **1982**, *5*, 159−172.
(54) Rosen, M. J.; Cohen, A. W.; Dahanayake, M.; Hua, X. Y. *J. Phys. Chem.* **1982**, *86*, 541−545.
(55) Mysels, K. J. *Langmuir* **1996**, *12*, 2325−2326.
(56) Carpena, P.; Aguiar, J.; Bernaola-Galván, P.; Carnero Ruiz, C. *Langmuir* **2002**, *18*, 6054−6058 and references therein. For the determination of counterion binding, see also: (a) Bakshi, M. S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 4323−4326. (b) Zana, R.; Levy, H.; Danino, D.; Talmon, Y.; Kwektat, K. *Langmuir* **1997**, *13*, 402−408. (c) De Lisi, R.; Inglese, A.; Milioto, S.; Pellerito, A. *Langmuir* **1997**, *13*, 192−202.

TABLE 1. Amphiphilic Properties of the Surfactants 11−15 at 25 °C

compd	spacer no. of methylenes	counterion X	T_k[a] (°C)	cmc[b] (mmol/L)	β[b] (%)	cmc[c] (mmol/L)	β[c] (%)
1	0	Cl	50.5				
2	3	Cl	50.9				
3	3	Br	63.6				
11b	2	CH_3SO_3	<0	2.07	74	2.08	70
12b	3	CH_3SO_3	<0	2.09	72	1.94	71
13b	4	CH_3SO_3	<0	1.93	40	1.93	40
14b	8	CH_3SO_3	<0	1.32	57	1.23	57
15b	12	CH_3SO_3	<0	0.750	57	0.681	57
12c	3	Cl	<0	1.51	69	1.45	68
				1.86[d]	64[d]	1.71[d]	64[d]
13c	4	Cl	<0	1.28	67	1.07	69
14c	8	Cl	<0	1.11	44	1.06	44
15c	12	Cl	<0	0.22	48	0.21	70
12d	3	Br	27.9	0.837[d]	82[d]	0.634[d]	80[d]
12e	3	I	65.3				
12f	3	p-$CH_3C_6H_4SO_3$	78.8				
16[e]		Cl	<0	17.1	60		

[a] Krafft Point. [b] From conductivity: classical method. [c] From conductivity: nonlinear fit. [d] At 30 °C. [e] lit.[53] 1.78 × 10^{-2} M.

in the fit, making it matter of taste and sensibility. Besides, the evaluation of the degree of counterion dissociation α, taken as the ratio of the slopes after and before the cmc respectively ($\alpha = S_{micellar}/S_{premicellar}$), and of counterion binding β ($\beta = 1 - \alpha$) could be affected by substantial errors.

Recently, a study concerning the evaluation of the cmc from conductivity data was reporting an interesting procedure, using a nonlinear fit.[56] The fit of the whole data set to a function, which represents the integral function of a sigmoid (equation 1), was proposed:

$$F(x) = F(0) + A_1x + \Delta x(A_2 - A_1)\ln\left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}}\right) \quad (1)$$

In this equation, the transition from two linear regimes at low and high concentration is described. The parameters have the following meaning: $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition; i.e., the cmc and Δx is the width of the transition. The α value can be deduced from the ratio A_2/A_1.

It was evident that the suggested function would represent exactly the physical model to which the conductivity data would adhere. The nonlinear fitting method avoids any treatment of the data and the consequent introduction of noise. Moreover, by the use of the non linear fit which simply searches for the best correlation, the evaluation of the degree of counterion binding β could be performed, avoiding artifacts due to the personal choice of points to be included in the linear fit of the linear regimes.

This method could be very useful when applied to gemini surfactants having the above-mentioned behavior, especially when the hydrophobic chains are lengthened.

In this paper, we tried to analyze our data concerning new gemini pyridinium surfactants, by the classical method and by this above-mentioned new method. The values of the cmc estimated by the two different data analysis approaches differ very slightly for most of the compounds, showing that the two methods are working well.

From Table 1 it is evident that the gemini pyridinium surfactants showing no Krafft Points, namely the chlorides and methanesulfonates, have a low cmc. The 1-dodecylpyidinium chloride (**16**), taken as a standard, shows a cmc of 1.71 × 10^{-2} M (lit.[53] 1.78 × 10^{-2} M). The cmc of 12Py(2)-3-(2)Py-12 2Cl (**12c**) is more than 10 times lower. This is in agreement with results obtained for other series of gemini surfactants.[15] The presence of two hydrophobic chains cause an effect on the cmc and on the micellization free energy (ΔG_{mic}) whose relation with the thermodynamic parameters was recently studied by Zana[57] since the introduction of gemini surfactants revealed that a new, more general, treatment was needed. This peculiarity discloses to gemini surfactants wide ranges of applicability in a number of fields. The structural features, that give the gemini surfactants a high opportunity of modulation of properties, are a key point for applications and, in particular, for formulators.

As a general trend, the chlorides (**12c**−**15c**) show slightly lower cmc than the methanesulfonates (**11b**−**15b**). When the cmc data were plotted against the number of carbon atoms in the spacer length (Figure 1), the methanesulfonates show a slight enhancement from $n = 2$ to $n = 3$ and a following decrease that is more pronounced for n being equal to or greater than 8 carbon atoms. The chlorides show nearly the same general behavior, but the decrease of the cmc is clearly evident for $n = 12$. Besides, in this series the compound having $n = 2$ (**11c**) is lacking, since it was impossible to produce it either by direct synthesis or by ionic exchange, and we could not notice the slight increase evidenced for methanesulfonates going from $n = 2$ to $n = 3$.

The increase in the cmc going from $n = 2$ to $n = 3$ (**12b**) is similar to the behavior shown by gemini ammonium surfactants[15] and it could be due to the small increase in conformational freedom when the spacer is lengthened. This fact could help the molecule to find a better conformation in solution, giving rise to the small increase in the cmc. This is only a hypothesis as far as our compounds are concerned, since the difference in cmc (**11b** vs **12b**) is very small. However, this kind of behavior

(57) Zana, R. *Langmuir* **1996**, *12*, 1208−1211.

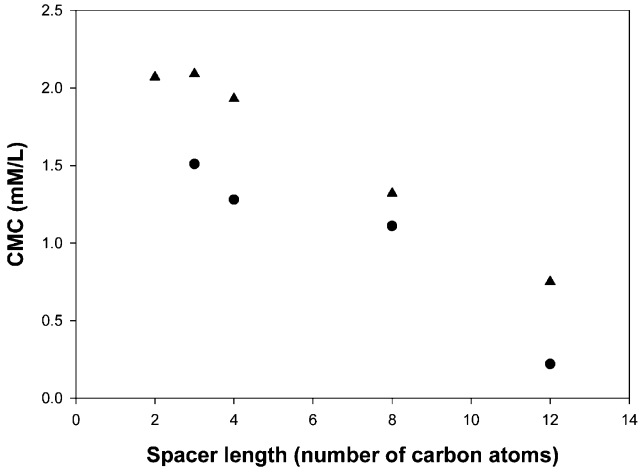


FIGURE 1. cmc vs spacer length for the compounds having a chloride **12c**−**15c** (●) or methanesulfonate **11b**−**15b** (▲) counterion.

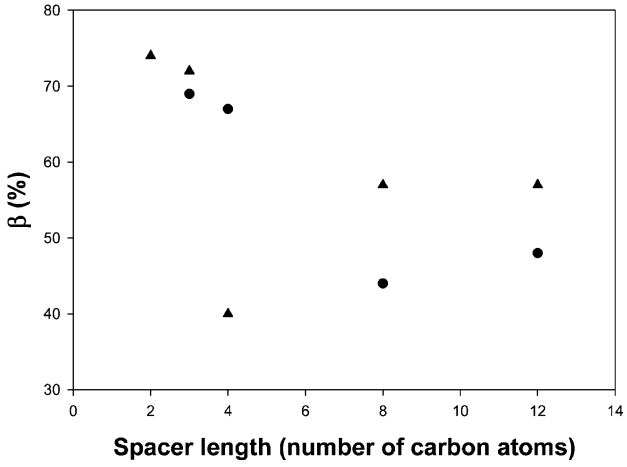


FIGURE 2. Degree of counterion binding β vs spacer length for the compounds having a chloride **12c**−**15c** (●) or methanesulfonate **11b**−**15b** (▲) counterion.

is markedly enhanced in other series of surfactants such as the gemini ammonium ones.

The cmc values for chlorides (**12c**−**15c**) are decreasing when the spacer is lengthened and seem to evidence an effect due to the increase of hydrophobicity of the spacer.

When the spacer length exceeds $n = 8$, e.g., $n = 12$, the contribution of the spacer to the whole hydrophobicity of the molecule has a dramatic effect on the cmc value, higher than that shown by n-s-n ammonium surfactants.[15] In effect, the cmc of 12-12-12 2Br is about one-third of the cmc of 12-3-12 2Br, while the cmc of 12Py(2)-12-(2)Py-12 2Cl (**15c**) is less than one-sixth of the 12Py(2)-3-(2)Py-12 2Cl (**12c**) cmc. The greater extension of this effect could be related to the different arrangement imposed by the nature of the headgroups. In this case, the pyridinium ring could decrease the conformational freedom with respect to the corresponding gemini ammonium surfactant. This hypothesis could explain why this behavior on the cmc is clearly evident starting from $n = 12$ since, when the spacer is quite short, the degree of conformational freedom is quite low and the headgroups does not have enough freedom to find a better arrangement, thus anticipating the aggregation. In fact, the presence of two charges on the pyridinium rings limits the ability to find better conformations since most of the possible conformations are experiencing the Coulombic repulsion. Another contribution to the lowering of the cmc for the compounds having $n = 12$, is probably connected with the great hydrophobicity of the spacer which, in some cases, was demonstrated to act as a further "third" hydrophobic chain by folding into the core of the monolayer or the micelle.[17] The higher degree of counterion binding of compounds having short spacers (**12c**−**13c**) with respect to the monomer (**16**) is another effect that could explain the lack of conformational freedom, since the two charges of the pyridinium rings are probably keeping one of the two counterion between them, so displaying a stabilizing effect.

Finally, to see the effect of the different halide counterions, a comparison was made between the compound **12c** and **12d**, working at 30 °C, since **12d** is showing a Krafft point at about 28 °C.

The 12Py(2)-3-(2)Py-12 2Br compound (**12d**), has a cmc of 8.37×10^{-4} M, while the corresponding chloride (**12c**) is micellizing at 1.86×10^{-3} M, so the cmc is about halved by changing the counterion from chloride to bromide, as expected. Since the iodide has a Krafft point of about 65 °C, its cmc was not measured.

Degree of Counterion Binding. The degree of counterion binding β is an important parameter since it is the expression of how many counterions are contained in the Stern layer to counterbalance the electrostatic force that opposes to the micelle formation. The evaluation of β by using the classical method could result very difficult, as described above, while the non linear fit give access to more reliable values. It should be stressed that a more reliable way to obtain the value of β is connected with the Corrin−Harkins plot reporting log CMC vs log(CMC + concentration of added salt).[58] However, since most of the previous literature was essentially based on β values obtained from the classical method, we prefer to report here values obtained according to the two methods shown above to permit an adequate comparison. The subject of the strict reliability of the β values will be worthy of a deeper study.

Normal micelles made up from 1-dodecylpyridinium chloride (**16**) show a β value of 60% and it is evident that the corresponding gemini surfactants having short spacers (**12c**−**15c**) have particular behavior since they bind their counterions more strongly than the "monomer" does. We have already explained above the possible reasons for this behavior. For longer spacers the degree of counterion binding is decreasing and reaches lower values than those shown by the monomer (see Figure 2). This seems to be a general trend for gemini surfactants, as the n-s-n ammonium gemini amphiphiles.[15] The conformational freedom connected with 8 and 12 methylenes is probably enough to leave the two headgroups far apart, so that the interaction with the hydrated counterions is substantially decreased. As a consequence, the short spacer surfactants are probably aggregating in non spherical micelles (at least spheroidal, elongated ones) since their packing parameter should be higher than 1/3.

(58) Sugihara, G.; Nakamura, A. A.; Nakashima, T.-H.; Araki, Y. I.; Okano, T.; Fujiwara, M. *Colloid Polym. Sci.* **1997**, *275*, 790−796.

As far as the long spacer surfactants are concerned, they probably can aggregate in spherical micelles or nearly spheroidal micelles, due to the higher conformational freedom that the spacer gives to the molecules. Their packing parameter should decrease with respect to that of the short spacer surfactants, according to spherical micelles. Besides, the low degree of counterion binding is normally related with small, nearly spherical, micelles.

A peculiar behavior occurs with the methanesulfonates, for which β follows a trend similar to those observed for the chlorides, except for the compound having four methylenes as spacer (**13b**) for which an "anomalous" value of 40% is obtained.

This particular behavior is presently under analysis, and we do not yet have clear background knowledge to explain it. As above depicted, this anomalous β value should evidence a particular nature of the aggregate. It seems that the compound **13b** forms small micelles with a low charge density. This could be explained by a molecular arrangement with the tetramethylenic spacer in an all s-trans conformation, which maintain the two rings and the two charges far apart. As a result of this conformation, the counterion could not be tightly linked between the two positive headgroups. In this situation, if the aggregation number is low, the charge density is low and water could enter deeper into the micellar core.

More work is needed, however, to get a deeper insight on the micellization behavior, thus measurements with several different techniques are currently in progress.

Conclusions

A novel series of gemini surfactants bearing the pyridinium ring as the headgroup was prepared. During the synthetic project it was found that the linkage point of the spacer on the pyridinium ring was crucial for the definition of the synthetic pathway and the surfactant properties.

The easiest series to be prepared, namely n-Py(4)-s-(4)Py-n 2X surfactants, revealed high Krafft points and thus, low potential toward practical applications. The second one, related to the n-Py(2)-s-(2)Py-n 2X, was a source of synthetic challenges. The use of alkyl methanesulfonates as quaternizing agents, even if successful in several cases, turned out to be a method lacking of generality. The resort to alkyl trifluoromethanesulfonates as the alkylating reagents opened the way to a quite general synthetic method. For the first time, pyridines bearing a substituent in the 2-position having a more crowding effect than methyl or ethyl, were efficiently alkylated with chains longer than ethyl or propyl. Surely, a well-addressed study of the synthetic opportunities offered by the long chain alkyl triflates in alkylating sterically hindered pyridines is opportune. In fact, the use of the hexadecyl trifluoromethanesulfonate could allow to overcome the lower reactivity connected with the longer alkyl chain, opening the way to the synthesis of the series having hexadecyl or longer chains. In view of the recent peculiar properties shown by pyridinium amphiphiles, even in the biological domain for their use as DNA carriers for transfection purposes, this possibility becomes very attractive.

The amphiphilic characterization was performed with conductivity measurements, obtaining the Krafft point, the cmc and the degree of counterion binding.

The obtained results showed a dependence of the cmc from the number of carbon atoms in the spacer, which is decreasing when the spacer is lengthened. This effect seems to be more pronounced than that found in the literature for gemini ammonium surfactants. A similar relationship was also found for the degree of counterion binding vs the spacer length, evidencing that short spacer surfactants give micelles with a high charge density. For these aggregates a conformational arrangement in which the headgroups bring one of the two counterions between them is postulated. Surfactants having long spacers seem to aggregate in micelles whose charge density is consistently lower. It could be guessed that the degree of counterion binding should probably indicate that the spacer has a crucial effect on the shape of the micelles.

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Supporting Information Available: General experimental procedures, ^{1}H NMR spectra for all new compounds, ^{1}H−^{1}H COSY spectra for compound (**13c**), and typical conductivity vs concentration plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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