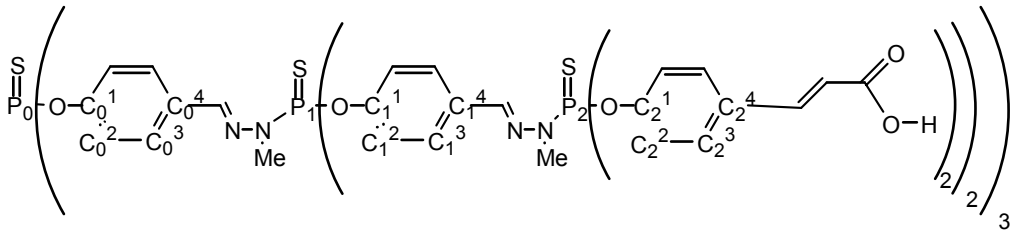
Electronic supplementary information

General. All manipulations were carried out with standard high vacuum and dry-argon techniques, excepted for the synthesis of the catanionic compounds. All solvents were dried and distilled before use, all other chemical were used as received. Instrumentation: Bruker AC80, AC200, AM250, DPX 300 (^{1}H, ^{13}C, ^{31}P NMR), Perkin Elmer 1725X (FT-IR). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France). Surface tensions were measured at 25 °C (± 0.1 °C) using the droplet method with a KRUSS GmbH Drop Shape Analysis instrument (DSA-10). The formation of vesicles was observed through transmission electron microscopy using a JEOL JEM 200 CX electron microscope, operating at 200 kV. Aliquots of solutions were applied on carbon-coated formvar grids, negatively stained with a 2% (w/v) solution of phosphotungstate (pH 7.5). The size of vesicles was also evaluated by dynamic light scattering using a Malvern Instruments zetasizer 3000. The numbering scheme used for NMR is depicted on the following picture:



2-[G$_2$]: A mixture of dendrimer **2-[G$_1$]** (500 mg, 0.146 mmol), malonic acid (547 mg, 4.38 mmol) and piperidine (52 µL, 0.44 mmol) was heated at 95°C in pyridine (10 mL) for four hours and then refluxed for 15 minutes to complete carbon dioxide removal. The brownish solution was cooled in an ice bath and poured onto 21 mL of 10M hydrochloric acid

mixed with a large amount of crushed ice. The precipitate of dendrimer was then washed with water and dried under vacuum. The crude white powder was ultimately washed with diethylether and dried to afford **2-[G_2]** as an amorphous white powder: yield 95%. $^{31}P\{^1H\}$ NMR ($DMSOd_6$) δ: 51.4 (s, P_0), 60.8 (s, P_2), 61.2 (s, P_1) ppm. ^1H NMR ($DMSOd_6$) δ: 3.43 (d, $^3J_{HP1,2}$ = 10.2 Hz, 27H, $P_{1,2}$-N-CH_3), 6.59 (d, $^3J_{HH}$ = 16 Hz , 12H, Ph-*CH*), 7.3-7.9 (m, 93H, CH_{arom} and CH=N), 7.65 (d, $^3J_{HH}$ = 16 Hz , 12H, *CH*-COOH). $^{13}C\{^1H\}$ NMR ($DMSOd_6$) δ: 34.6 (d, $^2J_{CP1,2}$ = 12.1 Hz, $P_{1,2}$-N-CH_3), 121.1 (s, Ph-*CH*), 123.0 (d, $^3J_{CP0,1,2}$ = 3.8 Hz, $C_{0,1,2}{}^2$), 130.0 (s, $C_{0,1}{}^3$), 131.5 (s, $C_2{}^3$), 133.2 (s, $C_2{}^4$), 133.6 (s, $C_{0,1}{}^4$), 142.4 (d, $^3J_{CP1,2}$ = 14.9 Hz, CH=N-N-$P_{1,2}$), 144.3 (s, *CH*-COOH), 152.2 (d, $^2J_{CP1}$ = 7.6 Hz, $C_1{}^1$), 152.4 (d, $^2J_{CP0}$ = 7.7 Hz, $C_0{}^1$), 152.8 (bd, $^2J_{CP2}$ = 7.8 Hz, $C_2{}^1$), 169.1 (s, COOH) ppm. IR (KBr): 1686 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{180}H_{156}N_{18}O_{45}P_{10}S_{10}$ (3921.7): C, 55.13; H, 4.01; N, 6.43. Found: C, 55.12; H, 4.11; N, 6.53.

3-[G_1]: A mixture of **2-[G_1]** (49 mg, 0.03 mmol) and aminolactitol **1** (100 mg, 0.18 mmol) in 20 mL distilled water was stirred 15 hours at room temperature to complete solubilization of the starting acidic dendrimer. The crude white powder of **3-[G_1]** was obtained quantitatively after lyophilization: yield 100%. $^{31}P\{^1H\}$ NMR (D_2O/CD_3CN, 2:1 v) δ: 50.0 (P_0); 60.7 (P_1) ppm. ^1H NMR (D_2O/CD_3CN, 2:1 v) δ: 7.91-7.19 (m, 45 H, CH_{arom} and CH=N, C<u>H</u>-COOH); 6.39 (d, $^3J_{HH}$ = 16.0 Hz, 6 H, Ph-C<u>H</u>=CH); 4.42 (d, $^3J_{HH}$ = 7.4 Hz, 6 H, H anomeric); 4.20-3.42 (m, 72 H, sugar: C<u>H</u>-OH and C<u>H_2</u>-OH); 3.40 (d, $^3J_{HP}$ = 7.3 Hz, 9 H, P-N-CH_3); 1.16 (br s, 90 H, CH_2); 0.79 (br s, 18 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (D_2O/CD_3CN, 2:1 v) δ: 175.1 (s, COO^-); 150.6 (d, $^2J_{CP0}$ = 6.9 Hz, $C_0{}^1$); 150.4 (d, $^2J_{CP1}$ = 5.4 Hz, $C_1{}^1$); 141.5 (br s, CH=N); 138.3 (s, <u>C</u>H-COO^-); 132.3 (s, $C_1{}^4$); 132.9 (s, $C_0{}^4$); 129.0 (s, $C_1{}^3$); 128.4 (s, $C_0{}^3$); 125.3 (s, Ph-CH); 121.0 (br s, $C_0{}^2$, $C_1{}^2$); 104.1 (s, CH anomeric); 75.9-53.9 (m, sugar: CH and CH_2); 35.4

(d, $^{2}J_{CP1}$ = 8.1 Hz, P-N-CH_3); 33.5-30.1 (m, CH_2); 14.4 (s, CH_3) ppm. IR (KBr) *cm*$^{-1}$: 1381 (ν_{COO}- symmetrical), 1559 (ν_{COO}- symmetrical).

3-[G$_2$]: A mixture of **2-[G$_2$]** (58 mg, 0.015 mmol) and aminolactitol **1** (100 mg, 0.18 mmol) in 20 mL distilled water was stirred 3 days at room temperature until complete solubilization of the starting acidic dendrimer. **3-[G$_2$]** was obtained quantitatively as a white powder after lyophilization: yield 100%. $^{31}P\{^{1}H\}$ NMR (D_2O/CD_3CN, 2:1 v) δ: 50.1 (P_0); 60.2 (P_1); 60.7 (P_2) ppm. ^{1}H NMR (D_2O/CD_3CN, 2:1 v) δ: 7.92-7.15 (m, 105 H, H_{arom} and CH=N, Ph-CH=C<u>H</u>); 6.41 (d, $^{3}J_{HH}$ = 16.9 Hz, 12 H, Ph-C<u>H</u>=CH); 4.42 (d, $^{3}J_{HH}$ = 7.6 Hz, 12 H, H anomeric); 4.60-3.40 (m, 171 H, sugar: C<u>H</u>-OH and C<u>H$_2$</u>-OH, P_1-N-CH_3, P_2-N-CH_3); 1.14 (br s, 180 H, CH_2); 0.81 (br s, 36 H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (D_2O/CD_3CN, 2:1 v) δ: 175.0 (s, COO^-); 150.8-150.0 (m, C_0^1, C_1^1, C_2^1); 141.3 (br s, CH=N); 138.0 (s, <u>C</u>H-COO^-); 133.0 (br s, C_0^4, C_1^4, C_2^4); 128.7 (s, C_2^3); 127.9 (br s, C_0^3, C_1^3); 125.4 (s, Ph-CH); 121.1 (br s, C_0^2, C_1^2, C_2^2); 104.9 (s, CH anomeric); 73.8-56.2 (m, sugar: CH and CH_2); 35.3 (bd, $^{2}J_{CP1}$ = $^{2}J_{CP2}$ = 8.2 Hz, P-N-CH_3); 32.9-30.2 (m, CH_2); 14.9 (s, CH_3) ppm. IR (KBr) *cm*$^{-1}$: 1381 (ν_{COO}- symmetrical), 1559 (ν_{COO}- non symmetrical).