**Supplementary information**

**Materials and methods**

All chemicals were purchased from Sigma Aldrich Co. (Steinheim, Germany) and were used without further purification. All solvents were dried and distilled before use. The purity of all compounds was checked by thin-layer chromatography (TLC-plates; Merck, Darmstadt, Germany) using silica gel 60 F_{254} plates (Merck) and common eluents. The plates were visualized under UV (254 nm) light or by usage of Bromothymol Blue. Purification of the products was carried out by recrystallization or by middle pressure liquid chromatography (MPLC; Büchi, Essen, Germany) on silica gel (0.040–0.063 mm, Merck). The MPLC was equipped with a Fraction Collector C-660, Pump Module C-601 (2×), Pump Manager C-615 and UV detector (cut off = 254 nm).

Melting points were determined with a Boetius apparatus. NMR spectra were recorded with either a 400 MHz spectrometer (Varian Gemini 2000) operating at 400 MHz for 1H nuclei and 100 MHz for 13C nuclei or a 500 MHz spectrometer (Varian Inova 500) operating at 500 MHz for 1H nuclei and 125 MHz for 13C nuclei. All chemical shifts are reported in parts per million (ppm) relative to CHCl3 at 1H-NMR (δ = 7.24 ppm) and at 13C-NMR (δ = 77.00 ppm), respectively. 1H-NMR spectroscopic data are reported as chemical shift, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signals), coupling constant (J in Hz) and assignment. Mass spectrometric data were obtained with a Finnigan mass spectrometer model MAT SSQ 710 C (ESI-MS) or were recorded on an AMD 402 (70 eV) spectrometer (EI-MS). Elemental analyses were recorded on a Leco CHNS-932. High resolution mass spectrometry (HR-MS) was performed using a LTQ-Orbitrap mass spectrometer with static nano-electrospray ionization (nano-ESI, positive modus) and a m/z range from 150 to 2000 (resolution: 30000). The mass spectrometric data were evaluated using XCalibur 2.0.7 software.

**Et2PE-C32Et2PE**

The synthesis of dotriacontane-1,32-diyl-bis[2-(diethylammonio)ethylphosphate] (Et2PE-C32-Et2PE) was carried out applying the general phosphorylation and quaternisation procedure of long-chain 1,ω-diols as described previously^{51} using 0.5 mmol of dotriacontane-1,32-diol (0.24 g).^{51}

Yield: 0.17 g (41%); 1H-NMR (500 MHz, CDCl3/CD3OD, 27 °C): δ = 1.22–1.28 (m, 56 H, CH2), 1.32 (t, 3J_{H,H} = 7.3 Hz, 12 H, 4× –CH2CH3), 1.57–1.63 (m, 4 H, –OCH2CH2(CH2)28CH2O–), 3.14 (q, 3J_{H,H} = 7.3 Hz, 8 H, 4× –CH2CH3), 3.23–3.25 (m, 4 H, 2× NCH2CH2O–), 3.83 („q“, J = 6.7 Hz, 4 H, –OCH2CH2(CH2)30CH2O–), 4.07–4.11 ppm (m, 4 H, 2× NCH2CH2O–); MS (ESI): m/z: 839.7 [M – H]+, 842.0 [M + H]+, 863.6 [M + Na]+, 1703.8 [2M + Na]+; elemental analysis calcld. (%) for C_{44}H_{90}N_{2}O_{8}P_{2} × 3H2O: C 59.03, H 11.26, N 3.13; found: 58.86, H 11.11, N 3.11.

**PC-C32Me2-PC**

The synthesis of 10,23-dimethyldotriacontane-1,32-diyl-bis[2-(trimethylammonio)-ethylphosphate] (PC-C32Me2-PC) was carried out applying the general
phosphorylation and quaternisation procedure of long-chain 1,ω-diols as described previously\textsuperscript{51} using 0.5 mmol of the methyl-modified diol (0.255 g).\textsuperscript{52}

Yield: 0.22 g (53%); \( R_f = 0.24 \) (CHCl\(_3\)/MeOH/NH\(_3\) = 10/10/3); \(^1\)H-NMR (500 MHz, CDCl\(_3\)/CD\(_3\)OD, 27 °C): \( \delta = 0.55 \) (d, \(^3\)J\(_{HH} = 6.6\) Hz, 6 H, 2× −CH\(_2\)H), 0.76–0.81 (m, 4 H, 2× −CH\(_2\)H\(_2\)(CH\(_3\))CHH−), 0.97–1.08 (m, 50 H, −CH\(_2\)−, −CH−), 1.31–1.37 (m, 4 H, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))−), 2.93 (s, 18 H, 2× −N(CH\(_3\))\(_3\)), 3.31–3.33 (m, 4 H, 2× NCH\(_2\)CH\(_2\)O−), 3.56–3.60 ("q", \( J = 6.7\) Hz, 4 H, 2× −OCH\(_2\)(CH\(_3\))−), 3.92–3.98 ppm (m, 4 H, 2× NCH\(_2\)CH\(_2\)O−); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)/CD\(_3\)OD, 27 °C): \( \delta = 10.18 \) (−CH\(_3\)), 25.27 (2× −O(CH\(_2\))\(_2\)CH\(_2\)−), 26.54 and 26.57 (2× −CH\(_2\)CH\(_2\)(CH\(_3\))CH\(_2\)−), 28.88, 29.13, 29.16, 29.47 and 29.51 (−CH\(_2\)−), 30.25 (d, \(^3\)J\(_{CP} = 7.3\) Hz, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))CH\(_2\)−), 32.25 (−CH−), 36.59 and 36.60 (2× −CH\(_2\)CH\(_2\)(CH\(_3\))CH\(_2\)−), 53.51 (t, \( J = 3.8\) Hz, 2× −N(CH\(_3\))\(_3\)), 58.47 (d, \(^2\)J\(_{CP} = 5\) Hz, 2× NCH\(_2\)CH\(_2\)O−), 65.55 (d, \(^2\)J\(_{CP} = 6\) Hz, 2× −OCH\(_2\)(CH\(_3\))−), 69.53 ppm (b, 2× 15 NCH\(_2\)CH\(_2\)O−); MS (EI): m/z: 841.34 [M + H]\(^+\), 863.25 [M + Na]\(^+\), 1703.76 [2M + Na]\(^+\); HR-MS (C\(_{44}H\(_{92}N\(_2\)O\(_8\)P\(_2\))): m/z: [M + H]\(^+\) exp. 841.6558, calc. 841.6558.

**Me\(_2\)PE-C32Me\(_2\)Me-2MePE**

The synthesis of 10,23-dimethyldotriacontane-1,32-diyl-bis[2-(dimethylammonio)-ethylphosphate] (Me\(_2\)PE-C32Me\(_2\)Me-2MePE) was carried out applying the general 20 phosphorylation and quaternisation procedure of long-chain 1,ω-diols as described previously\textsuperscript{51} using 0.5 mmol of the methyl-modified diol (0.255 g).\textsuperscript{52}

Yield: 0.27 g (67%); \(^1\)H-NMR (500 MHz, CDCl\(_3\)/CD\(_3\)OD, 27 °C): \( \delta = 0.69 \) (d, \(^3\)J\(_{HH} = 6.6\) Hz, 6 H, 2× −CH\(_2\)H), 0.91–0.94 (m, 4 H, 2× −CHHCH\(_2\)(CH\(_3\))CHH−), 1.12–1.22 (m, 50 H, −CH\(_2\)−, −CH−), 1.47–1.53 (m, 4 H, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))−), 2.76 (s, 12 H, 2× −N(CH\(_3\)\(_3\))), 3.17–3.18 (m, 4 H, 2× NCH\(_2\)CH\(_2\)O−), 3.75–3.79 ("q", \( J = 6.7\) Hz, 4 H, 2× −OCH\(_2\)(CH\(_3\))−), 4.03–4.07 ppm (m, 4 H, 2× NCH\(_2\)CH\(_2\)O−); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)/CD\(_3\)OD, 27 °C): \( \delta = 19.41 \) (−CH\(_3\)), 25.42 (2× −O(CH\(_2\))\(_2\)CH\(_2\)−), 26.76 and 26.82 (2× −CH\(_2\)CH\(_2\)(CH\(_3\))CH\(_2\)CH\(_2\)−), 29.07, 29.33, 29.37, 29.41, 29.69 and 29.75 (−CH\(_2\)−), 30.34 (d, \(^3\)J\(_{CP} = 6.9\) Hz, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))−), 32.47 (−CH−), 36.79 and 36.82 (2× −CH\(_2\)CH\(_2\)(CH\(_3\))CH\(_2\)−), 43.03 (2× −N(CH\(_3\)\(_3\))), 58.31 (d, \( J_{CP} = 5.5\) Hz) and 59.15 (d, \( J_{CP} = 5.0\) Hz, 2× NCH\(_2\)CH\(_2\)O−), 66.53 ppm (d, \(^2\)J\(_{CP} = 6.0\) Hz, 2× −OCH\(_2\)(CH\(_3\))−); MS (EI): m/z: 811.52 [M − H]\(^−\), 813.34 [M + H]\(^+\), 835.20 [M + Na]\(^+\), 1647.23 [2M + Na]\(^+\); HR-MS (C\(_{24}H\(_{46}N\(_2\)O\(_7\)P\(_2\))): m/z: [M + H]\(^+\) exp. 813.62213, calc. 813.62452.

**PC-C32Ac-PC**

The synthesis of dotriacont-16-in-1,32-diyl-bis[2-(trimethylammonio)ethylphosphate] (PC-C32Ac-PC) was carried out applying the general phosphorylation and quaternisation procedure of long-chain 1,ω-diols as described previously\textsuperscript{51} using 40.02 mmol of the acetylene-modified diol (95 mg), which was isolated during the synthesis of diacetylene-modified diols.\textsuperscript{53}

Yield: 65 mg (40%); \( R_f = 0.27 \) (CHCl\(_3\)/MeOH/NH\(_3\) = 10/10/3); \(^1\)H-NMR (400 MHz, CDCl\(_3\)/CD\(_3\)OD, 27 °C): \( \delta = 1.15–1.29 \) (m, 44 H, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))\(_1\)CH\(_2\)CH\(_2\)−), 1.33–1.39 (m, 4 H, −CH\(_2\)CH\(_2\)C\(_6\)H\(_5\)CH\(_2\)−), 1.48–1.54 (m, 4 H, 2× −OCH\(_2\)CH\(_2\)(CH\(_3\))−), 2.03 ("q", \( J = 6.9\) Hz, 4 H, −CH\(_2\)CH\(_2\)C\(_6\)H\(_5\)CH\(_2\)−), 3.12 (s, 18 H, 6× −CH\(_3\)), 3.53–3.55 (m, 4 H, 2× NCH\(_2\)CH\(_2\)O−), 3.76 ("q", \( J = 6.7\) Hz, 4 H, 2× −CH\(_3\))
−OCH$_2$(CH$_2$)$_{14}$−), 4.13–4.18 ppm (m, 4 H, 2× NCH$_2$CH$_2$O−); $^{13}$C-NMR (100 MHz, CDCl$_3$/CD$_3$OD, 27 °C): $\delta$ = 18.54 (−CH$_2$C≡CCH$_2$−), 25.63 (2× −O(CH$_2$)$_2$CH$_2$(CH$_2$)$_2$−), 28.61, 28.91, 29.03, 29.28, 29.46, 29.51, 29.53, 29.545, 29.575 and 29.582 (2× −O(CH$_2$)$_3$(CH$_2$)$_1$CH$_2$−), 30.61 (d, $^3$J$_{C,P}$ = 7.4 Hz, 2× −OCH$_2$CH$_2$(CH$_2$)$_{13}$−), 54.13 (t, $J = 3.7$ Hz, 6× −CH$_3$), 58.93 (d, $^2$J$_{C,P}$ = 5.1 Hz, 2× NCH$_2$CH$_2$O−), 66.03 (d, $^2$J$_{C,P}$ = 6.0 Hz, 2× −OCH$_2$(CH$_2$)$_{14}$−), 66.29 (b, 2× NCH$_2$CH$_2$O−), 80.22 ppm (−C≡C−); MS (ESI): $m/z$: 809.38 [M + H]$^+$, 831.12 [M + Na]$^+$, 1617.63 [2M + H]$^+$; HR-MS (C$_{42}$H$_{86}$N$_2$O$_8$P$_2$): $m/z$: [M + H]$^+$ exp. 809.5938, calc. 809.5932.

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References