Supporting Information.

Characterization of the surfactant propanediyl-1,3-bis(dodecyldimethylammonium dibromide), 12-3-12.2Br.

*Elemental analysis* (C₃₁H₆₈N₂Br₂, M<sub>r</sub>=628.693). Calc. for trihydrate (%): C 59.22; H 10.90; N 4.46; Found (%): C 57.74; H 10.91; N 4.06. ¹H-NMR (400 MHz, CDCl₃, δ in ppm): 3.85 (m, 4H, N+-C₆H₂-CH₂-C₆H₂-N+); 3.50 (m, 4H, N+-C₆H₂); 3.36 (s, 12H, N+-C₆H₃); 2.73 (m, 2H, N+-C₆H₂-CH₂-CH₂-N+); 1.80 (m, 4H, N+-CH₂-CH₂-); 1.37-1.25 (m, 36H, -(CH₂)₉-); 0.87 (t, 6H, -C₆H₃). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 67.2 (N+-C₆H₂-); 61.6 (N+-C₆H₂-CH₂-CH₂-N+); 51.7 (N+-C₆H₃); 32.3, 29.9, 29.8, 29.7, 29.6, 29.5, 26.7, 22.6 (-[(CH₂)₉]-); 23.1 (N+-C₆H₂-CH₂-); 19.1 (N+-C₆H₂-CH₂-CH₂-N+); 14.5 (-C₆H₃). Mass spectroscopy: (m/z) = 628.37; [M++ 79Br]- = 549.5; [M++ 81Br]- = 547.5; [(M - 2Br) / 2] = 234.3

*NMR Measurements.* The purity of the surfactant was checked by NMR analysis. Structure of the prepared compound was confirmed by NMR spectroscopic measurements. The Gemini surfactant was dissolved in 99.95% CDCl₃ (~10 mg in 0.7 mL) and transferred into 5 mm NMR sample tubes (Promochem, Wesel, Germany). Spectra were measured with Topspin 1.3 on a Bruker DRX-400 AVANCE spectrometer (Bruker, Rheinstetten, Germany) at 400.13 MHz (¹H) or 100.62 MHz (¹³C) or on a Bruker DRX-600 AVANCE spectrometer at 600.13 MHz (¹H) or 150.90 MHz (¹³C). For 1D spectra 32k data points were recorded and Fourier transformed to spectra with a range of 15 ppm (¹H) and 240 ppm (¹³C). COSY, TOCSY, NOESY, HMQC, and HMBC spectra were measured by 128 experiments with 1024 data points each. Appropriate linear forward prediction, sinusoidal multiplication and Fourier transformation led to 2D-spectra with a range of 12 ppm and 220 ppm for ¹H and ¹³C, respectively. Residual CHCl₃ was used as internal standard for ¹H (δH 7.24) and CDCl₃ for ¹³C (δC 77.0) spectra.

Figure 1S. NMR spectrum of the 12-3-12.2Br Gemini surfactant.
**Mass Spectrometry.** Solutions of surfactants were made in 50/50 mixture of water and acetonitrile (both: HPLC gradient grade, Baker HPLC analyzed) with 0.1% addition of formic acid (purris p.a., Sigma-Aldrich). Initial concentration was 0.05%. For measurements solutions were diluted with the same mixture 1:100, so finally they were approximately 10 µM. Solutions were stable over period of months. All measurements were done on triple quadrupole type of mass spectrometer: AB-Sciex model Q-TRAP 4000, equipped with electrospray (ESI) ionization chamber. Solutions were fed with syringe pump (Harvard Apparatus) with 5µL/min. In order to minimize in-source fragmentation all operating parameters of ion source and mass spectrometer were kept at lowest possible values that is, capillary voltage, nebulizing gas (set at 0), drying gas and entrance potential. Base pressure in the spectrometer is 1 x 10^{-5} Torr, the collision gas is nitrogen. Data were acquired by automatic ramp of collision energies using option of dynamic fill time (of the second quadrupole).

**Surface tension.** Surface tension of aqueous solution of gemini surfactants was determined from freshly prepared solution by Kruss 100 K tensiometer equipped with the Wilhelmy plate at 25°C. The platinum plate was always cleaned and heated to red color with a Bunsen burner before use. The critical micelle concentration (CMC) and the surface tension at CMC it was determined from the breakpoint of the surface tension vs concentration curve. A CMC of 0.87 mmol/l was determined by a reverse CMC measurements that means the measurement starts from a highly concentrated aqueous solution, which is next stepwise diluted with water. The sequence of concentrations is produced automatically from an initial stock of prepared surfactant solution.
Figure S2. Electromotive force vs total 12-3-12.2Br concentration at [NaCl] = 0.05M in sodium cacodylate buffer (pH = 7.0).

Figure S3. Stopped-flow kinetic curve for the DNA/12-3-12.2Br system, [12-3-12.2Br]T = 2.5x10⁻⁴ M, [NaCl] = 0.55M in sodium cacodylate buffer (pH = 7.0). The continuous red line has been calculated according to a biexponential data fit (eqn. 1S). The continuous black line is the best fit to monoexponential equation

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\frac{I}{I_0} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]  

(1S)

In this equation I(t) is the fluorescence at time t and I₀ is the fluorescence in the absence of 12-3-12.2Br surfactant.
Figure S4. Comparison between relative backward $k_{-1}/k_{-1,0}$ rate constants corresponding to the first step of Scheme II vs. the concentrations of NaCl in the media. (●) CTAB/DNA interaction (data obtained from reference 4). (●) 12-3-12.2Br/DNA interaction.