

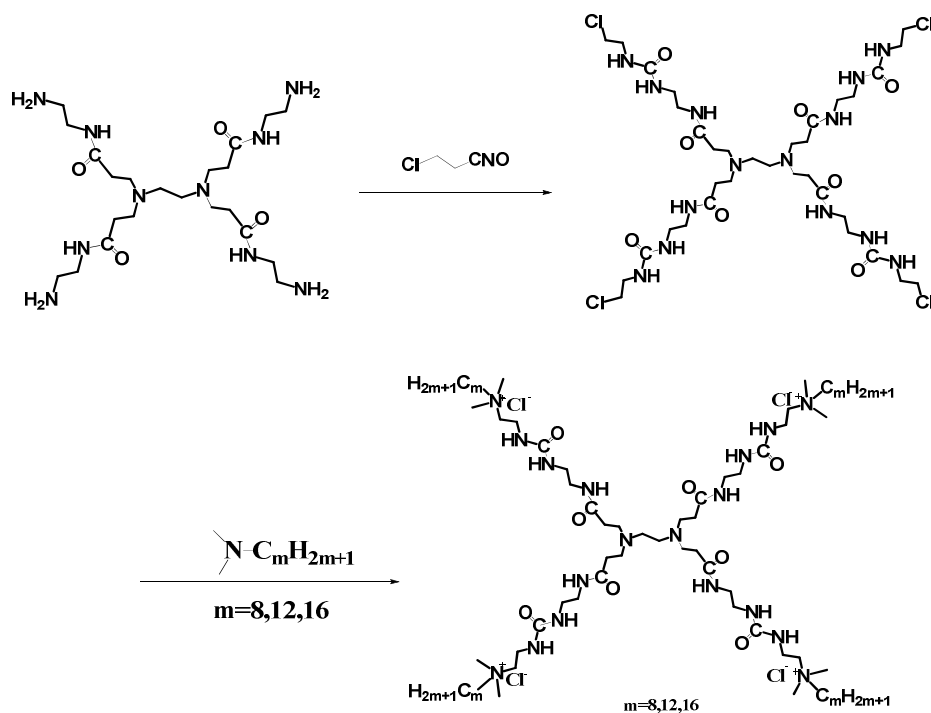
Dilational Properties of Novel Amphiphilic Dendrimers at Water-Air and Water-Heptane Interfaces

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QPAMC_m synthesis. The functionlization of dendrimers in a facile two-step reaction using PAMAM dendrimer as starting material which was prepared following the literature. The first involves introducing chlorine to the dendrimer by reacting the primary amine groups of the dendrimer with 2-chloroethyl isocyanate. The chlorine can then react with tertiary amines to form quaternary ammonium compounds. All the products were purified by acetone/ethanol repeatedly and characterized by ¹H NMR, ESI-MS and elemental analysis. A scheme of the reaction is shown in Scheme 1.



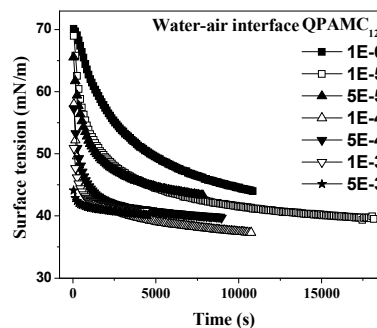
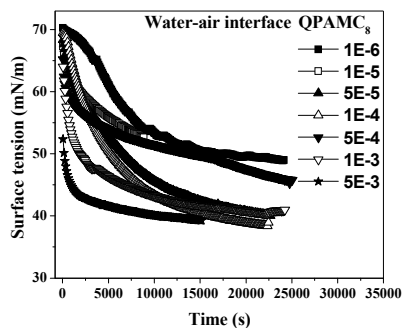
Scheme 1. The synthesis pathway of three amphiphilic dendrimers QPAMC_m.

QPAMC₈: To a solution of 5.00 g of PAMAM generation 1 dendrimer (1 equiv, 9.7 mmol) in 50 ml N,N-dimethyl formamide, added 4.1 g 2-chloroethyl isocyanate (4.04 equiv, 39.2 mmol) dropwise at room temperature. After the mixture was stirred overnight, 9.2 g of dimethyl dodecylamine (6 equiv, 58.2 mmol) were added. The solution was slowly heated to 80 °C for 72 h. After this, the solution was concentrated, and the concentrated solution was precipitated in acetone/ethanol, yellow powder was obtained (yield 58%). ¹H NMR (D₂O, 400MHz): δ : 3.63(t,8H, -CH₂-NH-CO), 3.50-3.57(m,8H,-CH₂-N-), 3.22-3.39(m,32H,CONH-CH₂-CH₂-N⁺), 3.17(s,24H,-N⁺-CH₃), 2.84-3.09(t,8H,-CH₂-CO-), 2.49(t,4H,-CH₂-CH₂-), 1.74(t,8H,-CH₂-CH₃), 1.13-1.31(m,40H,-(CH₂)₅-CH₃), 0.84(t,12H -CH₃). MS-ESI (m/z): 1421[(M-4Cl)⁺]; Anal. Calcd for C₇₀H₁₅₆Cl₄N₁₈O₈·H₂O: C, 56.68; H, 10.03; Cl, 9.04; N, 16.08. Found: C, 53.97; H, 9.37; Cl, 8.92; N, 16.27.

QPAMC₁₂: ¹H NMR(D₂O, 400MHz): δ :3.64-3.69(m,8H,-CH₂-NH-CO), 3.29-3.47(m, 40H, -CH₂-N-,CONH-CH₂-CH₂-N⁺), 3.17(s,24H,-N⁺-CH₃), 2.88(t,8H,-CH₂-CO-),2.50(t,4H,-CH₂-CH₂-),1.82(t,8H,-CH₂-CH₃),1.32-1.40(m,72H,-(CH₂)₉-CH₃), 0.93(t,12H -CH₃). MS-ESI (m/z): 412[(M-3Cl)⁺3/3]; Anal. Calcd for C₉₀H₁₈₈Cl₄N₁₈O₈·H₂O: C, 60.31; H, 10.57; Cl, 7.91; N, 14.07. Found: C, 56.64; H, 10.02; Cl, 7.78; N, 14.85.

QPAMC₁₆: ¹H NMR (DMSO, 400MHz): δ :3.22-3.56(m,32H,-CH₂-NH-CO, -CH₂-N-),3.05-3.39(m,40H,CONH-CH₂-CH₂-N⁺,24H,-N⁺-CH₃),2.65-2.88(t,8H,-CH₂-CO-), 2.22-2.42(m,4H,-CH₂-CH₂-),1.65(t,8H-CH₂-CH₃), 1.02-1.22(m,104H,-(CH₂)₁₃-CH₃), 0.84(t,12H -CH₃). MS-ESI (m/z): 468[(M-4Cl)⁺4/4]; Anal. Calcd for C₁₀₆H₂₂₀Cl₄N₁₈O₈·H₂O: C, 63.13; H, 10.99; Cl, 7.03; N, 12.50. Found: C, 53.98; H, 10.51; Cl, 6.72; N, 13.34.

Dynamic surface/interfacial tension.



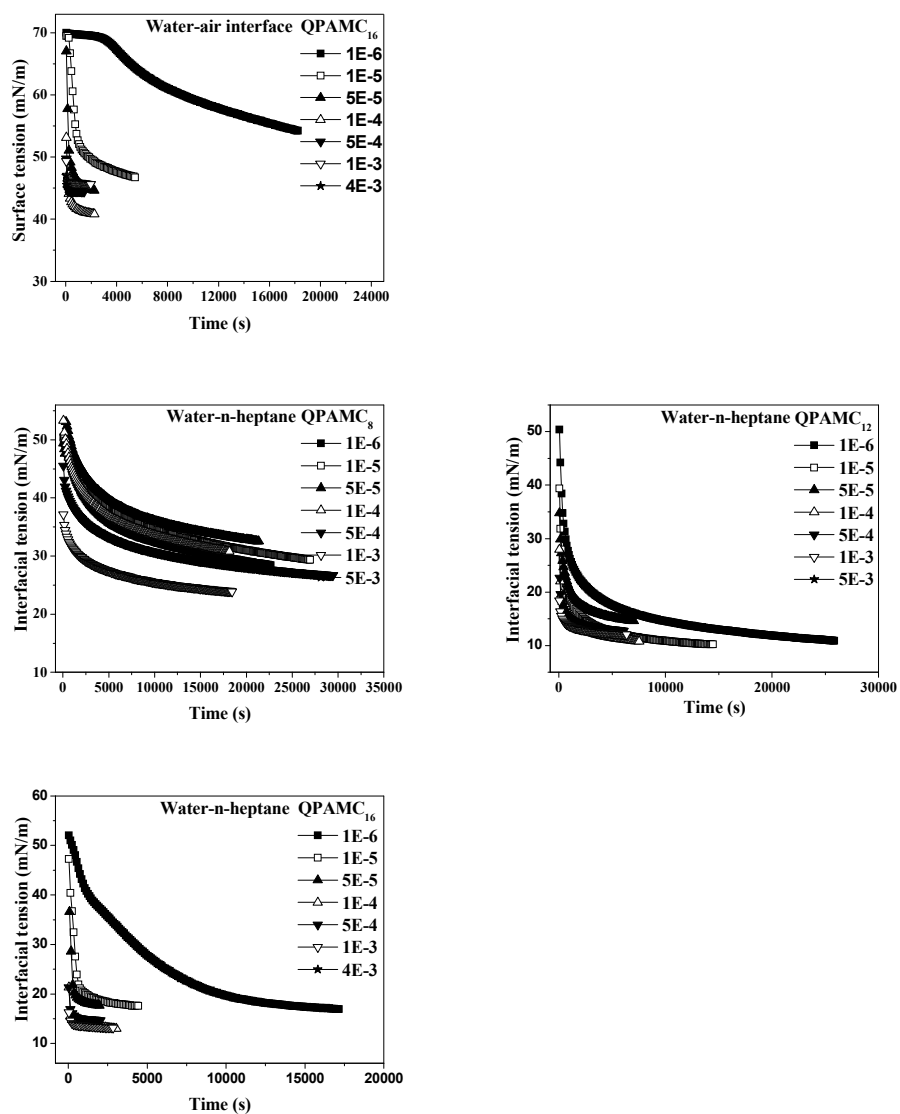


Figure 1S. The dynamic interfacial tension of QPAMC_m at two different interfaces.

DOSY Spectra. The 2D DOSY PGSE NMR spectra were also obtained with stebpgp1s pulse program at 25 °C with maximum gradient strength 50 G cm⁻¹. The obtained surfactant self-diffusion coefficients at 5×10^{-5} , 1×10^{-4} , 5×10^{-4} and 1×10^{-3} M • L⁻¹ are around 1.29×10^{-9} , 1.61×10^{-10} , 1.33×10^{-10} and 1.18×10^{-10} m²/s respectively.

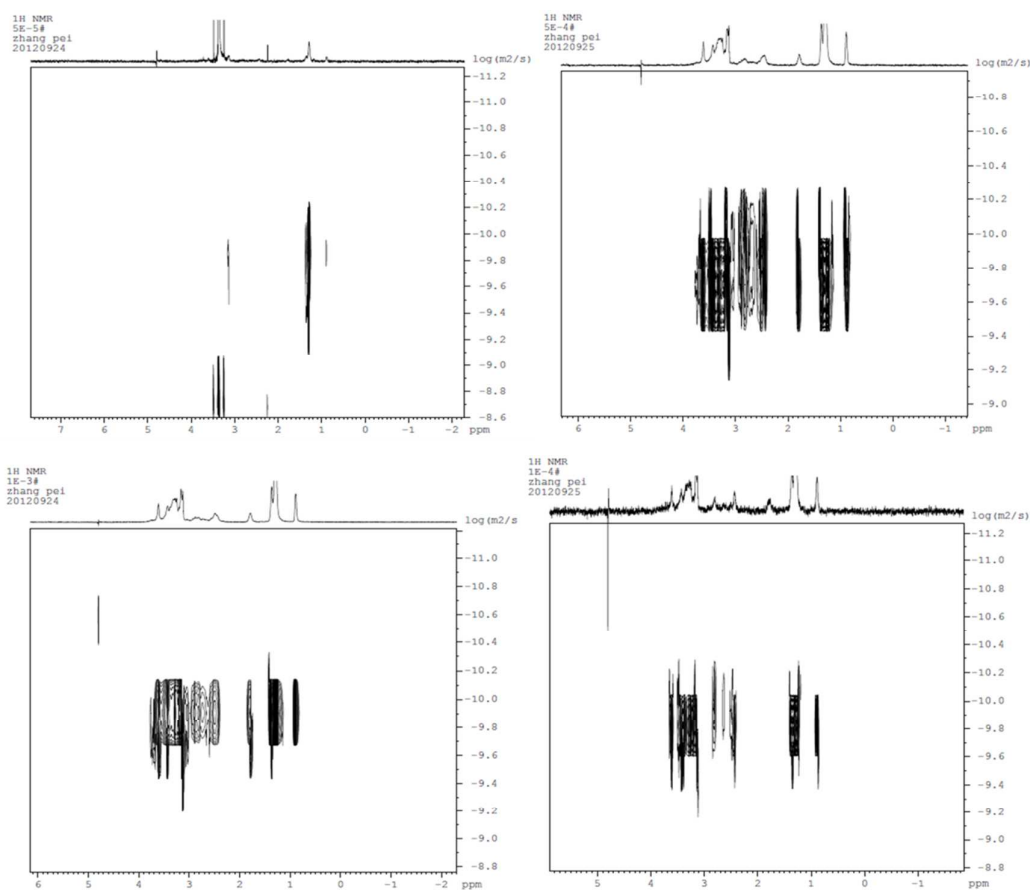


Figure 2S. 2D DOSY PGSE NMR spectra of QPAMC₁₂ at 5×10^{-5} , 1×10^{-4} , 5×10^{-4} and 1×10^{-3} M $\cdot$ L⁻¹ concentration (from the top to the bottom) obtained with stebppg1 s pulse program.