Supporting Information:

Can Molecules with Anionic Head and Poly(ethylene glycol) methyl ether Tail Self-assemble in Water? A Surface tension, Fluorescence Probe, Light Scattering, and Transmission Electron Microscopic Investigation

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Materials. Poly(ethylene glycol)methyl ether methacrylate (MW 300 and 1100), and 3-mercaptopropionic acid were obtained from Aldrich and were used without further purification. The fluorescence probes, 1-anilinonaphthalene (AN), 1,6-diphenyl-1,3,5-hexatriene (DPH), and pyrene (Py) were procured from Aldrich (Milwaukee, WI, USA) and were purified by repeated recrystallization from an ethanol-acetone mixture. Good quality organic solvents employed in this work were purified and dried whenever necessary. All aqueous solutions were prepared using Milli-Q water (~18 MΩ), pH 6.6.

Synthesis. Compound A was synthesized by thiol-ene “click” chemistry following a method reported in the literature. Briefly poly(ethylene glycol)methyl ether methacrylate was first freed from inhibitor by passing through a SiO₂ column and elution by methanol. Pure poly(ethylene glycol)methyl ether methacrylate was then reacted with 3-mercaptopropionic acid in methanol at room temperature for 6 hours. The compound A₁ and A₂ were obtained as white solid after evaporation of the solvent and were then purified by column (Al₂O₃) chromatography using 5:1 (v/v) ethyl acetate/pet ether mixture. The compounds were characterized by FT-IR, ¹H NMR, and ¹³C NMR spectroscopy. The reaction
of NaHCO$_3$ with $A_1$ or $A_2$ in THF-water mixture overnight gave the sodium salt, SA$_1$ or SA$_2$.

The solid product thus obtained was purified by repeated precipitation from diethylether.

**Chemical Identification**

**Amphiphile $A_1$.** State. Solid, and hygroscopic, Yield 79%, FTIR (KBr cm$^{-1}$). Peak at 3600 cm$^{-1}$ (broad) shows the presence of O-H stretching, 1742 cm$^{-1}$ shows presence of C=O stretching of ester group and 636 cm$^{-1}$ shows presence of C-S stretching. $^1$H NMR (CDCl$_3$, δ ppm): 1.45 (CH$_3$, t, 9H), 2.18 (CH$_3$-CH$_2$-N, m, 4H), 2.42 (2H, s, OH), 2.81 (6H, m, N-CH$_2$, S-CH$_2$-CH$_2$-N), 3.25 (5H, m, S(CH$_2$-CHCH$_3$)CH$_2$CH$_2$N), 3.88 (3H, s, CH$_3$-O), 4.10 (44H, m, long chain glycolic CH$_2$, CHCH$_2$OH), 4.23 (2H, m, CH-CH$_2$-OH), 4.77 (2H, t, C(O)OCH$_2$). $^{13}$C-NMR. (CDCl$_3$, 400 MHz) δ (ppm) 174.5 (COOCH$_2$), 169.1 (COOH), 68.7, 69.5, 70.5, 70.9, 73.6 (ether CH$_2$), 54.9 (OCH$_3$), 42.4 (SCH$_2$CH), 36.2 (SCH$_2$CH), 35.9 (SCH$_2$ CH$_2$COOH), 28.1 (SCH$_2$ CH$_2$COOH), 15.1 (CH$_3$).

**Amphiphile $A_2$.** State. Solid and hygroscopic, Yield 80%, FTIR (KBr cm$^{-1}$). Peak at 3600 cm$^{-1}$ (broad) shows the presence of O-H stretching, 1741 cm$^{-1}$ shows presence of C=O stretching of ester group and 637 cm$^{-1}$ shows presence of C-S stretching. $^1$H NMR (CDCl$_3$, δ ppm): 1.40 (CH$_3$, t, 9H), 2.127 (CH$_3$-CH$_2$-N, m, 4H), 1.92 (2H, s, OH), 2.31 (6H, m, N-CH$_2$, S-CH$_2$-CH$_2$-N), 2.75 (5H, m, S(CH$_2$-CHCH$_3$)CH$_2$CH$_2$N), 3.38 (3H, s, CH$_3$-O), 3.60 (m, long chain glycolic CH$_2$, CHCH$_2$OH), 3.73 (2H, m, CH-CH$_2$-OH), 4.27 (2H, t, C(O)OCH$_2$). $^{13}$C-NMR. (CDCl$_3$, 400 MHz) δ (ppm) 176.3 (COOCH$_2$), 168.4 (COOH), 67.8, 68.6, 70.9, 71.5, 74.1 (ether CH$_2$), 55.9 (OCH$_3$), 43.4 (SCH$_2$CH), 36.5 (SCH$_2$CH), 36.4 (SCH$_2$CH$_2$COOH), 27.9 (SCH$_2$ CH$_2$COOH), 14.8(CH$_3$).
References: