Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTRY INFORMATION

New Ester based Gemini Surfactants: Effect of Different Cationic Headgroups on Micellization Properties and Viscosity of Aqueous Micellar Solution

Avinash Bhadani*, Misako Tani, Takeshi Endo, Kenichi Sakai,
Masahiko Abe and Hideki Sakai*

Department of Pure and Applied Chemistry in Faculty of Science and Technology
and Research Institute for Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510, Japan.

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Synthesis and Characterization

Piperidine (42.58g, 0.50 mol) or pyrrolidine (35.56g, 0.50 mol) or morpholine (43.56g, 0.5 mol) was reacted with dodecyl bromide (49.85, 0.20 mol) in 200 ml of ethyl acetate for 24 hours at 60ºC. The crude reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure in a rotary flash evaporator at 45ºC. The crude reaction mixture was then washed twice with 200ml of deionized water followed by 100 ml of aqueous methanol (1:1 water:methanol). Thereafter it was dissolved in chloroform and dried using Na_2SO_4. The solvent was removed under reduced pressure in a rotary flash evaporator at 60°C to get respective linear tertiary amine (i. e. 1-dodecylpiperidine, 1-dodecylpyrrolidine and 4-dodecylmorpholine) in 78-84% isolated yield. Alternatively *N*,*N*-diethyldodecan-1-amine and ethane-1,2-diyl bis(2-bromoacetate) were synthesized using previous reported methodology.[1,2] Ethane-1,2-diyl bis(2-bromoacetate) was synthesized by reacting ethylene glycol (12.41g, 0.20 mol) and bromoacetic acid (55.58g, 0.40mol) in the presence of *p*-toluenesulfonic acid monohydrate (1.90g, 0.01mol) for 8 hours at 130ºC followed by workup as reported previously to get ethane-1,2-diyl bis(2-bromoacetate) in 55% isolated yield.[31] 1-dodecylpiperidine (25.35g, 0.1 mol) or 1-dodecylpyrrolidine (23.95g, 0.1 mol) or 4-dodecylmorpholine (25.55g, 0.1 mol) or *N*,*N*-diethyldodecan-1-amine (24.15g, 0.1 mol) was dissolved in 50 ml of dry chloroform at room temperature and ethane-1,2-diyl bis(2-bromoacetate) (14.59g, 0.048 mol) was slowly added to the stirred solution. After addition, the reaction mixture was stirred for 5 hours at 60ºC. The crude reaction mixture after the removal of chloroform under reduced pressure was subsequently washed twice with 100ml of diethylether and cold precipitated in acetone under inert nitrogen atmosphere. The precipitates after removal of solvent upon drying in a rotary flash evaporator at 70 °C for 3 hours give pure corresponding gemini surfactants in 58-78% isolated yield (Scheme-1).

1) *N*,*N*-diethyldodecan-1-amine: Slight yellowish liquid (38.68g, 65.6%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (q, J = 7.2 Hz, 4H), 2.42–2.37 (m, 2H), 1.43 (m, 2H), 1.26 (br s, 18H), 1.02 (t, J = 7.2 Hz, 6H), 0.90–0.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.95, 46.80, 31.86, 29.59, 29.30, 27.68, 26.95, 22.61, 14.01, 11.59. HRMS (ESI) *m/z:* 242.2848 calcd for $C_{16}H_{35}N$+H or (M+H), found 242.2846 (100%).

2) 1-Dodecylpyrrolidine: Slight yellowish liquid (42.85g, 89.5%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49–2.46 (m, 4H), 2.40 (dd, J = 8.7, 6.9 Hz, 2H), 1.78-1.76 (m, 4H), 1.48 (m, 2H), 1.30-1.26 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.67, 54.15, 31.84, 29.56, 29.28, 29.06, 27.69, 23.28, 22.60, 14.01. HRMS (ESI) *m/z:* 240.2691 calcd for $C_{16}H_{33}N$+H or (M+H), found 240.2691 (100%).

3) 1-Dodecylpiperidine: Slight yellowish liquid (37.11g, 73.2%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (br s, 4H), 2.28–2.24 (m, 2H), 1.60–1.56 (m, 4H), 1.48–1.43 (m, 4H), 1.26 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 59.66, 54.61, 31.90, 29.65, 29.60, 29.33, 27.76, 26.86, 25.90, 24.44, 22.66, 14.09. HRMS (ESI) *m/z:* 254.2848 calcd for $C_{17}H_{35}N$+H or (M+H), found 254.2848 (100%).

4) 4-Dodecylmorpholine: Slight yellowish liquid (41.02g, 80.3%); ^{1}H NMR (500 MHz, $CDCl_3$) 3.72-3.71 (br s, 4H), 2.43 (m, 4H), 2.31 (dd, J = 8.5, 7.0 Hz, 2H), 1.48 (m, 2H), 1.28-1.26 (m, 18H), 0.87 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 66.95, 59.19, 53.74, 31.85, 29.57, 29.53, 29.29, 27.47, 26.53, 22.62, 14.05. HRMS (ESI) *m/z:* 256.2640 calcd for $C_{16}H_{33}NO$+H or (M+H), found 256.2646 (100%).

5) 2,2'- [ethane-1,2-diylbis(oxy)] bis(*N*-dodecyl- *N*,*N*-diethyl- 2-oxoethanaminium) dibromide [C12QA(2Es)C12QA]2Br: White solid (18.26g, 46.4%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (s, 4H), 4.49 (s, 4H), 3.85 (q, J = 6.9 Hz, 8H), 3.62 (dd, J = 10.3, 6.7 Hz, 4H), 1.80 (m, 4H), 1.48 (t, J = 7.2 Hz, 12H), 1.35–1.25 (m, 36H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.95, 62.93, 59.74, 57.12, 55.95, 31.83, 29.53, 29.39, 29.25, 29.01, 26.41, 22.61, 22.45, 14.07, 8.70. HRMS (ESI-Positive) *m/z:* 314.3054 calcd for $C_{38}H_{78}N_2O_4^{2+}$/2+H or [(M^{2+}/2)+H], found 314.3063 (100%); 344.3159 calcd for $C_{20}H_{41}NO_3^{\bullet+}$+H (breaking of ester bond), found 344.3170.

6) 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpyrrolidin-1-ium) dibromide [C12PYR(2Es)C12PYR]2Br: White solid (22.81g, 62.6%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (s, 4H), 4.45 (s, 4H), 4.32–4.27 (m, 4H), 3.88-3.85 (m, 4H), 3.69–3.66 (m, 4H), 2.49 (m, 4H), 2.17 (m, 4H), 1.81 (m, 4H), 1.33-1.24 (m, 36H), 0.89–0.87 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.37, 64.53, 62.82, 61.82, 59.53, 31.76, 29.46, 29.35, 29.18, 28.95, 26.32, 23.93, 22.73, 22.55, 14.00. HRMS (ESI-Positive) *m/z:* 312.2897 calcd for $C_{38}H_{74}N_2O_4^{2+}$/2+H or [(M^{2+}/2)+H], found 312.2874 (100%); 342.3003 calcd for $C_{20}H_{39}NO_3^{\bullet+}$+H (breaking of ester bond), found 342.2994.

7) 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpiperidin-1-ium) dibromide [C12PIP(2Es)C12PIP]2Br: White solid (29.60g, 73.00%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 4H), 4.47 (s, 4H), 4.28-4.24 (m, 4H), 3.79–3.73 (m, 8H), 2.09 (m, 4H), 1.89-1.74 (m, 12H), 1.36–1.25 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.83, 62.68, 59.60, 58.21, 31.85, 29.55, 29.44, 29.41, 29.28, 29.03, 26.49, 22.64, 22.26, 20.65, 19.90, 14.09. HRMS (ESI-Positive) *m/z:* 326.3054 calcd for $C_{40}H_{78}N_2O_4^{2+}$/2+H or [(M^{2+}/2)+H], found 326.3079 (100%); 356.3159 calcd for $C_{21}H_{41}NO_3^{\bullet+}$+H (breaking of ester bond), found 356.3177.

8) 4,4'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(4-dodecylmorpholin-4-ium) dibromide [C12MOR(2Es)C12MOR]2Br: White solid (23.02g, 56.5%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (s, 4H), 4.51 (s, 4H), 4.47-4.43 (m, 4H), 4.36- 4.34 (m, 4H), 4.05 -4.02 (m, 4H), 3.89- 3.80 (m, 8H), 1.85 (br s, 4H), 1.35- 1.24 (m, 36H), 0.88 (t, J = 6.96 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.73, 63.07, 61.46, 60.35, 58.83, 56.79, 31.76, 29.47, 29.35, 29.19, 28.92, 26.27, 22.54, 22.23, 14.00. HRMS (ESI-Positive) *m/z:* 328.2846 calcd for $C_{38}H_{74}N_2O_6^{2+}$/2+H or [(M^{2+}/2)+H], found 328.2821 (100%); 358.2952 calcd for $C_{20}H_{39}N_2O_4^{\bullet+}$+H (breaking of ester bond), found 358.2994.

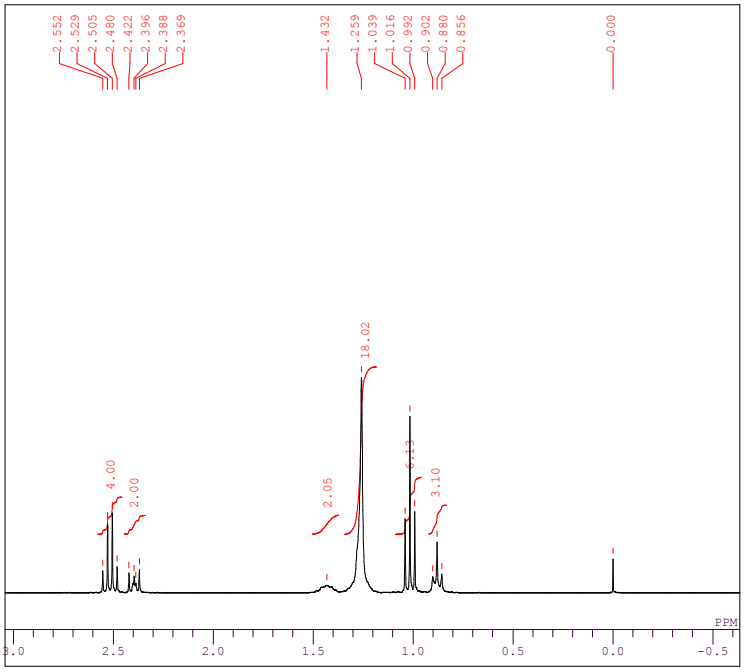

Figure S1: [1]H NMR spectra of *N*,*N*-diethyldodecan-1-amine.

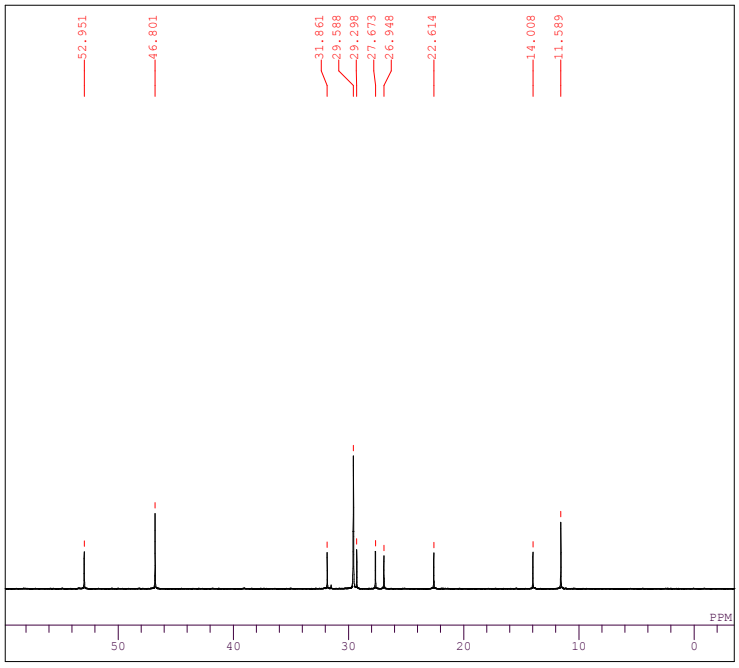

Figure S2: [13]C NMR spectra of *N*,*N*-diethyldodecan-1-amine.

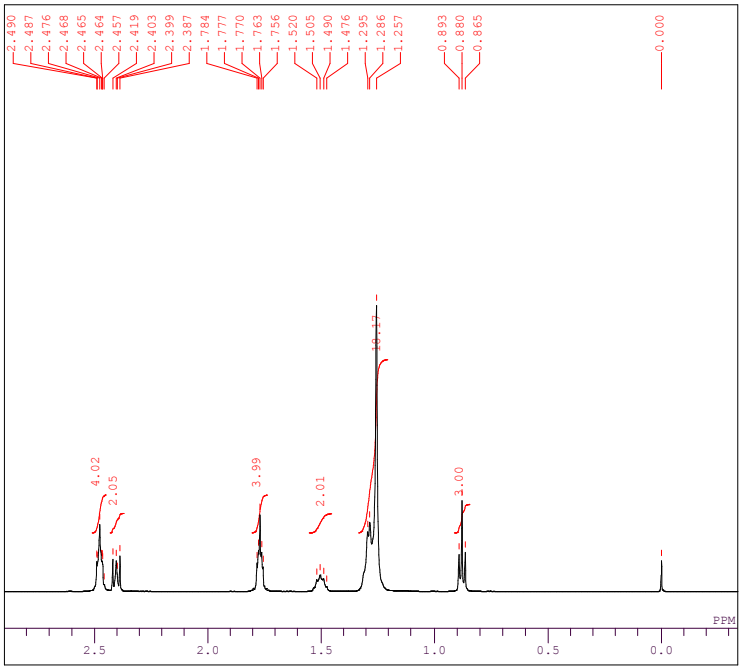

Figure S3: ^{1}H NMR spectra of 1-dodecylpyrrolidine.

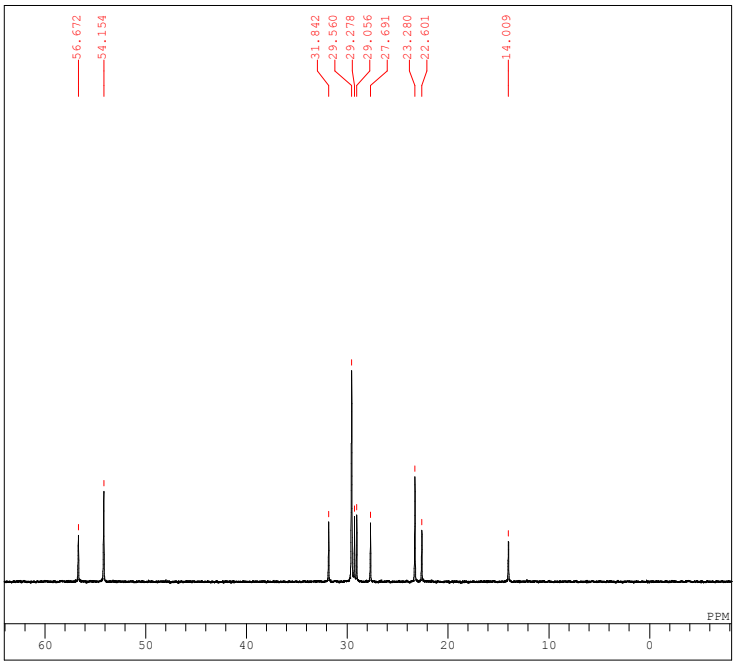

Figure S4: ^{13}C NMR spectra of 1-dodecylpyrrolidine.

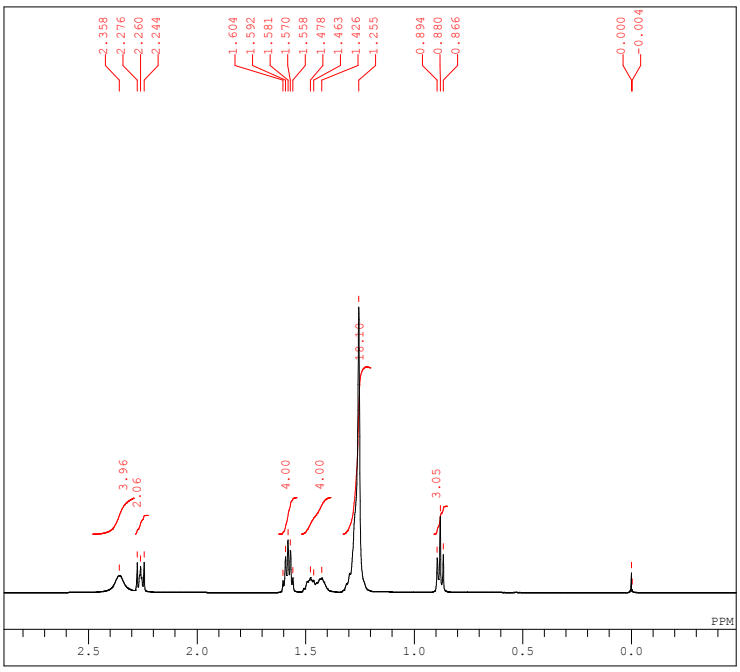

Figure S5: ^{1}H NMR spectra of 1-dodecylpiperidine.

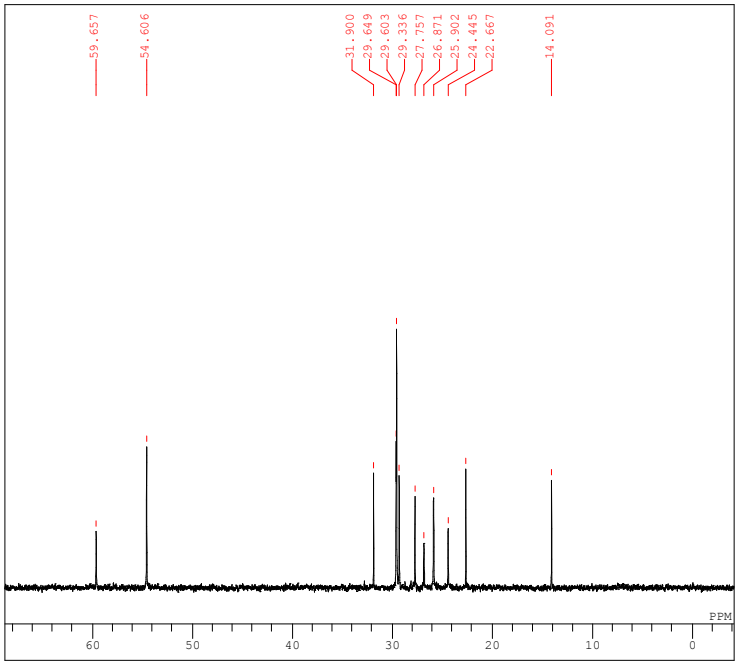

Figure S6: ^{13}C NMR spectra of 1-dodecylpiperidine.

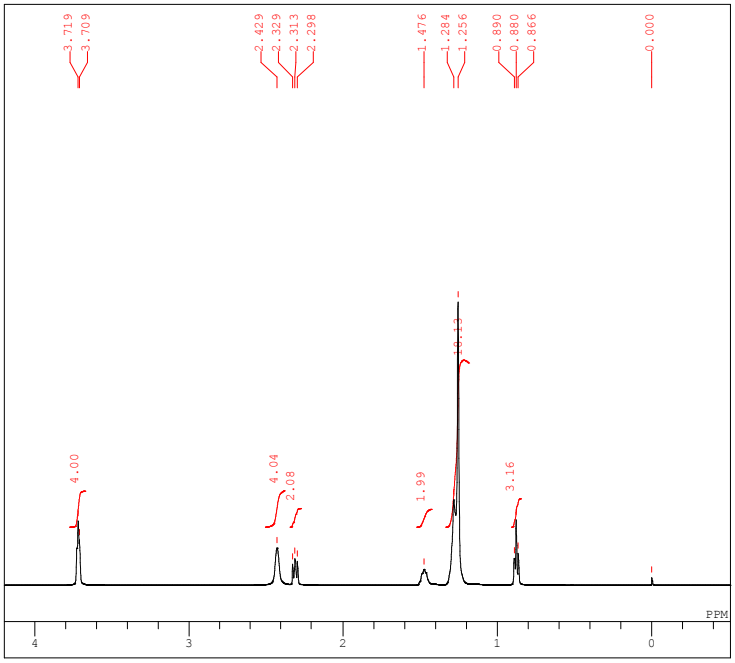

Figure S7: ^{1}H NMR spectra of 4-dodecylmorpholine.

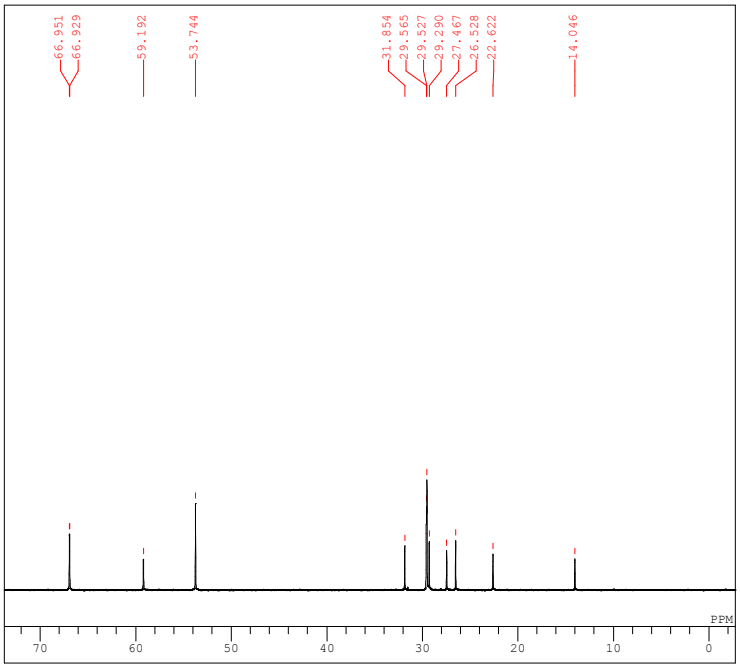

Figure S8: ^{13}C NMR spectra of 4-dodecylmorpholine.

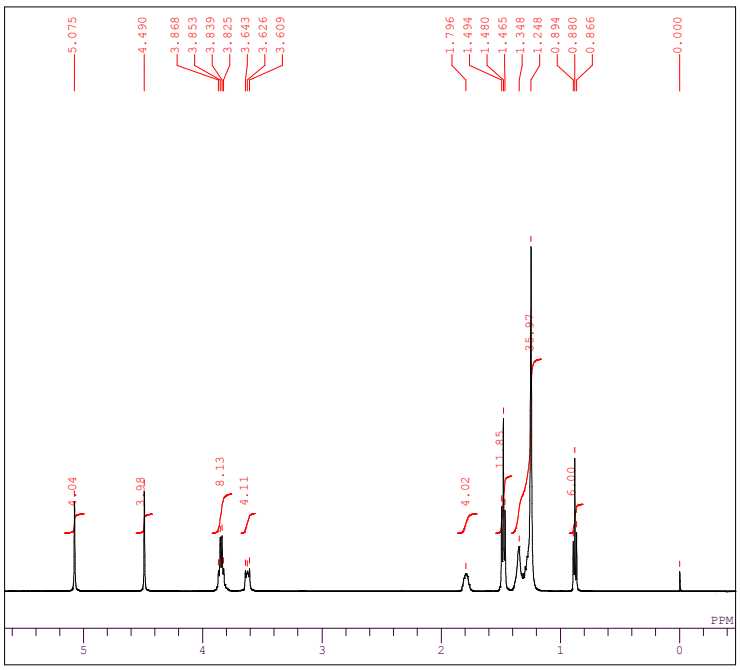

Figure S9: ^{1}H NMR spectra of 2,2'- [ethane-1,2-diylbis(oxy)] bis(*N*-dodecyl- *N*,*N*-diethyl- 2-oxoethanaminium) dibromide **[C12QA(2Es)C12QA]2Br.**

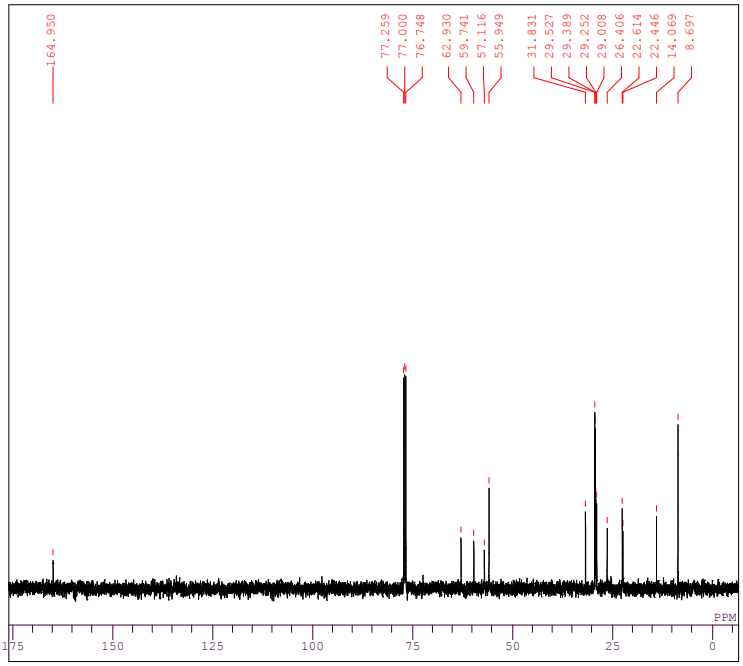

Figure S10: ^{13}C NMR spectra of 2,2'- [ethane-1,2-diylbis(oxy)] bis(*N*-dodecyl- *N*,*N*-diethyl- 2-oxoethanaminium) dibromide **[C12QA(2Es)C12QA]2Br.**

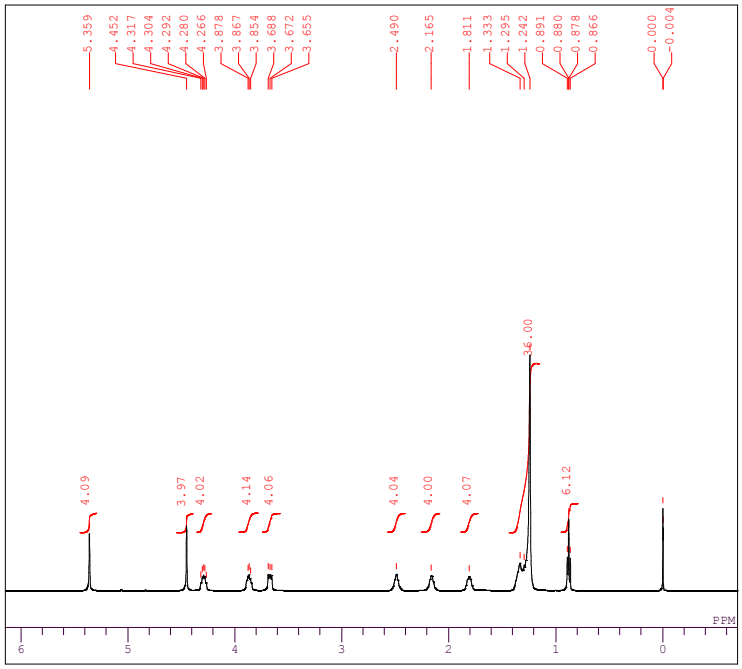

Figure S11: ^{1}H NMR spectra of 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpyrrolidin-1-ium) dibromide **[C12PYR(2Es)C12PYR]2Br.**

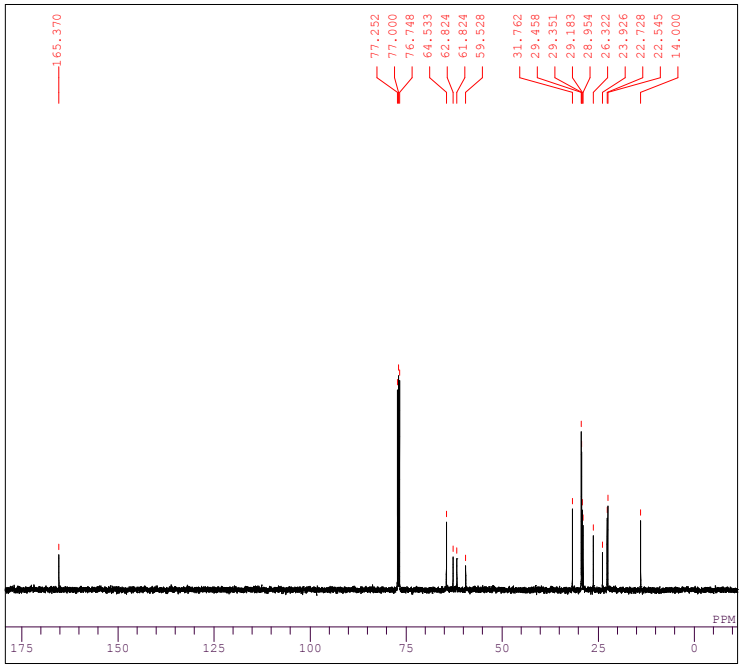

Figure S12: ^{13}C NMR spectra of 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpyrrolidin-1-ium) dibromide **[C12PYR(2Es)C12PYR]2Br.**

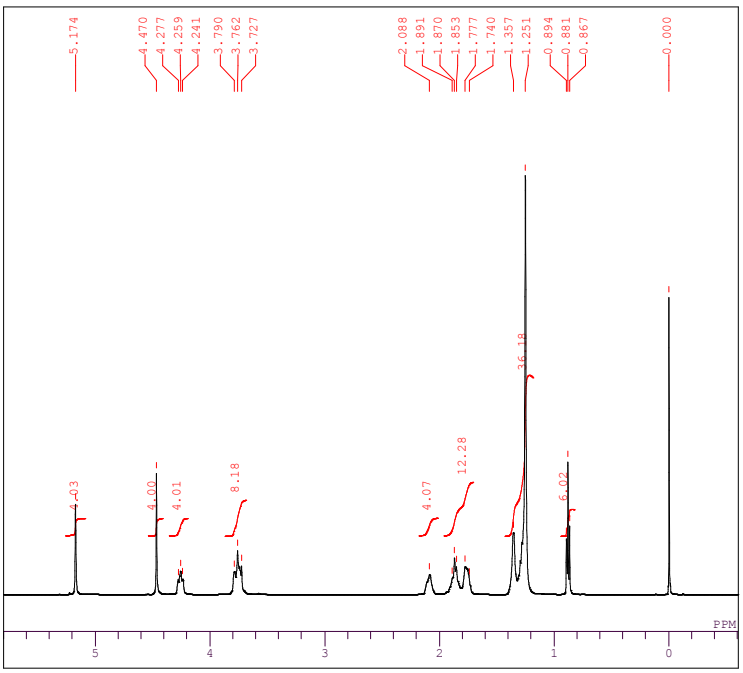

Figure S13: ^{1}H NMR spectra of 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpiperidin-1-ium) dibromide **[C12PIP(2Es)C12PIP]2Br.**

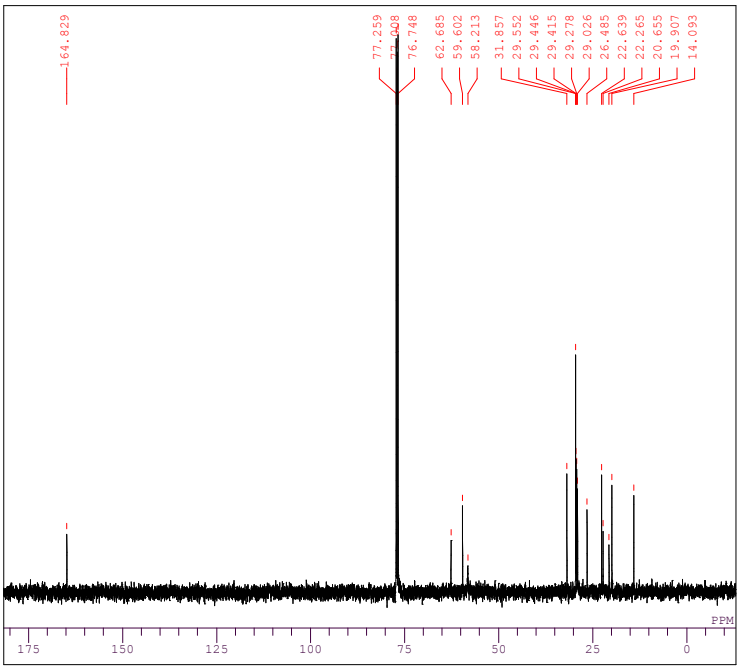

Figure S14: ^{13}C NMR spectra of 1,1'-(ethane-1,2-diylbis(oxy))bis(2-oxoethane-1,2-diyl)bis(1-dodecylpiperidin-1-ium) dibromide **[C12PIP(2Es)C12PIP]2Br.**

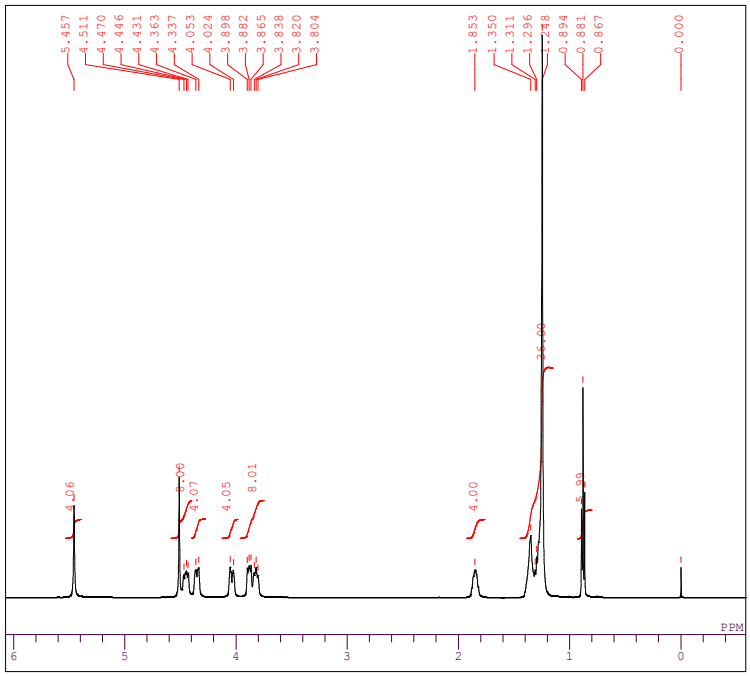

Figure S15: [1]H NMR spectra of 4,4'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(4-dodecylmorpholin-4-ium) dibromide **[C12MOR(2Es)C12MOR]2Br.**

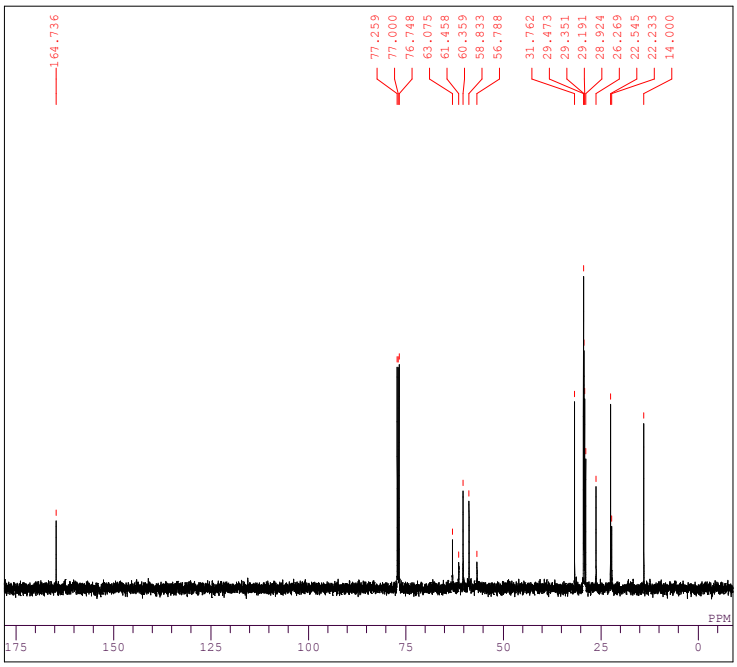

Figure S16: [13]C NMR spectra of 4,4'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(4-dodecylmorpholin-4-ium) dibromide **[C12MOR(2Es)C12MOR]2Br.**

Reference:

1) Q. Zhang, Z. Gao, F. Xu, S. Tai, X. Liu, S. Mo and F. Niu, *Langmuir,* 2012, **28**, 11979−11987.

2) A. Bhadani, T. Endo, K. Sakai, H. Sakai and M. Abe, *Colloid Polym Sci.,* 2014, **292**, 1685–1692.