

Electronic Supplementary Information

A Family of Novel Bio-based Zwitterionic Surfactants Derived from Oleic Acid

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1. Material

Oleic acid (>85%, GC, TCI), AlCl₃ (99%, Aladdin), *N, N*-dimethyl-1,3-propanediamine (99%, GC, Sigma), *N, N*-Dimethylethylenediamine (99%, J&K), *N, N*-Diethylethylenediamine (99%, J&K), Sodium chloroacetate (99%, Aladdin) were used without further purification. All other chemicals used were of analytical reagent grade.

Daqing Crude Oil were dehydrated and degassed. The acid value is 0.06 mg KOH/g. The density of the crude oil is 0.84 g/cm³ and the viscosity was 19.2 mPa·s at 50 °C. The composition was listed in Table S1. The main hydrocarbons are alkanes from C13-C31, among which C23 was the most abundant.

Table S1 Content of each fraction in crude oil

Composition	Mass fraction %
Asphaltene	8.12
Resins	24.12
Hydrocarbon	65.88
Organic acids	0.13

2. Characterization

2.1 EI-MS spectra

EI-MS spectra were recorded on an Agilent 5975 inert Mass Selective Detector.

2.2 ESI-HRMS spectra

ESI HRMS spectra were recorded on the Waters LCT Premier XE Mass Spectrometers.

2.3 ¹H NMR spectra

¹H NMR spectra of all the intermediates and final surfactants were recorded on a Bruker Avance 400 spectrometer (400 MHz) in CDCl₃ at room temperature. Tetramethylsilane (TMS) was used as reference.

2.4 HPLC chromatograph spectra

The purity of bio-based zwitterionic surfactants was measured on a WuFeng LC-100 liquid chromatograph with RI100 as the detector and Elite Hypersil-ODS2 5 μm (4.6 \times 250 mm) as the reversed-phase chromatography column. The ratio of methanol and water in the mobile phase is chosen as 90:10.

3. Synthesis

3.1 Synthesis of Phenyl octadecanoic acid (POA)

2.82 g (10 mmol) of oleic acid and 1.34 g (10 mmol) of AlCl_3 were added to 15 mL benzene in a round-bottom flask. The reaction mixture was refluxed at 65 $^\circ\text{C}$, and anhydrous CaCl_2 was placed in a drying tube above the reactor. After 6 h of reaction, the product was washed by 10 mL hydrochloric acids (6 mol/L) for 3 times and extracted. AlCl_3 was dissolved in water phase and then recycled. The organic phase was for the next step.

0.5 mL of the organic phase was taken out, for characterization and yield calculation. Excess benzene was recycled on a rotary evaporator giving a yellow residue, Phenyl octadecanoic acid (POA), 3.54 g (9.83 mmol), yielded 98.3%.

EI-MS (Fig. S1): Phenyl octadecanoic acid butylester, Found: $m/z=416$.

^1H NMR (400 MHz, CDCl_3) (Fig. S2): $\delta=0.856$ (t, $J=3.20$ Hz, 3H), 1.201 (m, 22H), 1.516-1.593 (m, 6H), 2.293-2.352 (m, 2H), 2.414-2.462 (m, 1H), 7.128-7.263 (m, 5H).

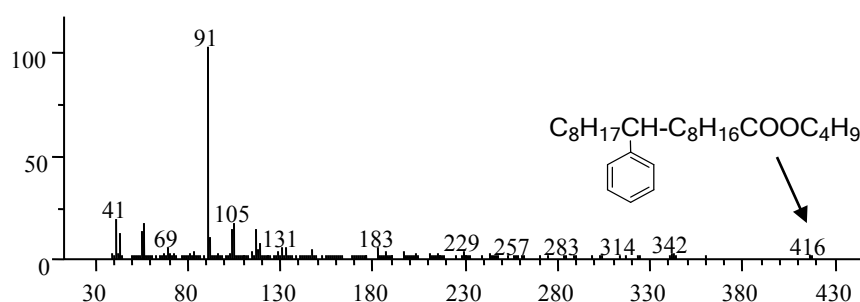


Fig. S1 EI-MS spectrum of Phenyl octadecanoic acid butylester

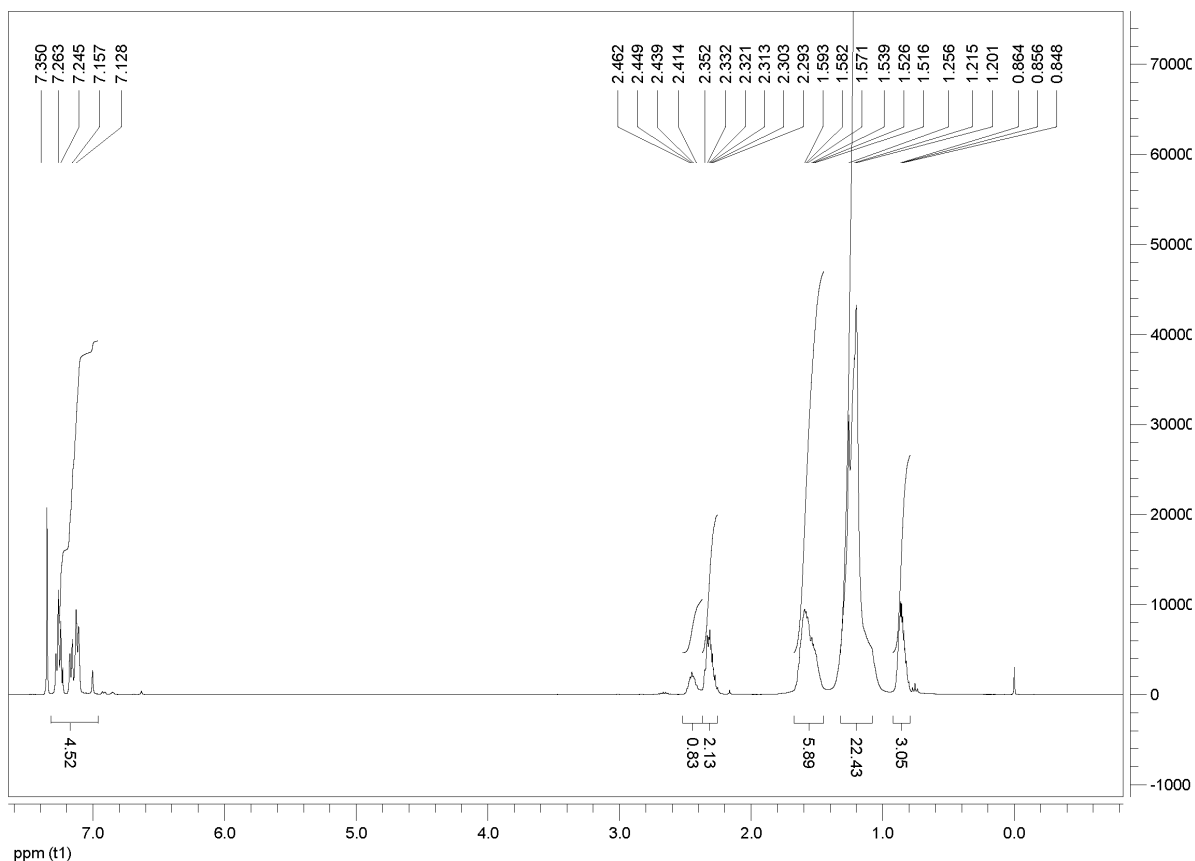


Fig. S2 ¹H NMR spectrum of Phenyl octadecanoic acid. (chloroform: $\delta=7.350$)

3.2 Synthesis of *N*-phenyl octadecanoicamidopropyl-*N,N*-dimethylamine (POAPMA)

The solution of POA (3.60 g, 10 mmol) mentioned above was added dropwise to a drying flask with 0.8 mL SOCl₂ (11 mmol) in it, and the mixture was stirred at 40 °C for 2 h. Then the mixture was distilled to remove excess SOCl₂. 1.4 mL *N,N*-dimethyl-1,3-propanediamine (11 mmol) was slowly added in to the residue at 0 °C. The reaction mixture was then warmed to 40 °C and stirred for 2 h. The excess diamine and solvent were recycled on a rotary evaporator giving a brown residue, *N*-phenyl octadecanoicamidopropyl-*N,N*-dimethylamine (POAPMA), 4.00 g (9.02 mmol), yielded 90.2%.

ESI HRMS (Fig. S3): m/z [M+H]⁺ calcd for 445.4158; found: 445.4133.

¹H NMR (400 MHz, CDCl₃) (Fig. S4): $\delta=0.850$ (t, $J=3.20$ Hz, 3H), 1.199 (m, 22H), 1.535-1.643 (m, 8H), 2.118-2.136 (m, 2H), 2.210-2.229 (m, 6H), 2.261-2.298 (m, 1H), 2.374-2.452 (m, 2H), 3.321-3.453 (m, 2H), 6.924 (br, 1H), 7.129-7.269 (m, 5H).

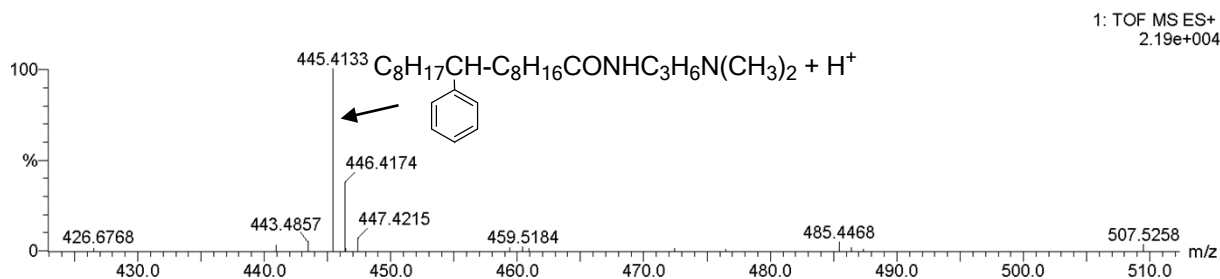


Fig. S3 ESI-HRMS spectrum of POAPMA

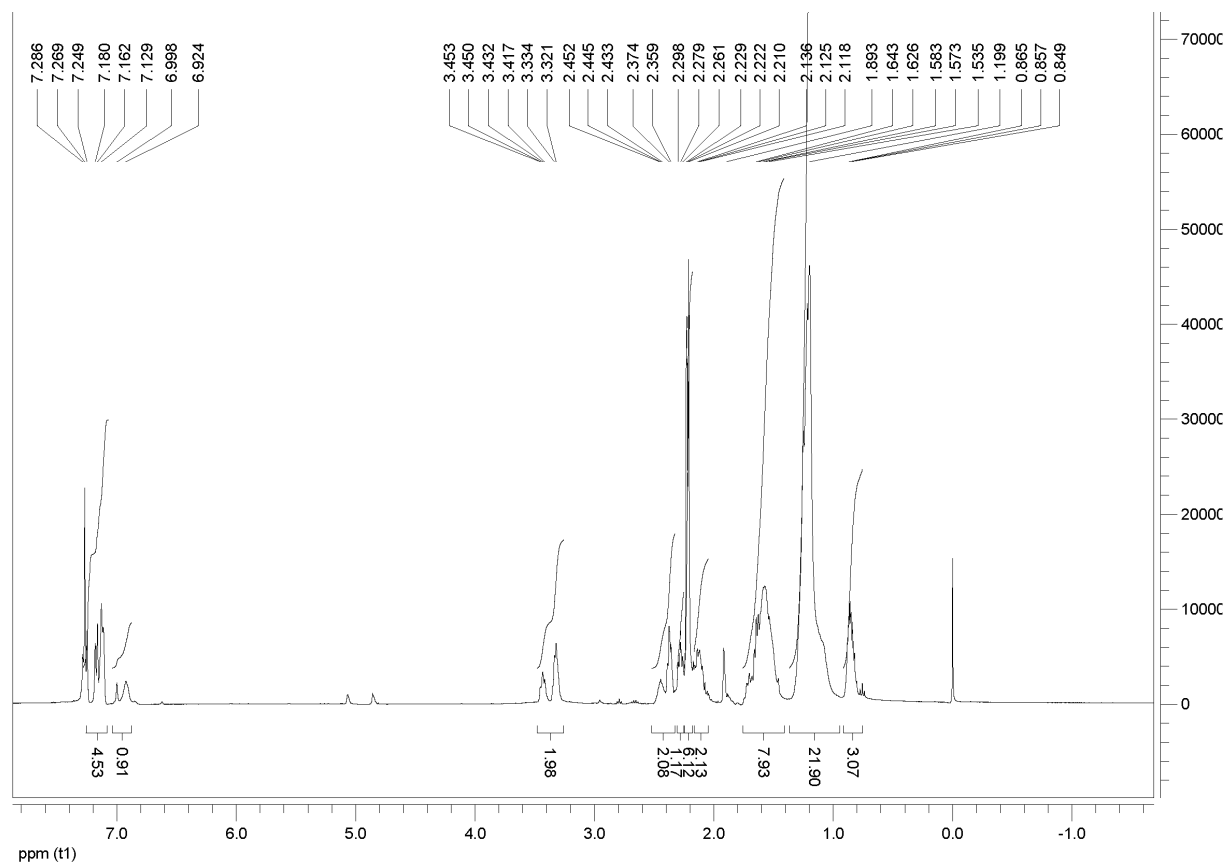


Fig. S4 1H NMR spectrum of POAPMA. (chloroform: $\delta=7.286$)

3.3 Synthesis of *N*-phenyloctadecanoicamidopropyl-*N,N*-dimethylcarboxylbetaine (POAPMB)

POAPMA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a solvent mixture of methanol and water ($v_{\text{methanol}}/v_{\text{water}} = 1:4$). The final products were refluxed at 75 °C for about 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filter liquor was distilled to remove ethanol and purified by recrystallization in ethyl acetate. A brown precipitate, *N*-phenyloctadecanoicamidopropyl-*N,N*-dimethylcarboxylbetaine (POAPMB), 4.29 g (8.54 mmol) was received and yielded 85.4%.

ESI HRMS (Fig. S5): m/z $[M+Na]^+$ calcd for 525.4134; found: 525.4137.

1H NMR (400 MHz, $CDCl_3$) (Fig. S6): $\delta=0.857$ (t, $J=3.00$ Hz, 3H), 1.199 (m, 22H), 1.538-1.556 (m, 6H), 1.913-1.942 (m, 2H), 2.157-2.258 (m, 2H), 2.355-2.385 (m, 1H), 3.213-3.253 (m, 6H), 3.418-3.457 (m, 2H), 3.500-3.629 (m, 2H), 3.854-3.905 (m, 2H), 6.998 (br, 1H), 7.114-7.250 (m, 5H).

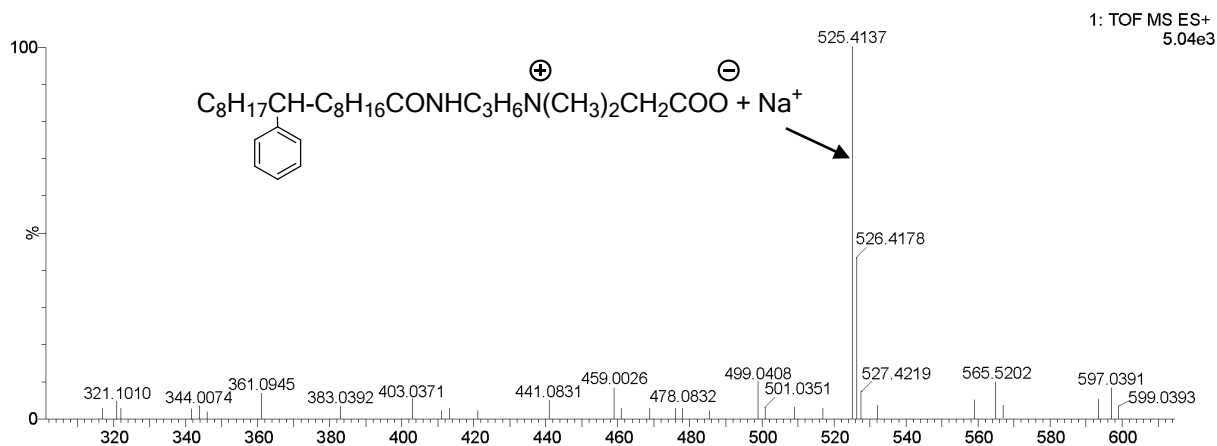


Fig. S5 ESI-HRMS spectrum of POAPMB

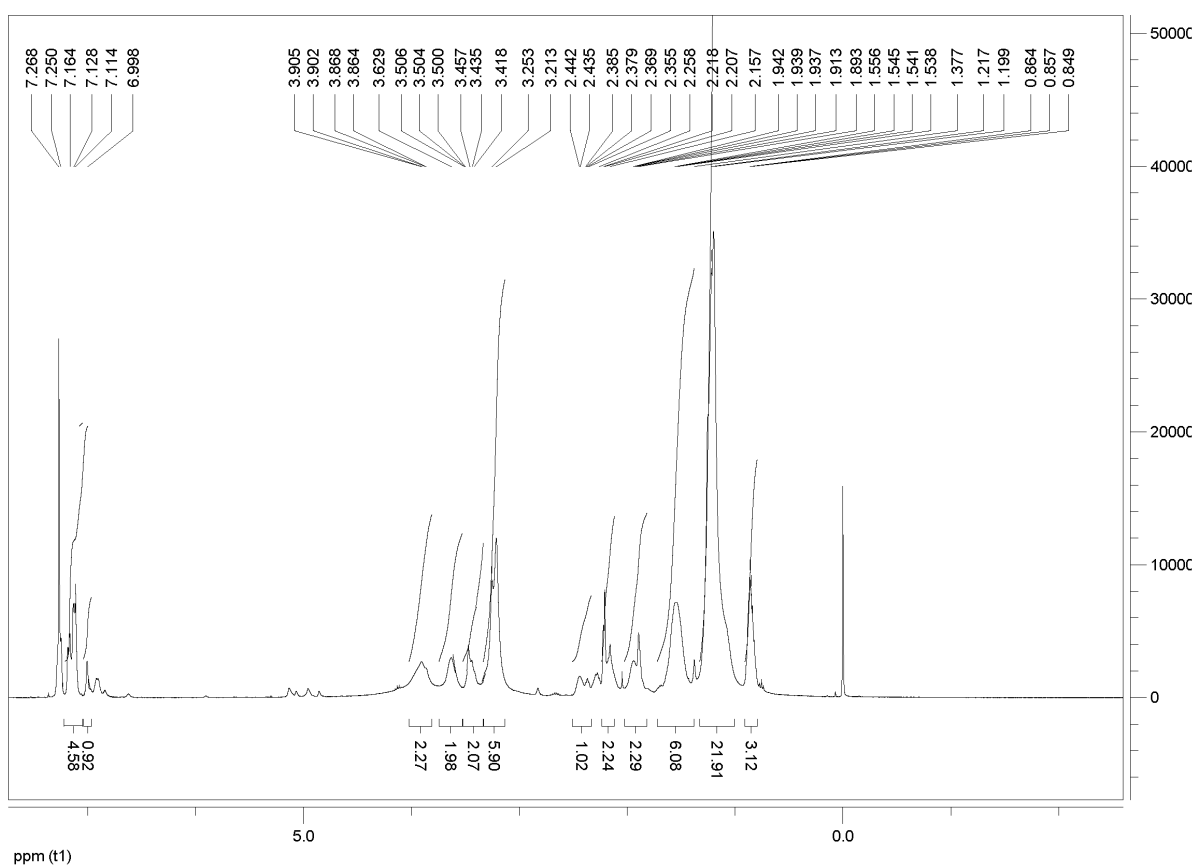


Fig. S6 1H NMR spectrum of POAPMB. (chloroform: $\delta=7.268$)

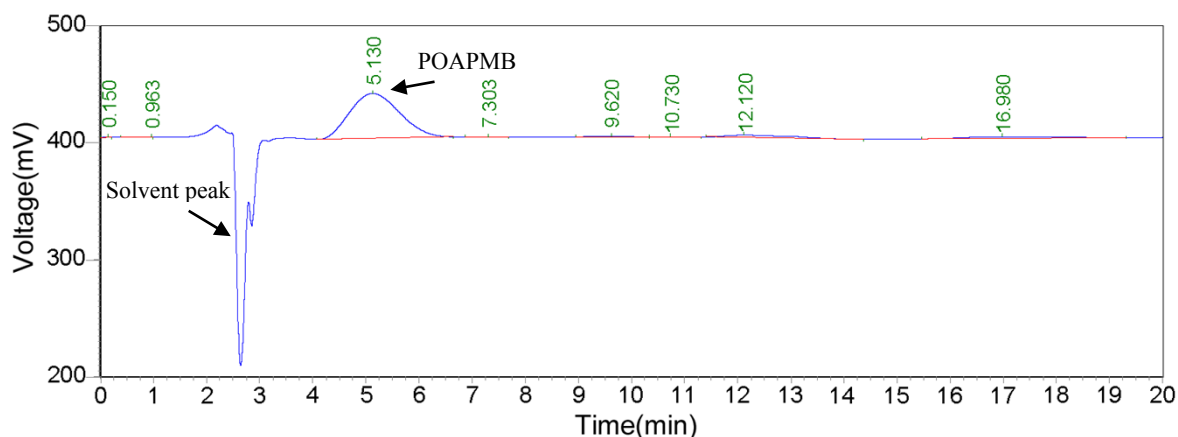


Fig. S7 HPLC chromatography spectrum of POAPMB

3.4 Synthesis of Tolyloctadecanoic acid (TOA)

2.82 g (10 mmol) of oleic acid and 1.34 g (10 mmol) of AlCl_3 were added to 15 mL toluene in a round-bottom flask. The reaction mixture was refluxed at 65 °C and anhydrous CaCl_2 was placed in a drying tube above the reactor. After 6 h of reaction, the product was washed by 10 mL hydrochloric acids (6 mol/L) for 3 times and extracted. AlCl_3 was dissolved in water phase and then recycled. The organic phase was for the next step.

0.5 mL of the organic phase was taken out, for characterization and yield calculation. Excess benzene was removed on a rotary evaporator giving a yellow residue, Tolyloctadecanoic acid (TOA), 3.62 g (9.69 mmol), yielded 96.9%.

EI-MS (Fig. S8): Tolyloctadecanoic acid butylester, Found: $m/z=430$.

^1H NMR (400 MHz, CDCl_3) (Fig. S9): $\delta=0.858$ (t, $J=2.60$ Hz, 3H), 1.202 (m, 22H), 1.499-1.583 (m, 6H), 2.296-2.351 (m, 5H), 2.400 (s, 1H), 7.128-7.350 (m, 4H).

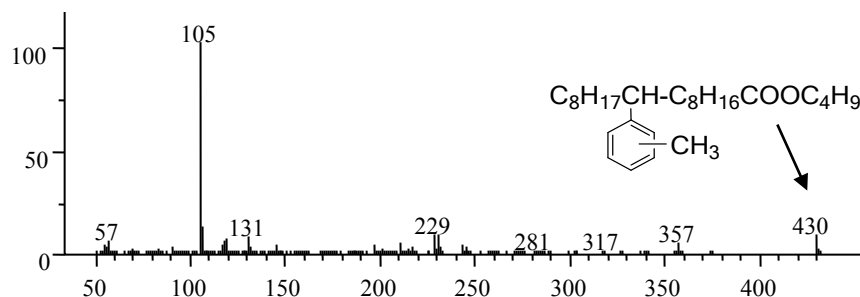


Fig. S8 EI-MS spectrum of Tolyloctadecanoic acid butylester

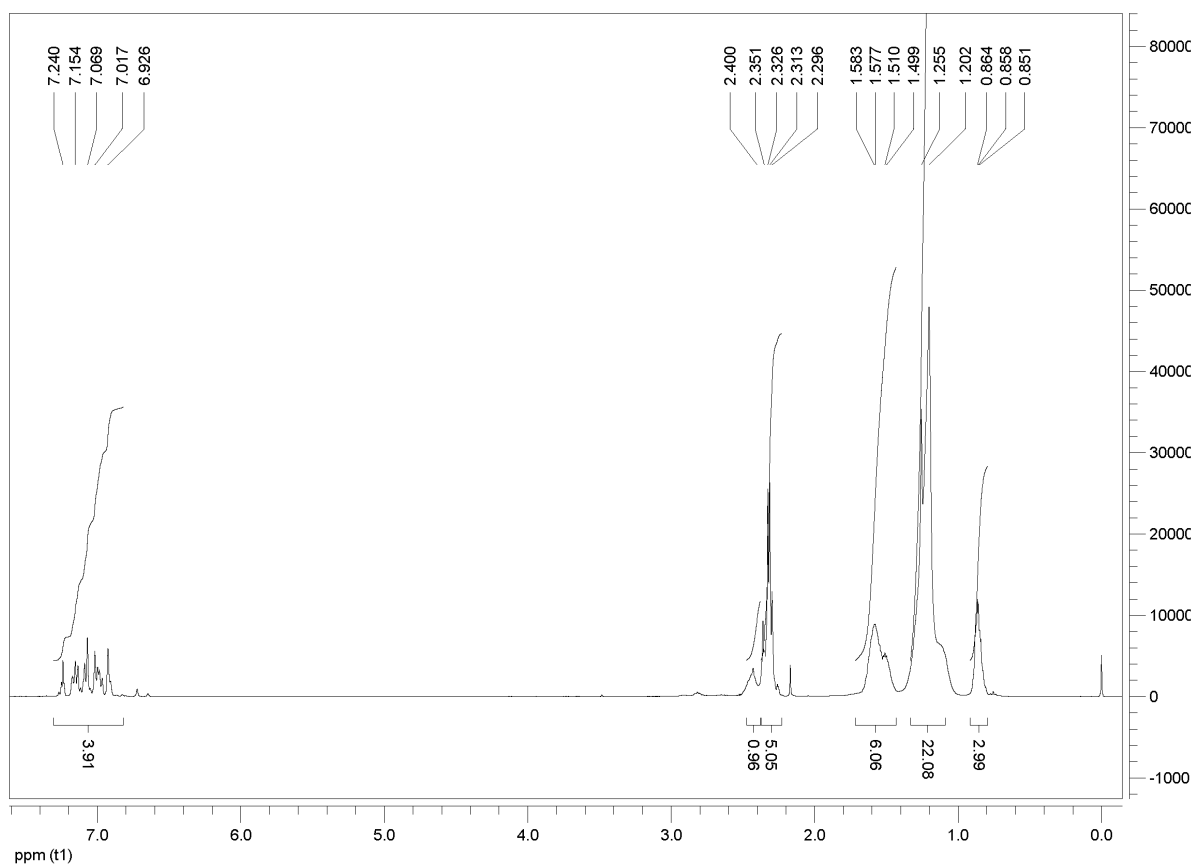


Fig. S9 ¹H NMR spectrum of TOA

3.5 Synthesis of *N*-tolyloctadecanoicamidopropyl-*N,N*-dimethylamine (TOAPMA)

A solution of TOA (3.74 g, 10 mmol) mentioned above was added dropwise to a drying flask with 0.8 mL SOCl₂ (11 mmol) in it, and the mixture was stirred at 40 °C for 2 h. Then the mixture was distilled to remove excess SOCl₂. 1.4 mL *N,N*-dimethyl-1,3-propanediamine (11 mmol) was slowly added in to the residue at 0 °C. The reaction mixture was then warmed to 40 °C and stirred for 2 h. The excess diamine and solvent were recycled on a rotary evaporator giving a brown residue, *N*-tolyloctadecanoicamidopropyl-*N,N*-dimethylamine (TOAPMA), 4.32 g (9.43 mmol), yielded 94.3%.

ESI HRMS (Fig. S10): *m/z* [M+H]⁺ calcd for 459.4314; found: 459.4334.

¹H NMR (400 MHz, CDCl₃) (Fig. S11): δ=0.857 (t, J=2.80 Hz, 3H), 1.201 (m, 22H), 1.479-1.508 (m, 6H), 1.902-1.977(m, 2H), 2.170-2.208 (m, 2H), 2.296-2.328 (m, 3H), 2.405 (m, 1H), 2.643-2.734 (m, 6H), 2.925-2.934 (m, 2H), 3.367 (m, 2H), 6.925 (br, 1H), 7.017-7.154 (m, 4H).

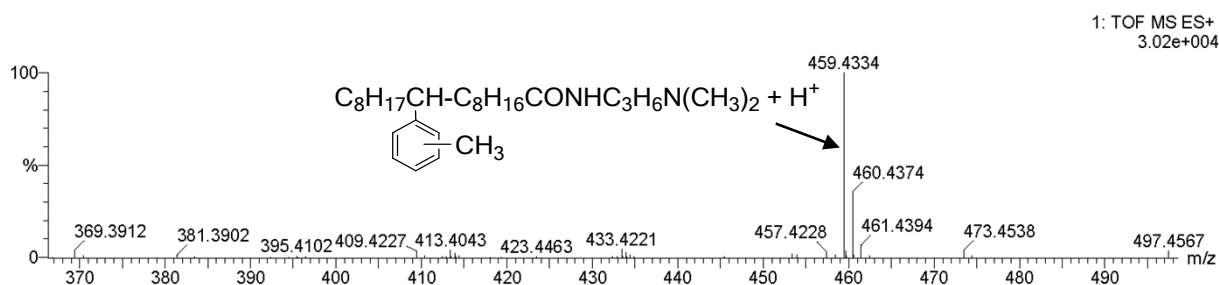


Fig. S10 ESI-HRMS spectrum of TOAPMA

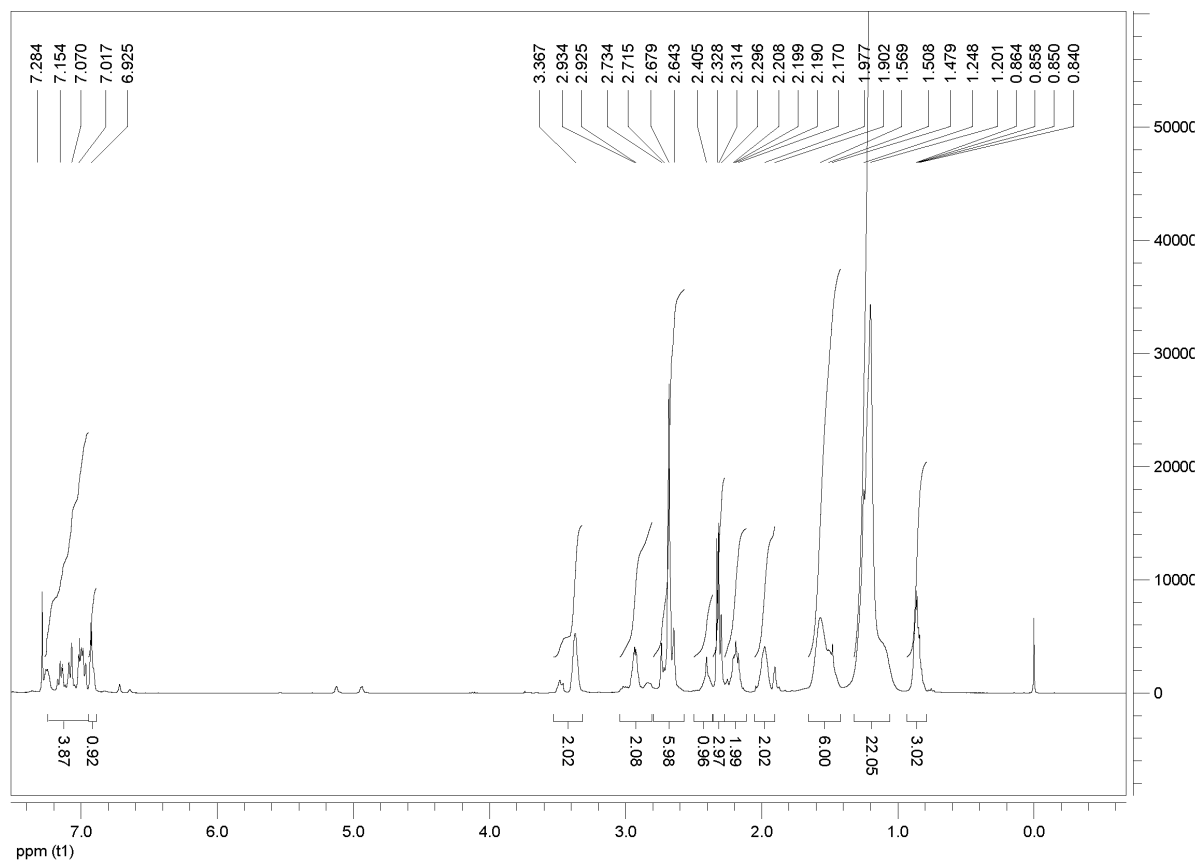


Fig. S11 1H NMR spectrum of TOAPMA. (chloroform: $\delta=7.284$)

3.6 Synthesis of *N*-tolyloctadecanoicamidopropyl-*N,N*-dimethylaminocarboxylbetaine (TOAPMB)

In the last step, TOAPMA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a mixture solvent of methanol and water ($v_{\text{methanol}}/v_{\text{water}} = 1:4$). The final products were refluxed at 75 °C for about 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filter liquor was distilled to remove ethanol and purified by recrystallization in ethyl acetate. A brown precipitate, *N*-tolyloctadecanoicamidopropyl-*N,N*-

dimethylcarboxylbetaine (TOAPMB), 4.32 g (8.36 mmol) was received and yielded 83.6%.

ESI HRMS (Fig. S12): m/z $[M+Na]^+$ calcd for 539.4188; found: 539.4208.

1H NMR (400 MHz, $CDCl_3$) (Fig. S13): $\delta=0.857$ (t, $J=2.60$ Hz, 3H), 1.200 (m, 22H), 1.542 (m, 6H), 1.945 (m, 2H), 2.170-2.224 (m, 2H), 2.293-2.324 (m, 3H), 2.4002 (m, 1H), 3.218-3.268 (m, 6H), 3.448 (m, 2H), 3.659 (m, 2H), 3.895 (m, 2H), 6.922 (br, 1H), 7.013-7.133 (m, 4H).

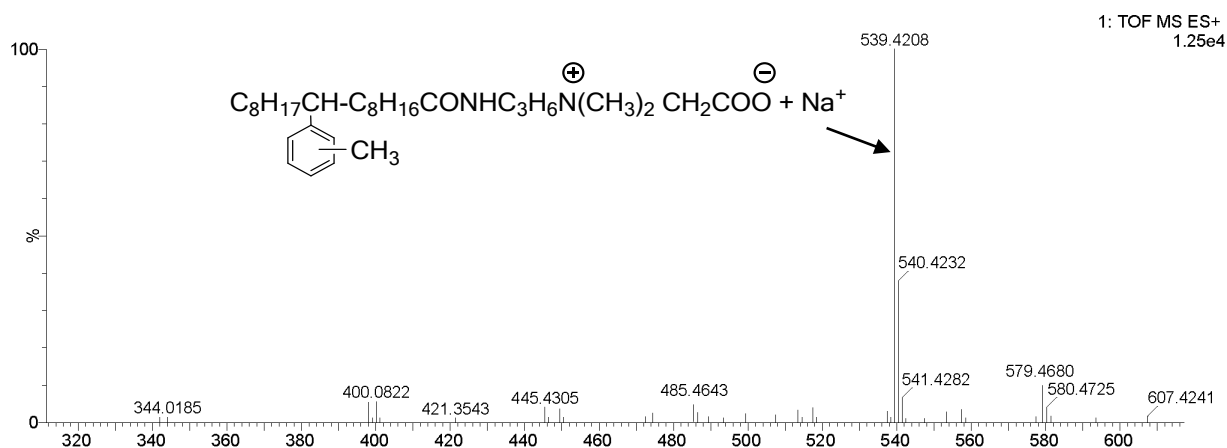


Fig. S12 ESI-HRMS spectrum of TOAPMB

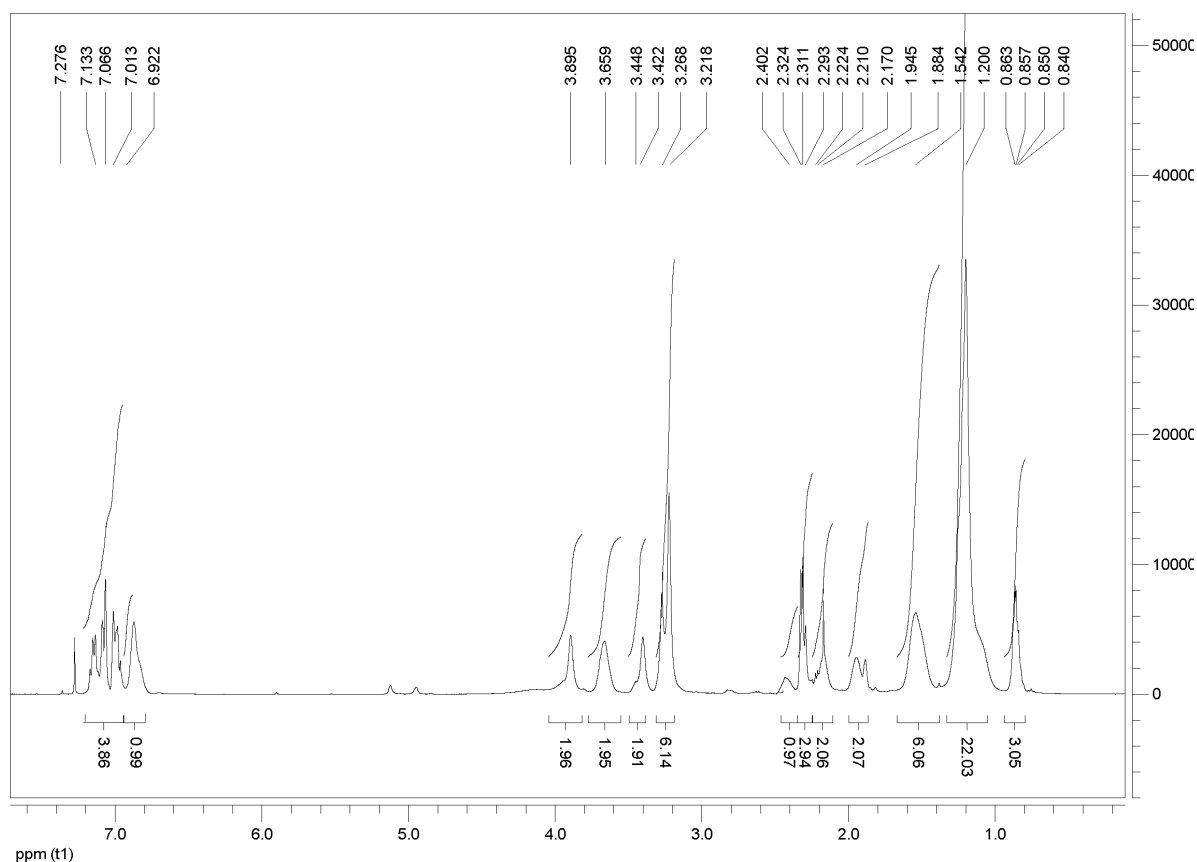


Fig. S13 1H NMR spectrum of TOAPMB. (chloroform: $\delta=7.276$)

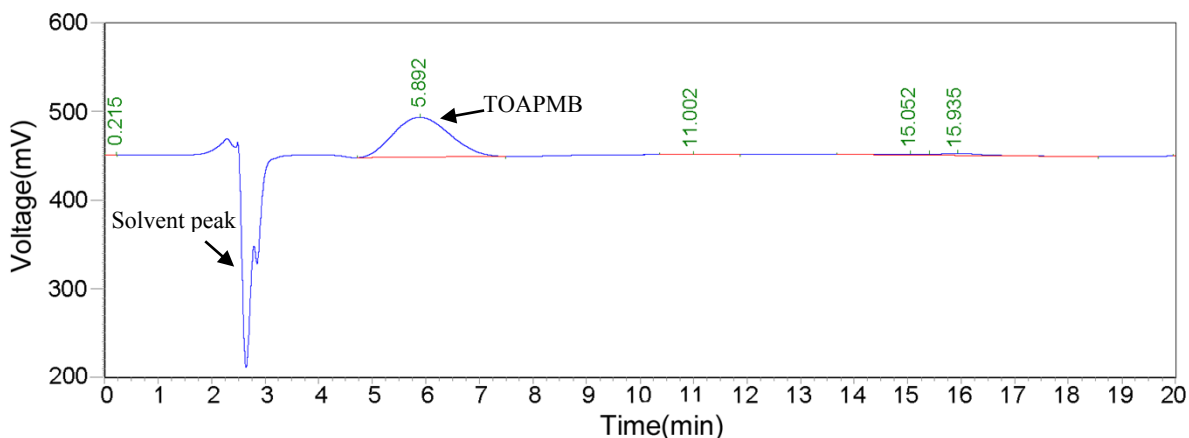


Fig. S14 HPLC chromatography spectrum of TOAPMB

3.7 Synthesis of Ethylphenyloctadecanoic acid (EOA)

2.82 g (10 mmol) of oleic acid and 1.34 g (10 mmol) of AlCl_3 were added to 15 mL ethylbenzene in a round-bottom flask. The reaction mixture was refluxed at 65 °C, and anhydrous CaCl_2 was placed in a drying tube above the reactor. After 6 h of reaction, the product was washed by 10 mL hydrochloric acids (6 mol/L) for 3 times and extracted. AlCl_3 was dissolved in water phase and then recycled. The organic phase was for the next step.

0.5 mL of the organic phase was taken out, for characterization and yield calculation. Excess benzene was recycled on a rotary evaporator giving a yellow residue, Ethylphenyloctadecanoic acid (EOA), 3.58 g (9.23 mmol), yielded 92.3%.

EI-MS (Fig. S15): Ethylphenyloctadecanoic acid butylester, Found: $m/z=444$.

^1H NMR (400 MHz, CDCl_3) (Fig. S16): $\delta=0.858$ (t, $J=2.80$ Hz, 3H), 1.209-1.256 (m, 25H), 1.505-1.593 (m, 6H), 2.289-2.336 (m, 2H), 2.420 (s, 1H), 2.611-2.647 (m, 2H), 6.943-7.236 (m, 4H).

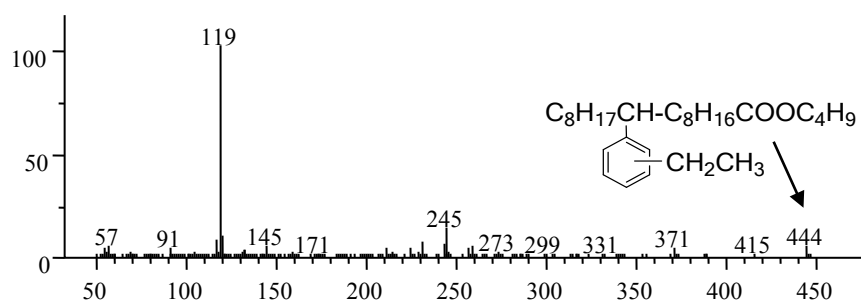


Fig. S15 EI-MS spectrum of Ethylphenyloctadecanoic acid butylester

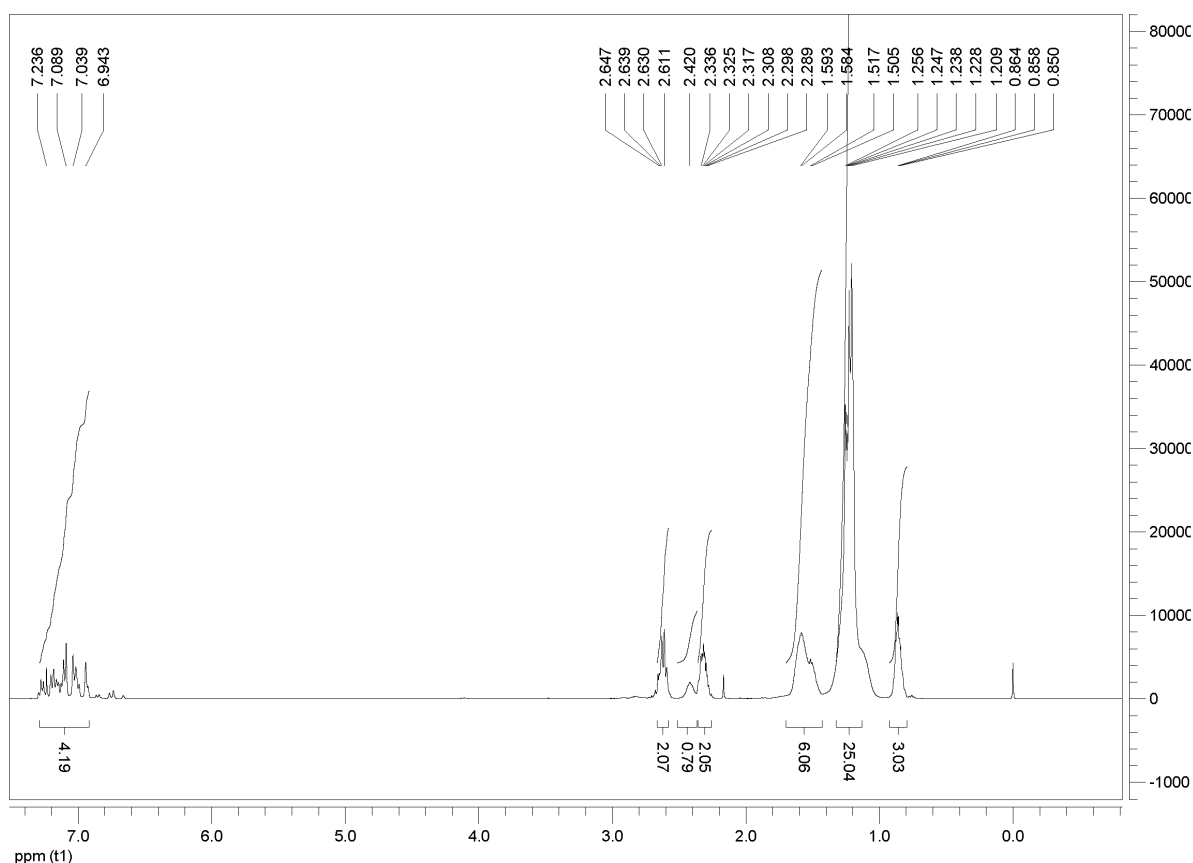


Fig. S16 ^1H NMR spectrum of EOA

3.8 Synthesis of *N*-ethylphenyloctadecanoicamidopropyl-*N,N*-dimethylamine (EOAPMA)

A solution of EOA (3.88 g, 10 mmol) mentioned above was added dropwise to a drying flask with 0.8 mL SOCl_2 (11 mmol) in it, and the mixture was stirred at 40 °C for 2 h. Then the mixture was distilled to remove excess SOCl_2 . 1.4 mL *N,N*-dimethyl-1,3-propanediamine (11 mmol) was slowly added in to the residue at 0 °C. The reaction mixture was then warmed to 40 °C and stirred for 2 h. The excess diamine and solvent were recycled on a rotary evaporator giving a brown residue, *N*-

ethylphenyloctadecanoicamidopropyl-*N,N*-dimethylamine (EOAPMA), 4.54 g (9.63 mmol), yielded 96.3%.

ESI HRMS (Fig. S17): m/z $[M+H]^+$ calcd for 473.4471; found: 473.4477.

^1H NMR (400 MHz, CDCl_3) (Fig. S18): $\delta=0.857$ (t, $J=3.00$ Hz, 3H), 1.210-1.249 (m, 25H), 1.512-1.576 (m, 6H), 2.045 (m, 2H), 2.187-2.224 (m, 2H), 2.414 (m, 1H), 2.593-2.649 (m, 2H), 2.712-2.971 (m, 6H), 3.037-3.113 (m, 2H), 3.384-3.498 (m, 2H), 6.943 (br, 1H), 7.017-7.091 (m, 4H).

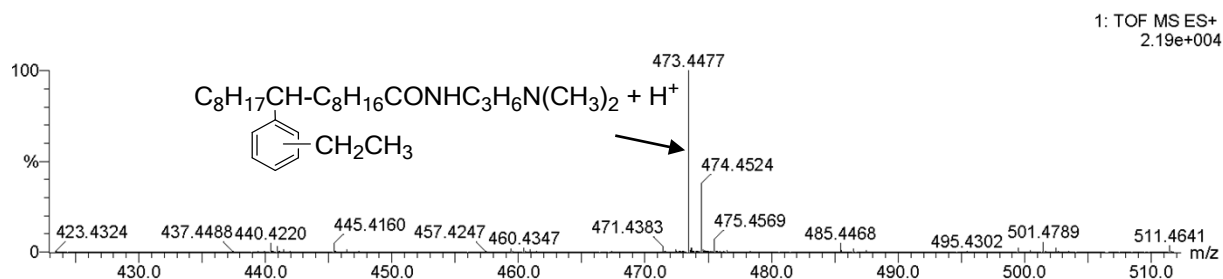


Fig. S17 ESI-HRMS spectrum of EOAPMA

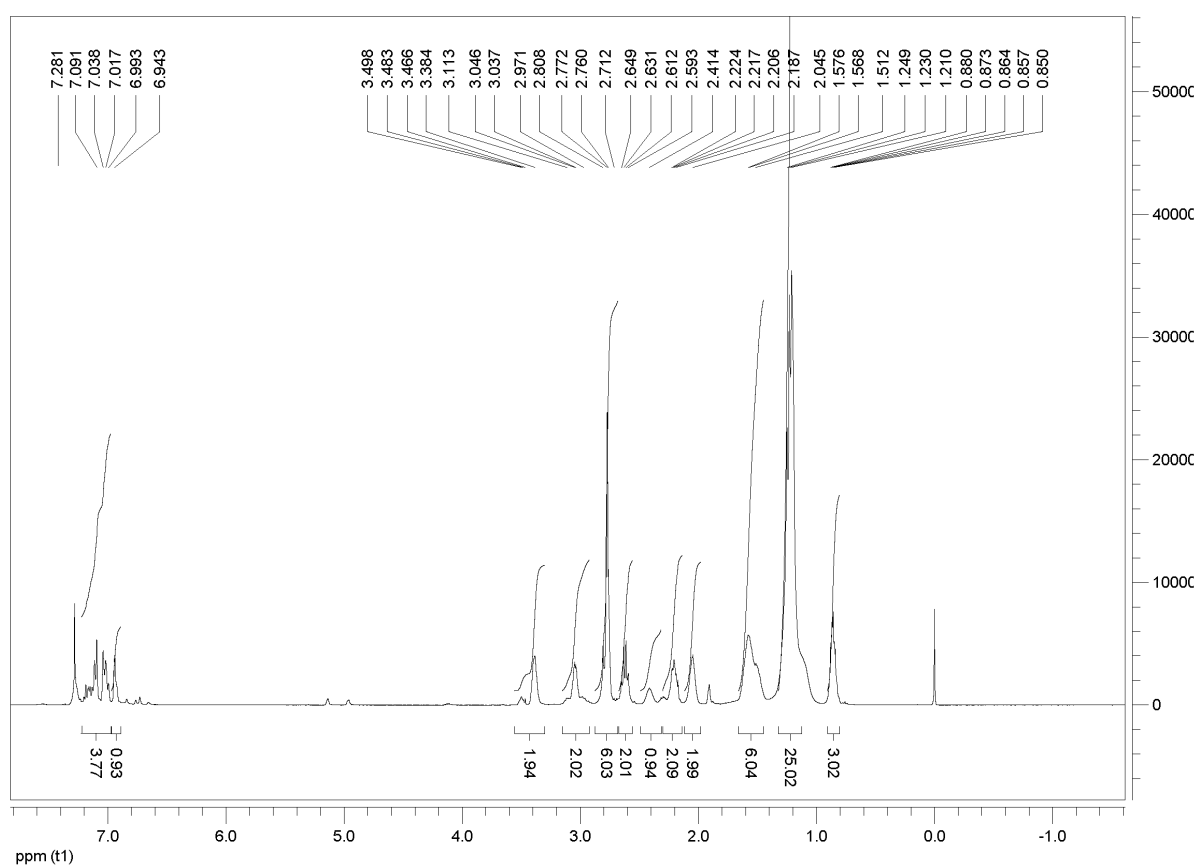


Fig. S18 ^1H NMR spectrum of EOAPMA. (chloroform: $\delta=7.281$)

3.9 Synthesis of *N*-ethylphenyloctadecanoicamidopropyl-*N,N*-dimethylcarboxylbetaine (EOAPMB)

In the last step, EOAPMA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a mixture solvent of methanol and water ($v_{\text{methanol}}/v_{\text{water}} = 1:4$). The final products were refluxed at 75 °C for about 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filter liquor was distilled to remove ethanol and purified by recrystallization in ethyl acetate. A brown precipitate, *N*-ethylphenyloctadecanoicamidopropyl-*N,N*-dimethylcarboxylbetaine (EOAPMB), 4.46 g (8.42 mmol) was received and yielded 84.2%.

ESI HRMS (Fig. S19): m/z $[M+Na]^+$ calcd for 553.4345; found: 553.4362.

^1H NMR (400 MHz, CDCl_3) (Fig. S20): $\delta=0.856$ (t, $J=3.00$ Hz, 3H), 1.227 (m, 25H), 1.544 (m, 6H), 1.884-1.949 (m, 2H), 2.169-2.223 (m, 2H), 2.408-2.411 (m, 1H), 2.591-2.647 (m, 2H), 3.225-3.273 (m, 6H), 3.416-3.451 (m, 2H), 3.671-3.688 (m, 2H), 3.894 (m, 2H), 6.940 (br, 1H), 7.014-7.107 (m, 4H).

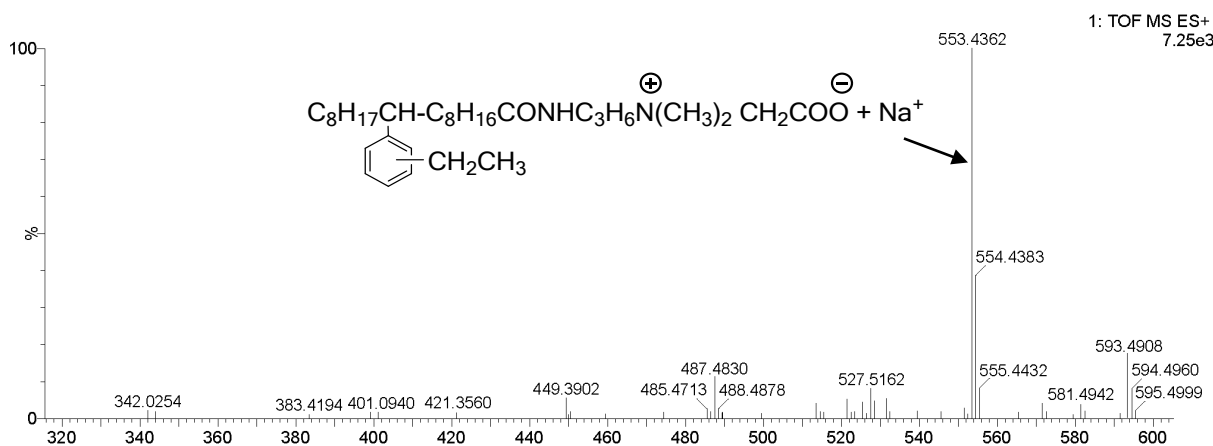


Fig. S19 ESI-HRMS spectrum of EOAPMB

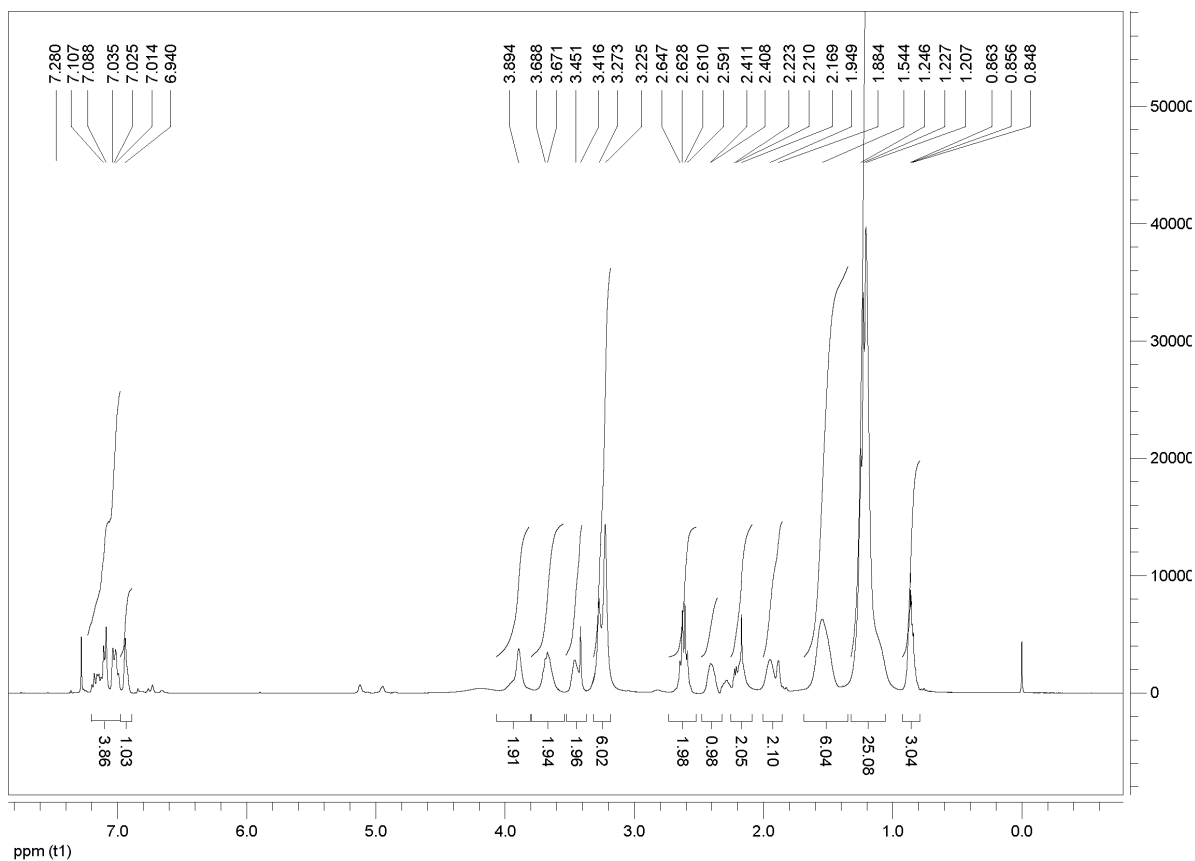


Fig. S20 ^1H NMR spectrum of EOAPMB. (chloroform: $\delta=7.280$)

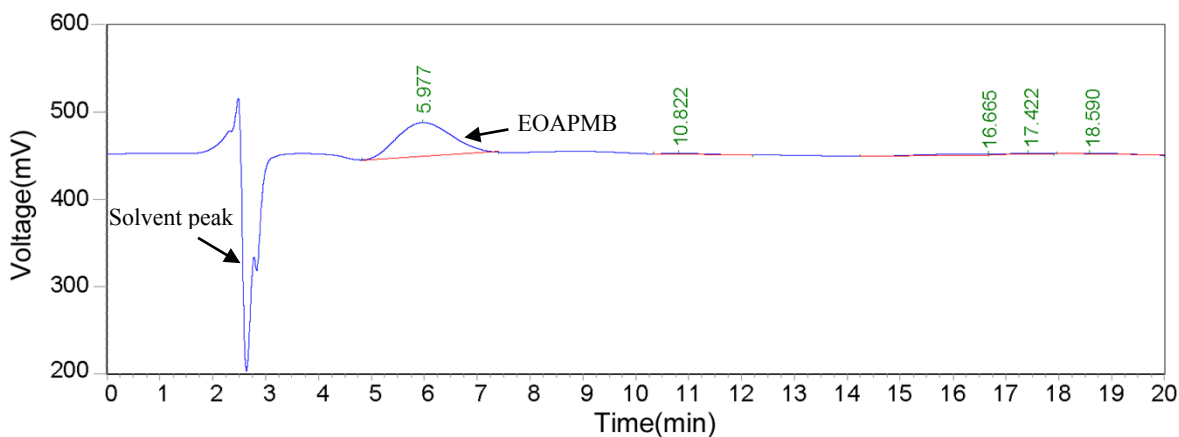


Fig. S21 HPLC chromatography spectrum of EOAPMB

3.10 Synthesis of *N*-phenyloctadecanoicamidoethyl-*N,N*-dimethylamine (POAEMA)

A solution of POA (3.60 g, 10 mmol) mentioned above was added dropwise to a drying flask with 0.8 mL SOCl_2 (11 mmol) in it, and the mixture was stirred at 40 °C for 2 h. Then the mixture was distilled to remove excess SOCl_2 . 1.4 mL *N,N*-Dimethylethylenediamine (11 mmol) was slowly

added in to the residue at 0 °C. The reaction mixture was then warmed to 40 °C and stirred for 2 h. The excess diamine and solvent were recycled on a rotary evaporator giving a brown residue, *N*-phenyloctadecanoicamidoethyl-*N,N*-dimethylamine (POAEMA), 4.05 g (9.42 mmol), yielded 94.2%.

ESI HRMS (Fig. S22): m/z $[M+H]^+$ calcd for 431.4001; found: 431.3990.

^1H NMR (400 MHz, CDCl_3) (Fig. S23): δ =0.857 (t, J =3.00 Hz, 3H), 1.198-1.250 (m, 22H), 1.534-1.588 (m, 6H), 2.133-2.194 (m, 2H), 2.271 (m, 6H), 2.448-2.532 (m, 3H), 3.338-3.350 (m, 2H), 7.000 (br, 1H), 7.131-7.183 (m, 5H).

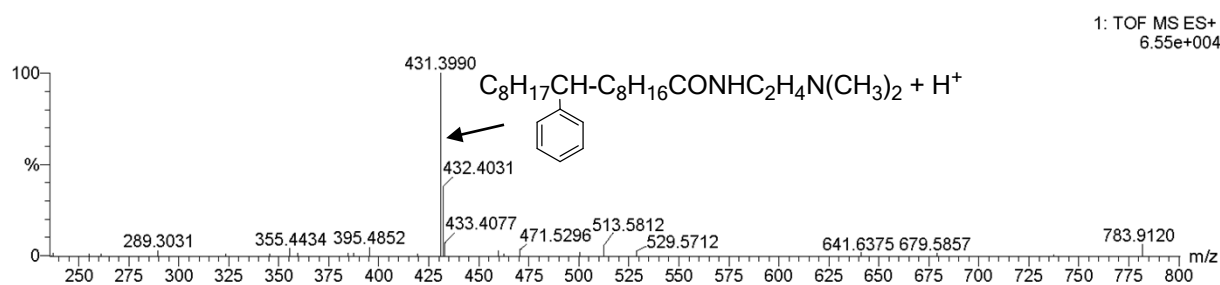


Fig. S22 ESI-HRMS spectrum of POAEMA

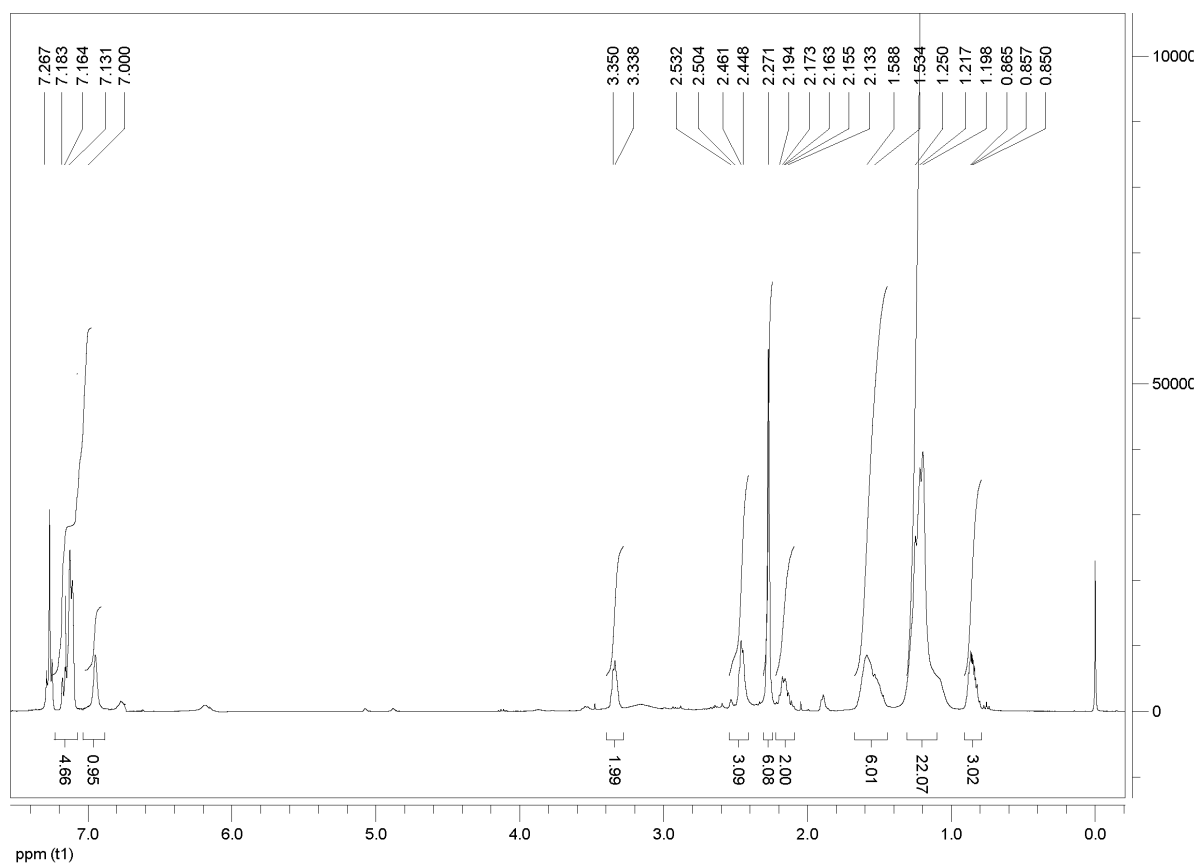


Fig. S23 ¹H NMR spectrum of POAEMA. (chloroform: δ=7.267)

3.11 Synthesis of *N*-phenyloctadecanoicamidoethyl-*N,N*-dimethylcarboxylbetaine (POAEMB)

POAEMA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a mixture solvent of methanol and water ($v_{\text{methanol}}/v_{\text{water}} = 1:4$). The final products were refluxed at 75 °C for about 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filter liquor was distilled to remove ethanol and purified by recrystallization in ethyl acetate. A brown precipitate, *N*-phenyloctadecanoicamidoethyl-*N,N*-dimethylcarboxylbetaine (POAEMB), 4.05 g (8.30 mmol) was received and yielded 83.0%.

ESI HRMS (Fig. S24): m/z $[M+Na]^+$ calcd for 511.3875; found: 511.3862.

¹H NMR (400 MHz, CDCl₃) (Fig. S25): δ=0.857 (t, J=3.00 Hz, 3H), 1.200-1.217 (m, 22H), 1.540-1.544 (m, 6H), 2.174-2.260 (m, 2H), 2.401-2.438 (m, 1H), 3.271 (m, 6H), 3.623-3.739 (m, 2H), 3.794-3.804 (m, 2H), 3.969-4.016 (m, 2H), 7.000 (br, 1H), 7.128-7.248 (m, 5H).

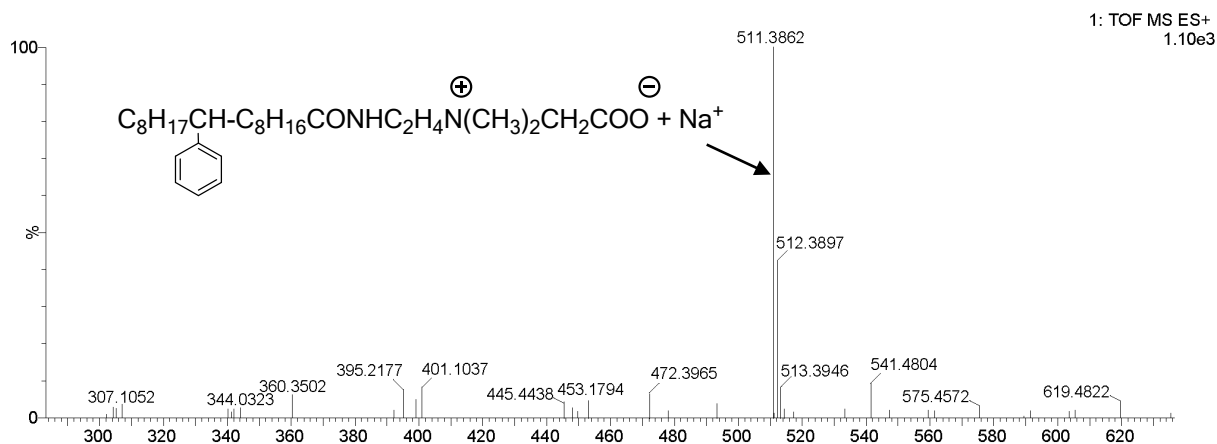


Fig. S24 ESI-HRMS spectrum of POAEMB

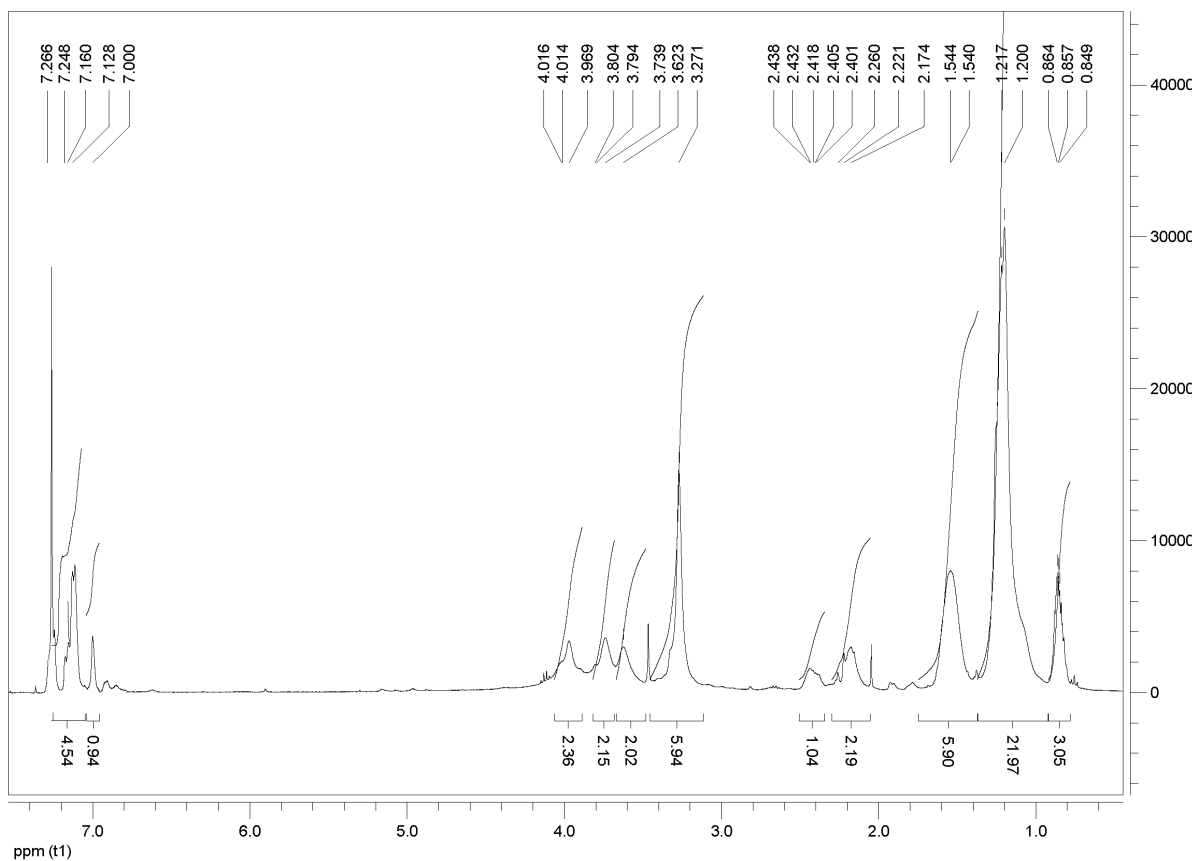


Fig. S25 ^1H NMR spectrum of POAEMB. (chloroform: $\delta=7.266$)

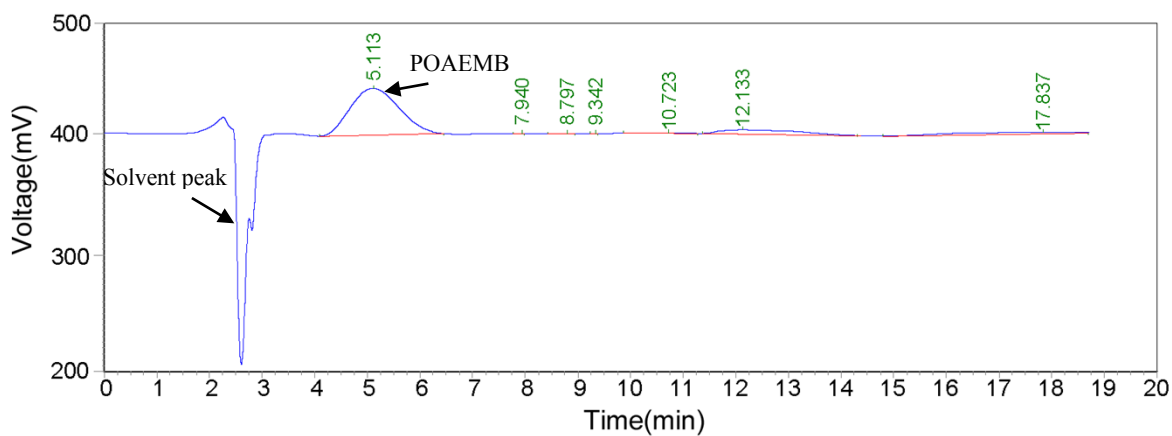


Fig. S26 HPLC chromatography spectrum of POAEMB

3.12 Synthesis of *N*-phenyloctadecanoicamidoethyl-*N,N*-diethylamine (POAEEA)

A solution of POA (3.60 g, 10 mmol) mentioned above was added dropwise to a drying flask with 0.8 mL SOCl_2 (11 mmol) in it, and the mixture was stirred at 40 °C for 2 h. Then the mixture was distilled to remove excess SOCl_2 . 1.4 mL *N,N*-Diethylethylenediamine (11 mmol) was slowly

added in to the residue at 0 °C. The reaction mixture was then warmed to 40 °C and stirred for 2 h. The excess diamine and solvent were recycled on a rotary evaporator giving a brown residue, *N*-phenyloctadecanoicamidoethyl-*N,N*-diethylamine (POAEEA), 40.8 g (8.91 mmol), yielded 89.1%.

ESI HRMS (Fig. S27): Calcd: 459.4314 (M + H⁺). Found: m/z=459.4299.

¹H NMR (400 MHz, CDCl₃) (Fig. S28): δ=0.858 (t, J=3.00 Hz, 3H), 0.992-1.056 (m, 6H), 1.130-1.250(m, 22H), 1.476-1.589 (m, 6H), 2.125-2.186 (m, 2H), 2.432 (s, 1H), 2.514-2.620 (m, 6H), 3.280-3.349 (m, 2H), 6.999 (br, 1H), 7.130-7.182 (m, 5H).

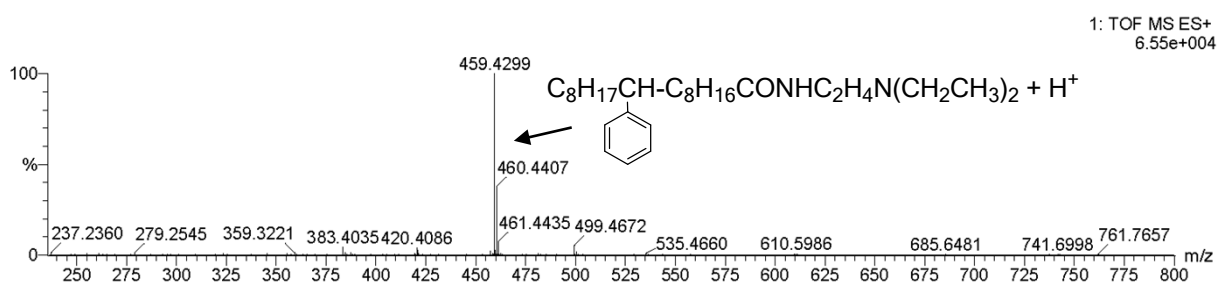


Fig. S27 ESI-HRMS spectrum of POAEEA

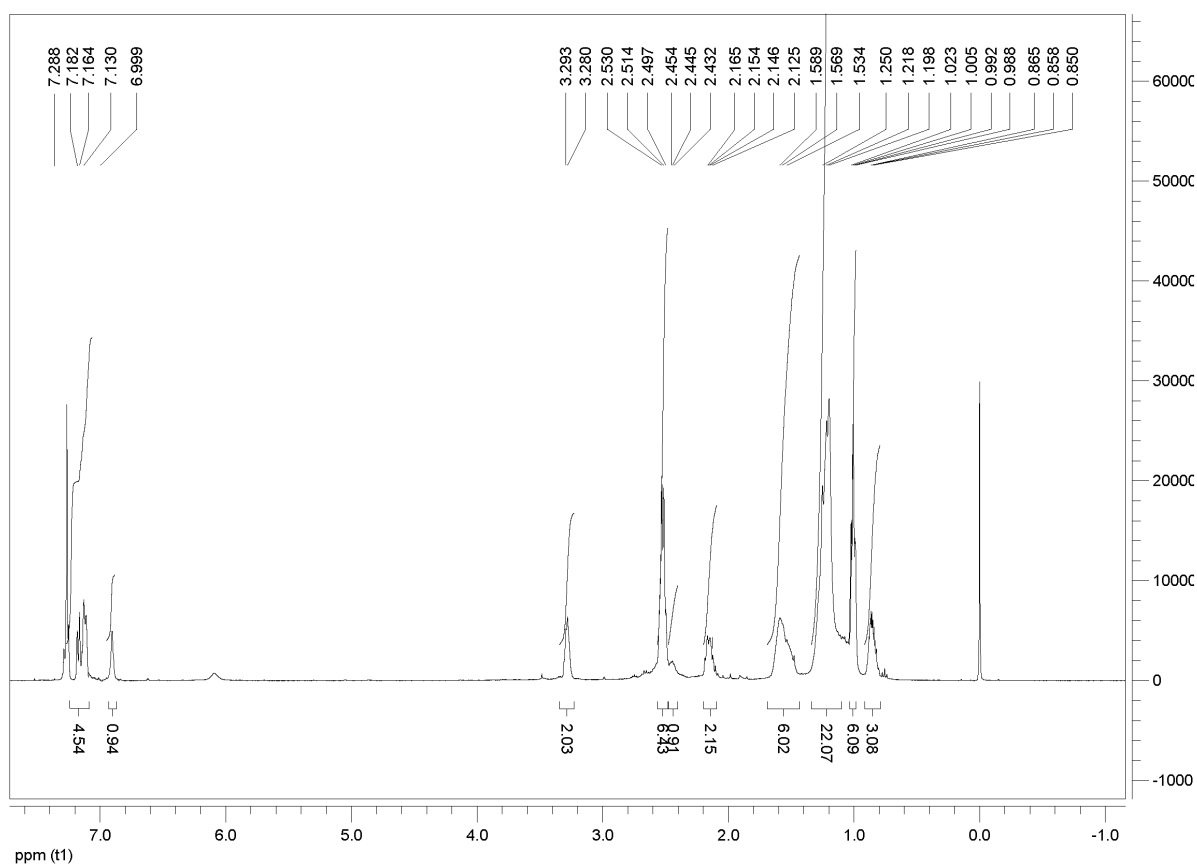


Fig. S28 ¹H NMR spectrum of POAEEA. (chloroform: δ=7.288)

3.13 Synthesis of *N*-phenyloctadecanoicamidoethyl-*N,N*-diethyl carboxyl betaine (POAEEB)

POAEMA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a mixture solvent of methanol and water ($v_{\text{methanol}}/v_{\text{water}} = 1:4$). The final products were refluxed at 75 °C for about 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filter liquor was distilled to remove ethanol and purified by recrystallization in ethyl acetate. A brown precipitate, *N*-phenyloctadecanoicamidoethyl-*N,N*-diethyl carboxyl betaine (POAEEB), 3.86 g (7.51 mmol) was received and yielded 75.1%.

ESI HRMS (Fig. S29): Calcd: 539.4188 (M + H⁺). Found: m/z=539.4173.

¹H NMR (400 MHz, CDCl₃) (Fig. S30): δ =0.858 (t, J=3.00 Hz, 3H), 0.993-1.024 (m, 6H), 1.198-1.251(m, 22H), 1.534-1.588 (m, 6H), 2.147-2.175 (m, 2H), 2.431-2.453 (s, 1H), 2.517-2.533 (m, 4H), 3.283 (m, 2H), 3.489 (m, 2H), 6.999 (br, 1H), 7.131-7.184 (m, 5H).

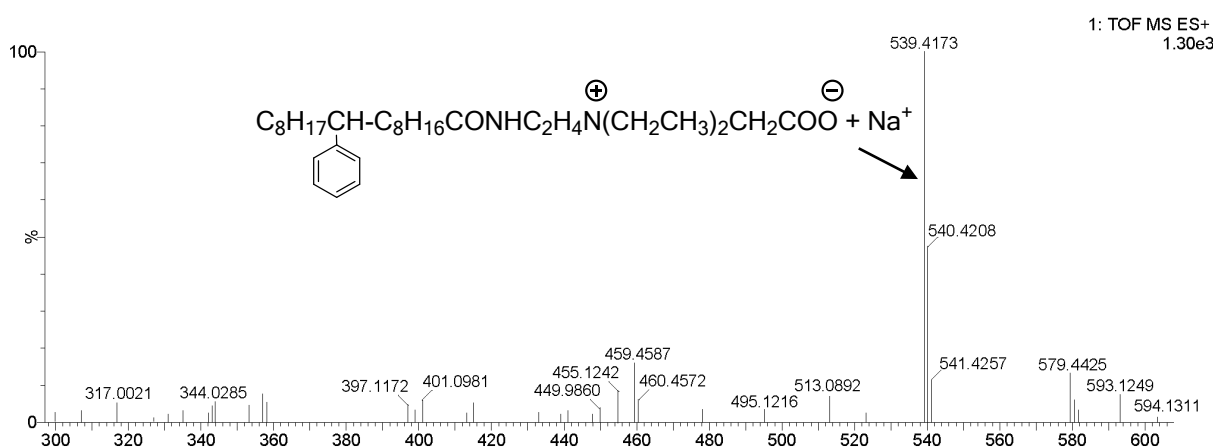


Fig. S29 ESI-HRMS spectrum of POAEEB

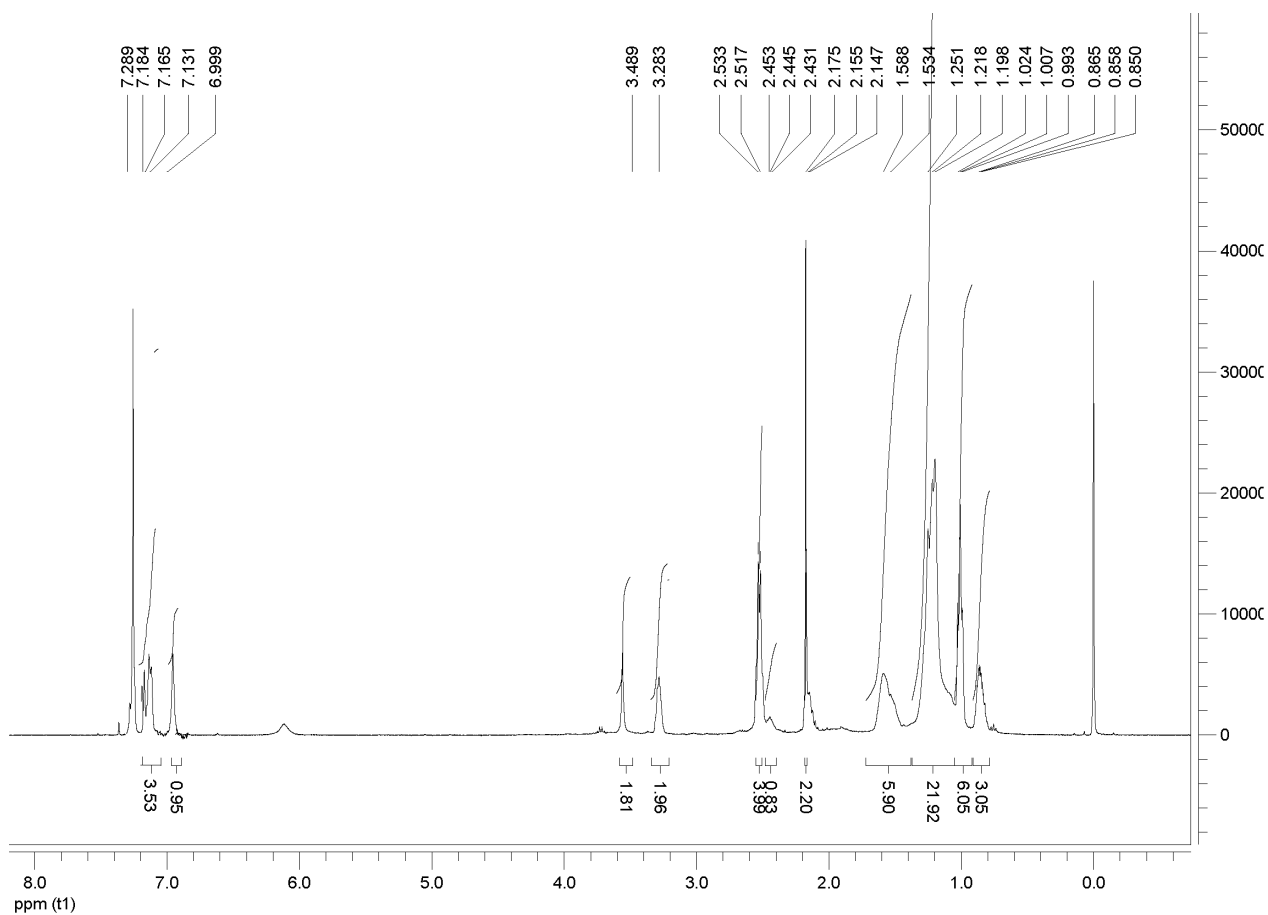


Fig. S30 ¹H NMR spectrum of POAEEB. (chloroform: $\delta=7.289$)

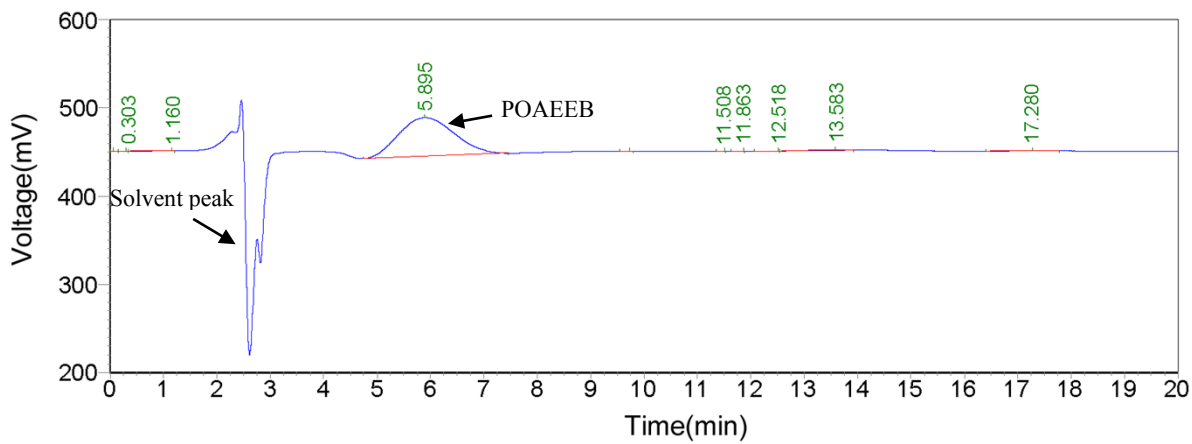


Fig. S31 HPLC chromatography spectrum of POAEEB

4. Surface and interfacial properties

4.1 Surface properties

The surface tensions (SFT) of the aqueous solution at different surfactant concentrations were measured by using a DCAT 21 tensiometer (Dataphysics, Germany) with the plate method and the temperature was controlled at 25.0 ± 0.1 °C. Before each measurement, the quartz plate was briefly heated above an alcohol burner until glowing. In order to attain equilibrium conditions, the quartz plate should be cooled to room temperature and dipped in the solution for a while. The measurement should be repeated three times and an average value was obtained. The surface tension between air and double distilled water was 71.8 mN/m at 25 °C.

The inflection point in the plot of SFT versus surfactant concentration is commonly referred to as the critical micelle concentration (CMC, as indicated e.g. by the arrow in Fig. 2) and indicates the point where the air-water surface is saturated with surfactant monomers and, thus, micelles start to form. Critical surface tension (SFT_{CMC}) refers to the SFT at CMC. Because the CMC values of bio-based zwitterionic surfactants are low enough and surfactants are purified. So the activity coefficients can be approximated to 1, the concentration of surfactant can be used to replace the activity of surfactant in the usual form of Gibbs equation. Maximum surface excess concentration (Γ_{max}) calculated by the following Gibbs equation (1).

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{\partial SFT}{\partial \lg C} \right)_T \quad (1)$$

where C is the concentration of surfactant aqueous solution, $R = 8.314$ J/mol/K, $T = 298.15$ K, SFT is expressed in mN/m, n is a constant and depends on the number of species constituting the surfactant adsorbed at the interface. For zwitterionic surfactants, it is generally assumed that the value of n should be set at 1, because no counterion adsorption is expected if the cationic and anionic portions of the molecule are genuinely internally associated. The minimum area occupied per surfactant molecule (A_{min}) at air/water interface is related to the surface excess Γ_{max} as follows.

$$A_{min} = (N_A \Gamma_{max})^{-1} \times 10^{16} \quad (2)$$

where N_A is the Avogadro constant.

The contact angles were measured by using the sessile drop technique. The apparatus consisted of a camera with a micro lens and a horizontal platform. The platform was connected to the thermostat to control temperature. Before measurement, the platform environment was preheated at $25 \pm 1^\circ\text{C}$ by switching on the thermostat. When the temperature reached 25°C , the solid substrate was placed in middle of the platform. A $2 \mu\text{L}$ solution drop was introduced onto the solid substrate through a microsyringe. The contact angles were measured by taking photographic images after adding the solution for 60 s. The contact angles were determined directly from the photographs by drawing tangent lines between the liquid drop and the solid surface. The measurements were repeated 5 times for every samples and the average angle was taken. The average contact angle on the three phase contact gas/double distilled water/solid was 92° at 25°C .

4.2 Interfacial Properties

Interfacial tensions were measured by the spinning-drop method at $50 \pm 0.1^\circ\text{C}$ using SVT 20 tensiometer (Dataphysics, Germany). Equilibrium was affirmed to be obtained when successive values taken at 10 min intervals agreed to within 0.001 mN m^{-1} . The volumetric ratio of water to oil in the spinning-drop tensiometer is about 2000. Daqing crude oil was used as oil phase. Surfactant solutions were prepared with Daqing oil field simulated formation water and the concentration of the solutions was 0.5 g L^{-1} . The formation water consists of $112.7 \text{ mg L}^{-1} \text{ CaCl}_2$, $42.8 \text{ mg L}^{-1} \text{ MgCl}_2$, $1597.1 \text{ mg L}^{-1} \text{ NaCl}$, $17.0 \text{ mg L}^{-1} \text{ Na}_2\text{SO}_4$, $381.6 \text{ mg L}^{-1} \text{ Na}_2\text{CO}_3$ and $3176.0 \text{ mg L}^{-1} \text{ NaHCO}_3$. The total dissolved substance is 5327.2 mg L^{-1} . IFT_{\min} is the minimum of the interfacial tensions as indicated e.g. by the arrow in Fig. 3. The interfacial tension between Daqing crude oil and simulated formation water was 9.70 mN/m at 50°C .