Supporting Information

Locomotion Mode of Micrometer-Sized Oil Droplets in Solution of Cationic Surfactants Having Ester or Ether Linkages

Ayana Hirono[1], Taro Toyota[2], Kouichi Asakura[1], Taisuke Banno[1,*]

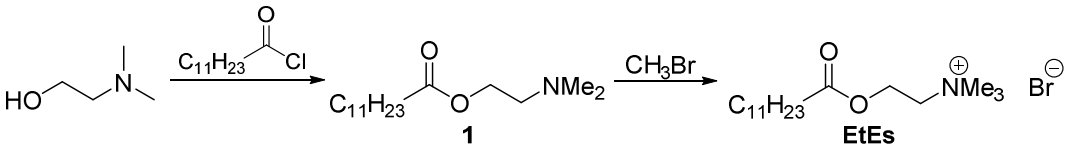
[1]Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

[2] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

Supporting Information Index

Synthetic procedures of cationic surfactants

1. Synthesis of lauroyloxyethylene-*N*,*N*,*N*-trimethylammonium bromide (EtEs)



Scheme S1

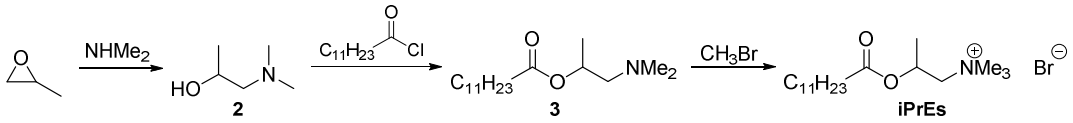
2-dimethylaminoethanol (0.93 g, 10 mmol) in an anhydrous dichloromethane (2 mL) was added dropwise to an anhydrous dichloromethane solution (3 mL) of lauroylchloride (1.14 g, 5 mmol). The reaction mixture was stirred under argon atmosphere at room temperature for 4 h. The mixture was then concentrated under reduced pressure, and the residue was dissolved in ethyl acetate (20 mL). The organic layer was washed three times with a 5% sodium hydrogen carbonate aqueous solution (15 mL), and then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to obtain 2-lauroyloxyethylene-dimethylamine (**1**), at a yield of 90% (1.27 g), as a yellow syrup.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.15 (2H, t, J = 5.5 Hz), 2.54 (2H, t, J = 5.7 Hz), 2.33–2.27 (8H, m), 1.64–1.60 (2H, m), 1.38–1.13 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 272.5472 $[M + H]^+$; calcd 272.4387 $[M + H]^+$.

2 M THF solution of methyl bromide (8 mL) was added to **1** (1.27 g, 4.68 mmol) at 0 ^{o}C and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by reprecipitation using chloroform (5 mL) and ethyl acetate (6 mL) to obtain **EtEs** at a yield of 56% (0.956 g), as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.57–4.56 (2H, m), 4.19–4.11 (2H, m), 3.57–3.50 (9H, m), 2.35 (2H, t, J = 7.6 Hz), 1.65–1.56 (2H, m), 1.38–1.19 (16H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.2733 $[M - Br]^{+}$; calcd 286.4732 $[M - Br]^{+}$.

2. Synthesis of 2-lauroyloxypropylene-*N*,*N*,*N*-trimethylammonium bromide (iPrEs)



Scheme S2

rac-Propylene oxide (4.36 g, 74.9 mmol) was added to 9.5 mol/L aqueous solution of dimethylamine (10 mL) at 0 °C. Then the mixture was stirred at room temperature for 2

h. After the reaction, the crude product was washed four times with dichloromethane (20 mL), and then dried over anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure to obtain *rac*-1-dimethylamino-2-propanol (**2**), a yield of 60% (4.62 g), as a yellow syrup. In a similar procedure, optically active (*R*)-**2** and (*S*)-**2** were obtained using (*R*)-propylene oxide and (*S*)-propylene oxide in 81% and 86% yields, respectively, as a yellow syrup.

rac-**2**; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.95–3.85 (1H, m), 2.45–2.32 (7H, m), 2.29–2.23 (1H, m), 1.12 (3H, t, J = 6.0 Hz). ESI-MS in CH_3CN (*m*/*z*): 104.5379 [M + H]$^+$; calcd 104.1628 [M + H]$^+$.

(*R*)-**2**; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82–3.74 (1H, m), 2.33–2.19 (7H, m), 2.17–2.11 (1H, m), 1.12 (3H, t, J = 6.0 Hz). ESI-MS in CH_3CN (*m*/*z*): 104.5110 [M + H]$^+$; calcd 104.1628 [M + H]$^+$.

(*S*)-**2**; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82–3.75 (1H, m), 2.27 (6H, s), 2.26–2.20 (1H, m), 2.16–2.10 (1H, m), 1.12 (3H, t, J = 6.0 Hz). ESI-MS in CH_3CN (*m*/*z*): 104.4963 [M + H]$^+$; calcd 104.1628 [M + H]$^+$.

rac-**2** (1.70 g, 16 mmol) in an anhydrous dichloromethane (5 mL) was added dropwise to an anhydrous dichloromethane solution (4 mL) of lauroylchloride (2.19 g, 10 mmol).

The reaction mixture was stirred under argon atmosphere at room temperature for 4 h. The mixture was then concentrated under reduced pressure, and the residue was dissolved in ethyl acetate (30 mL). The organic layer was washed three times with a 5% sodium hydrogen carbonate aqueous solution (15 mL), and then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to obtain *rac*-2-lauroyloxypropylene-dimethylamine (**3**), at a yield of 79% (2.24 g), as a yellow syrup. In a similar procedure, optically active (*R*)-**3** and (*S*)-**3** were obtained using (*R*)-**2** and (*S*)-**2** in 24% and 71% yields, respectively, as a yellow syrup.

rac-**3**; ^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ 5.12–4.94 (1H, m), 2.52–2.42 (1H, m), 2.33–2.16 (9H, m), 1.65–1.56 (2H, m), 1.40–1.20 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.2609 $[M + H]^+$; calcd 286.4653 $[M + H]^+$.

(*R*)-**3**; ^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ 5.14–4.97 (1H, m), 2.53–2.45 (1H, m), 2.31–2.19 (9H, m), 1.65–1.56 (2H, m), 1.36–1.15 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.2622 $[M + H]^+$; calcd 286.4653 $[M + H]^+$.

(*S*)-**3**; ^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ 5.18–4.97 (1H, m), 2.52–2.45 (1H, m), 2.31–2.20 (9H, m), 1.65–1.56 (2H, m), 1.37–1.17 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.2604 $[M + H]^+$; calcd 286.4653 $[M + H]^+$.

2 M THF solution of methyl bromide (16 mL) was added to *rac*-**3** (2.24 g, 8.26 mmol) at 0 ^{o}C and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by reprecipitation from mixture of chloroform (1 mL) and ethyl acetate (2 mL) to obtain *rac*-**iPrEs** at a yield of 54% (1.61 g), as a white powder. In a similar procedure, optically active (*R*)-**iPrEs** and (*S*)-**iPrEs** were obtained using (*R*)-**3** and (*S*)-**3** in 74% and 82% yields, respectively, as a white powder.

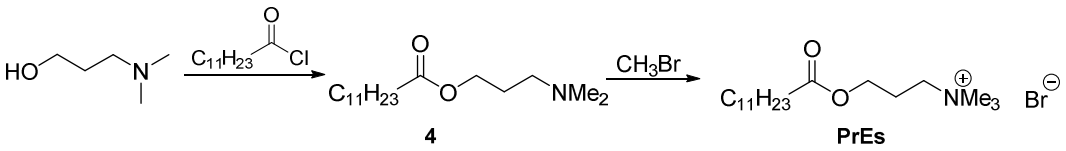
rac-**iPrEs**; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.55–5.37 (1H, m), 4.47–4.40 (1H, m), 3.79–3.68 (1H, m), 3.50 (9H, s), 2.35–2.25 (2H, m), 1.65–1.56 (2H, m), 1.40–1.18 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 300.2930 $[M - Br]^{+}$; calcd 300.4998 $[M - Br]^{+}$.

(*R*)-iPrEs: ^{1}H NMR (500 MHz, $CDCl_3$); δ 5.56–5.39 (1H, m), 4.47–4.40 (1H, m), 3.79–3.68 (1H, m), 3.51 (9H, s), 2.37–2.17 (2H, m), 1.67–1.52 (2H, m), 1.42–1.19 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 300.2748 $[M - Br]^{+}$; calcd 300.4998 $[M - Br]^{+}$.

(*S*)-iPrEs: ^{1}H NMR (500 MHz, $CDCl_3$); δ 5.54–5.40 (1H, m), 4.50–4.40 (1H, m), 3.80–3.68 (1H, m), 3.53 (9H, s), 2.40–2.27 (2H, m), 1.68–1.55 (2H, m), 1.43–1.18

(19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 300.2733 $[M - Br]^+$; calcd 300.4998 $[M - Br]^+$.

3. Synthesis of lauroyloxypropylene-*N*,*N*,*N*-trimethylammonium bromide (PrEs)



Scheme S3

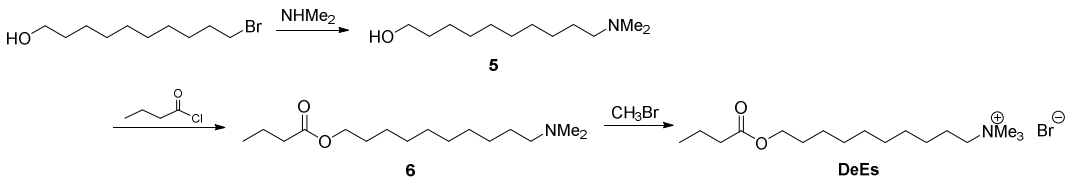
3-Dimethylamino-1-propanol (1.03 g, 10 mmol) in an anhydrous dichloromethane (2 mL) was added dropwise to an anhydrous dichloromethane solution (3 mL) of lauroylchloride (1.33 g, 6 mmol). The reaction mixture was stirred under argon atmosphere at room temperature for 4 h. The mixture was then concentrated under reduced pressure, and the residue was dissolved in ethyl acetate (20 mL). The organic layer was washed three times with a 5% sodium hydrogen carbonate aqueous solution (15 mL), and then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to obtain lauroyloxyethylene-*N*,*N*-dimethylamine (**4**), at a yield of 78% (1.34 g), as a colorless syrup.

^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ 4.11 (2H, t, J = 6.6 Hz), 2.39–2.24 (4H, m), 2.21 (6H, s), 1.85–1.72 (2H, m), 1.66–1.55 (2H, m), 1.38–1.13 (19H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.3185 $[M + H]^+$; calcd 286.4732 $[M + H]^+$.

2 M THF solution of methyl bromide (8 mL) was added to **4** (1.37 g, 4.79 mmol) at 0 ^oC and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by reprecipitation using chloroform (4 mL) and ethyl acetate (12 mL) to obtain **PrEs** at a yield of 74% (1.01 g), as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.29–4.15 (2H, m), 3.83–3.70 (2H, m), 3.53 (9H, s), 2.33 (2H, t, J = 7.2 Hz), 2.27–2.13 (2H, m), 1.68–1.56 (2H, m), 1.38–1.18 (16H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 300.0254 $[M – Br]^+$; calcd 300.4998 $[M – Br]^+$.

4. Synthesis of propanoyloxydecamethylene-*N*,*N*,*N*-trimethylammonium bromide (DeEs)



Scheme S4

A mixture of a 9.5 mol/L aqueous solution of dimethylamine (4.51 g, 50.0 mmol), 10-bromo-1-decanol (2.84 g, 12 mmol), a 20 mM NaOH solution (0.7 mL) was stirred in ethanol (8 mL) for 24 h at 70 °C. After the reaction, the solvent were removed by evaporation under reduced pressure to obtain crude product. The crude product was purified by silicagel column chromatography [chloroform/methanol = 9/1 (v/v), R_f = 0.50] to obtain 10-dimethylaminodecanol (**5**), at a yield of 88% (2.42 g), as a white powder.

^{1}H NMR (500 MHz, CD_3OD-d_4): δ 3.54 (2H, t, J = 6.4 Hz), 2.86–2.73 (2H, m), 2.62 (6H, s), 1.70–1.48 (4H, m), 1.45–1.26 (12H, m). ESI-MS in CH_3CN (m/z): 202.4114 $[M + H]^+$; calcd 202.3489 $[M + H]^+$.

A mixture of **5** (0.49 g, 2.43 mmol) and butyryl chloride (0.78 g, 7.30 mmol) was stirred in anhydrous acetonitrile (82 mL) for 18 h at 100 °C. After the reaction, the mixture was concentrated under reduced pressure, and the residue was dissolved in ethyl acetate (30

mL). The organic layer was washed three times with a 5% sodium hydrogen carbonate aqueous solution (10 mL), then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to obtain propanoyloxydecamethylene-*N*,*N*-dimethylamine (**6**), at a yield of 52% (0.347 g), as a yellow syrup.

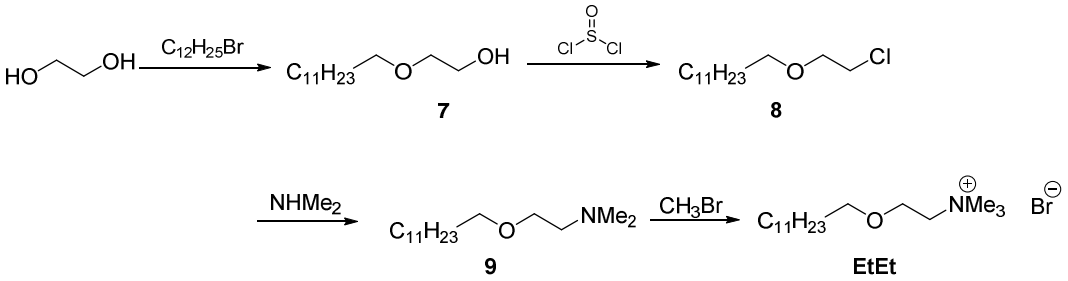
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.05 (2H, t, J = 6.6 Hz), 2.35–2.15 (10H, m), 1.70–1.58 (4H, m), 1.53–1.18 (14H, m), 0.94 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 272.1946 $[M + H]^+$; calcd 272.4387 $[M + H]^+$.

2 M THF solution of methyl bromide (15 mL) was added to **6 (**1.30 g, 4.79 mmol) at 0 ^{o}C and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by reprecipitation using ethyl acetate (2 mL) and hexane (4 mL) to obtain **DeEs**, at a yield of 58% (1.01 g), as an orange powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (2H, t, J = 6.6. Hz), 3.57–3.51 (2H, m), 3.44 (9H, m), 2.26 (2H, t, J = 6.6 Hz), 1.78–1.68 (2H, m), 1.66–1.57 (4H, m), 1.40–1.22 (12H, m), 0.94 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 286.2177 $[M - Br]^+$; calcd 286.4732

$[M - Br]^+$.

5. Synthesis of dodecyloxyethylene-*N*,*N*,*N*-trimethylammonium bromide (EtEt)



Scheme S5

A mixture of bromododecane (3.00 g, 12.0 mmol) and tetrabutylammonium bromide (0.192 g, 0.595 mmol) in dioxane (7 mL) were added to a solution of KOH (0.903 g, 13.7 mmol) in ethyleneglycol (3.83 g, 61.7 mmol). The reaction mixture was stirred with reflux for 5 h. After the reaction, the mixture was diluted with chloroform (10 mL) and water (10 mL). The organic layer was washed with water (20 mL) three times, and then dried over anhydrous magnesium sulfate. The crude product was purified by silica gel column chromatography [*n*-hexane/ethyl acetate = 3/2 (v/v), R_f = 0.64] to obtain dodecyloxyethanol (**7**), a yield of 51% (1.41 g), as a colorless syrup.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75–3.67 (2H, m), 3.55–3.38 (4H, m), 2.20–2.08 (1H, m), 1.64–1.50 (2H, m), 1.38–1.15 (18H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in

CH_3CN (*m*/*z*): 231.2304 $[M + H]^+$; calcd 231.3868 $[M + H]^+$.

Thionyl chloride (1.22 g, 10.2 mmol) was added dropwise with stirring to a mixture of **7** (2.05 g, 8.90 mmol) and anhydrous pyridine (0.808 g, 10.2 mmol) in anhydrous toluene (3 mL) at 0 °C. Then, the mixture was stirred for 2 h at 110 °C. After the reaction, the mixture was diluted with water (10 mL). The organic layer was washed with 30 wt% HCl (30 mL) three times, and then dried over anhydrous magnesium sulfate. The solvent was under reduced pressure to obtain the crude product. Purification was carried out by silica gel column chromatography [*n*-hexane/ethyl acetate = 3/2 (v/v), R_f = 0.86] to obtain dodecyloxyethylenechloride (**8**), a yield of 74% (1.63 g), as a yellow syrup. ^1H NMR (500 MHz, $CDCl_3$): δ 3.73–3.58 (4H, m), 3.54–3.45 (2H, m), 1.67–1.53 (2H, m), 1.40–1.16 (18H, m), 0.87 (3H, t, J = 6.6 Hz). ESI-MS in CH_3CN (*m*/*z*): 249.7827 $[M + H]^+$; calcd 249.8325 $[M + H]^+$.

A mixture of a 9.5 mol/L aqueous solution of dimethylamine (3.5 mL), **8** (1.63 g, 6.55 mmol) and a 20 mM NaOH solution (0.43 mL) was stirred in ethanol (6 mL) for 24 h at 70 °C. After the reaction, the solvent and unreacted dimethylamine were removed by evaporation under reduced pressure to obtain crude product. The crude product was

purified by silicagel column chromatography [chloroform/methanol = 9/1 (v/v), R_f = 0.26] to obtain dodecyloxyethylene-dimethylamine (**9**), a yield of 64% (1.08 g), as a colorless syrup.

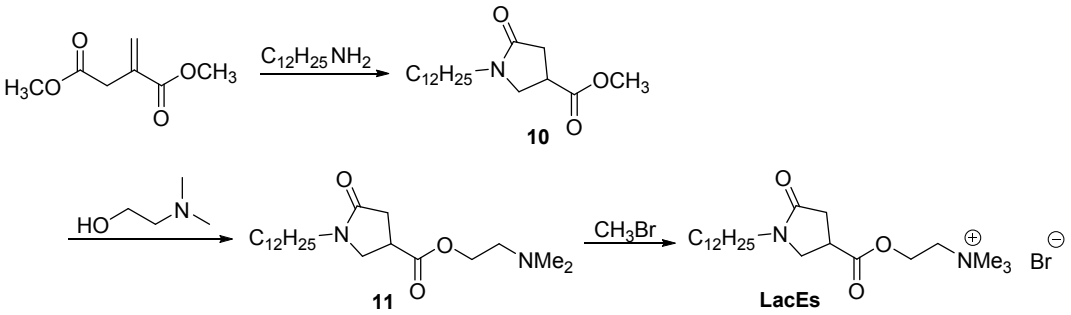
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.51 (2H, t, J = 6.1 Hz), 3.42 (2H, t, J = 6.8 Hz), 2.49 (2H, t, J = 6.1 Hz), 2.24 (6H, s), 1.63–1.52 (2H,m), 1.37–1.15 (18H, m), 0.87 (3H, m, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 258.2671 $[M + H]^+$; calcd 258.4552 $[M + H]^+$.

2 M THF solution of methyl bromide (8 mL) was added to **9** (1.08 g, 4.20 mmol) at 0 ^{o}C and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by recrystallization using ethyl acetate (1 mL) to obtain **EtEt** at a yield of 50% (0.75 g), as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.98–3.94 (2H, m), 3.90–3.86 (2H, m), 3.57–3.44 (11H, m), 1.58–1.50 (2H, m), 1.35–1.19 (18H, m), 0.87 (3H, m, J = 6.6 Hz). ESI-MS in CH_3CN (m/z): 272.2875 $[M – Br]^+$; calcd 272.4897 $[M – Br]^+$.

6. Synthesis of (*N*-dodecyl-2-pyrrolidone-4-yl)carbonyloxyethylene-*N*,*N*,*N*-

trimethylammonoium bromide (LacEs)



Scheme S6

A mixture of dimethyl itaconate (0.475 g, 3.0 mmol) and *n*-dodecylamine (0.565 g, 3.0 mmol) were reacted under argon atmosphere for 24 h at 40 °C with stirring. After the reaction, the crude product was purified by silica gel column chromatography [*n*-hexane/ethyl acetate = 2/3 (v/v), R_f = 0.50] to obtain *N*-dodecyl-2-pyrrolidone-4-methylester (**10**), a yield of 63% (0.55 g), as a colorless syrup.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.74 (3H, s), 3.66–3.43 (2H, m), 3.39–3.17 (3H, m), 2.78–2.49 (2H, m), 1.55–1.45 (2H, m), 1.37–1.15 (18H, m), 0.87 (3H, t, J = 6.6 Hz).

ESI-MS in CH_3CN (*m*/*z*): 312.1782 $[M + H]^+$; calcd 312.4595 $[M + H]^+$.

10 (1.03 g, 3.29 mmol) and 2-dimethylaminoethanol (0.330 g, 3.29 mmol) were reacted

in the presence of molecular sieve 4A for 24 h at 90 °C with stirring. After the reaction, the first in the crude product was purified by silica gel column chromatography [chloroform/methanol = 9/1 (v/v), R_f = 0.40] to obtain a mixture of **10** and (*N*-dodecyl-2-pyrrolidone-4-yl)carbonyloxyethylene-*N*,*N*-dimethylamine (**11**) as a yellow syrup. The molar ratio was 59/100, as calculated from the ^{1}H NMR spectrum of the $CDCl_3$ solution.

2 M THF solution of methyl bromide (1.0 mL) was added to a mixture of **10** and **11** at 0 ^oC and then the mixture was stirred for 30 min at room temperature. After the reaction, the solvent and unreacted methyl bromide were removed by evaporation under reduced pressure to obtain the crude product. Purification was carried out by reprecipitation using chloroform (1 mL) and ethyl acetate (4 mL) to obtain **LacEs**, a yield of 5% (72.2 mg) over two steps, as a white crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.73–4.66 (2H, m), 4.30–4.22 (2H, m), 3.76–3.15 (15H, m), 2.75–2.67 (2H, m), 1.56–1.43 (2H, m), 1.38–1.16 (18H, m), 0.87 (3H, t, J = 6.6 Hz).

ESI-MS in CH_3CN (m/z): 383.3157 $[M - Br]^+$; calcd 383.5885 $[M - Br]^+$.

Figure

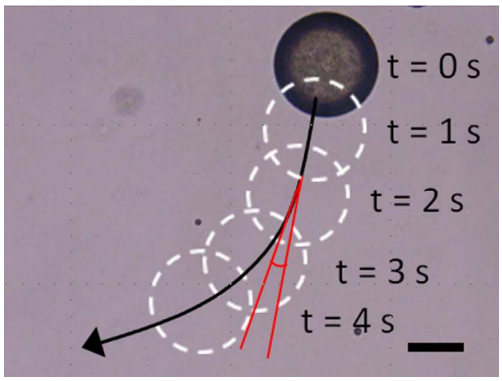


Figure S1. Illustration of the analytical method used to describe the self-propelled motion of micrometer-sized oil droplets in C16TAB solution. In the driven trajectory of the oil droplet as indicated by the black arrow, a change in direction was observed when the angle formed by the straight line and the tangent to the center of droplets was ≥ 0.25 immediately after the change in direction during the self-propelling motion. The angle indicated by the red color is 0.25 rad. The white dashed circles indicate the trajectory followed for the oil droplet. From the coordinates of the centers of oil droplets, we calculated the moving distance per unit time (s) and obtained the motion speed by dividing the moving distance by the analysis time. Scale bar: 100 μm.

Description of video clips

Four video clips are attached that depict the motions of micrometer-sized oil droplets in solutions of 50 mM surfactants (**EtEs**, **C16TAB**, and **DeEs**) at room temperature (23–25 ^{o}C). All the movies are shown at a real-time speed.

Movie S1: The high-speed motion of **HBA** oil droplets in aqueous **EtEs** within 1 min of the start of observation.

Movie S2: Self-propelled motion of **HBA** oil droplets in an aqueous solution of **C16TAB** within 1 min of the start of the observation.

Movie S3: Formation of aggregates at the rear of a self-propelled oil droplet in aqueous **C16TAB** solution 15 min after the start of observation.

Movie S4: Stationary **HBA** oil droplets in aqueous **DeEs** solution within 1 min of the start of observation.