Supporting Information

Recyclable and re-usable smart surfactant for stabilization of various multi-responsive emulsions alone or with nanoparticles

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No. Tables: 1

No. Figures: 20

EXPERIMENTAL

Materials

Silica nanoparticles with a purity > 99.8% were provided by Wuxi Jinding Longhua Chemical Co., China of primary diameter 20 nm and BET surface area = 200 ± 20 m^2/g. Alumina nanoparticles were purchased from Sigma-Aldrich and have a purity > 99.8%, a primary diameter of 13 nm and a BET surface area of 85-115 m^2/g. SEM and TEM images of both particle types are shown in Figures S3 and S7, respectively. 8-bromooctanoic acid (purity > 98%), dimethylamine hydrochloride (purity > 99%), hydroquinone (purity > 98%), lithium aluminum hydride (purity > 97%), methyl bromide (purity > 98%), n-decane (purity > 98%) and the cationic surfactant cetyltrimethylammonium bromide (CTAB, purity > 99%) were purchased from Aladdin (Shanghai). Other chemicals used were all analytically pure and purchased from Sinopharm Chemical Reagent Co. (Shanghai). High purity N$_2$ and CO$_2$ were provided by Wuxi Xinnan Chemical Gas Co. Ltd, China. Pure water with a pH close to 6.8 and a resistance of 18.2 MΩ cm was produced from a Simplicity Pure Water System (Merck Millipore, Shanghai). All chemicals were used as received unless specified otherwise.

Synthesis and characterization of novel surfactant N$^+$-8P8-N

The novel smart surfactant was synthesized in five steps as shown in Scheme S1, and the detailed process is described below.
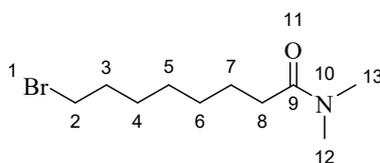
(1) *Synthesis of compound I*

8-bromooctanoic acid (30 g, 0.135 mol) was added to a three-necked flask fitted with a reflux condenser and exhaust gas absorption device. A few drops of N,N-dimethylformamide (DMF) was added dropwise as a catalyst. After that thionyl chloride (21 g, 0.178 mol) was added slowly dropwise and the mixture was stirred for 1 h at 60 °C. After completion of the reaction, excess thionyl chloride was removed by distillation under reduced pressure to give intermediate **I**.
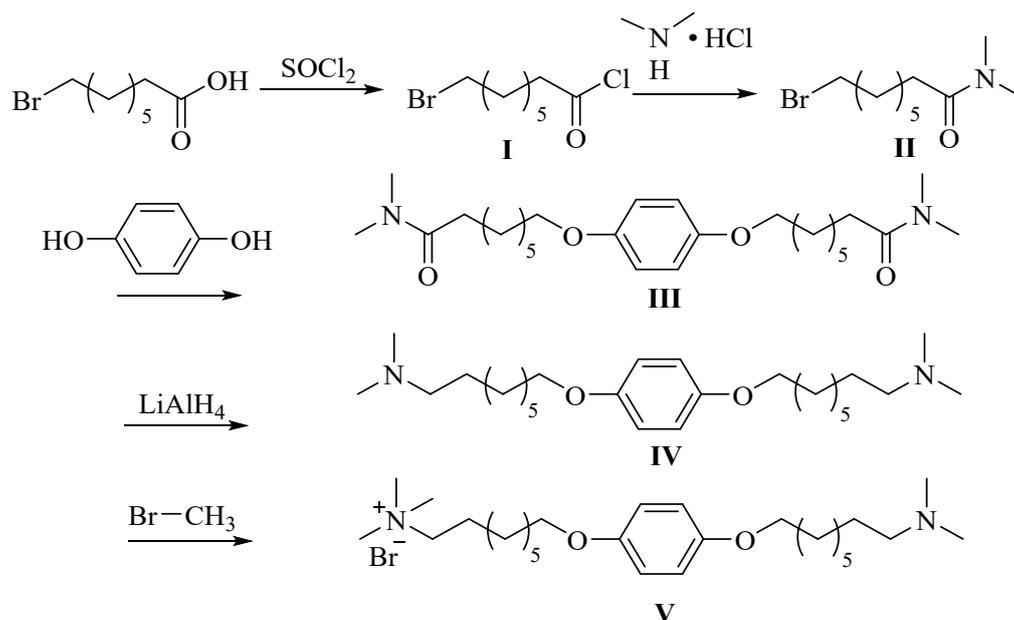
Scheme S1. Synthesis of N+-8P8-N surfactant.

(2) *Synthesis of compound II*

Dimethylamine hydrochloride (14 g, 0.172 mol) and trimethylamine (50 g, 0.494 mol) were added to a three-necked flask which was immersed in a low-temperature bath at -10 °C and the intermediate **I** (32.61 g, 0.135 mol) dissolved in dichloromethane (10 ml) was added dropwise under magnetic stirring. The mixture was continuously stirred for 2 h, followed by extraction with deionized water (200 mL×3) to remove excess dimethylamine and trimethylamine. Then, dichloromethane (200 mL×2) was used to strip the collected aqueous phase. The organic extracts were combined, dried with anhydrous Na$_2$SO$_4$ and filtered and then evaporated to give a deep red liquid, which is further purified by column chromatography (petroleum ether:ethyl acetate = 1:1) yielding compound **II** as a white solid with a yield of 75.4 %. ^{1}H-NMR is shown in Figure S1 (400 MHz, CDCl$_3$, δ): 3.46 – 3.36 (s, C2-2H), 3.08 – 2.90 (s, C12-3H, C13-3H), 2.36 – 2.27 (s, C8-2H), 1.91 – 1.81 (s, C3-2H), 1.70 – 1.58 (s, C7-2H), 1.50 – 1.31 (s, C4-2H, C5-2H, C6-2H).
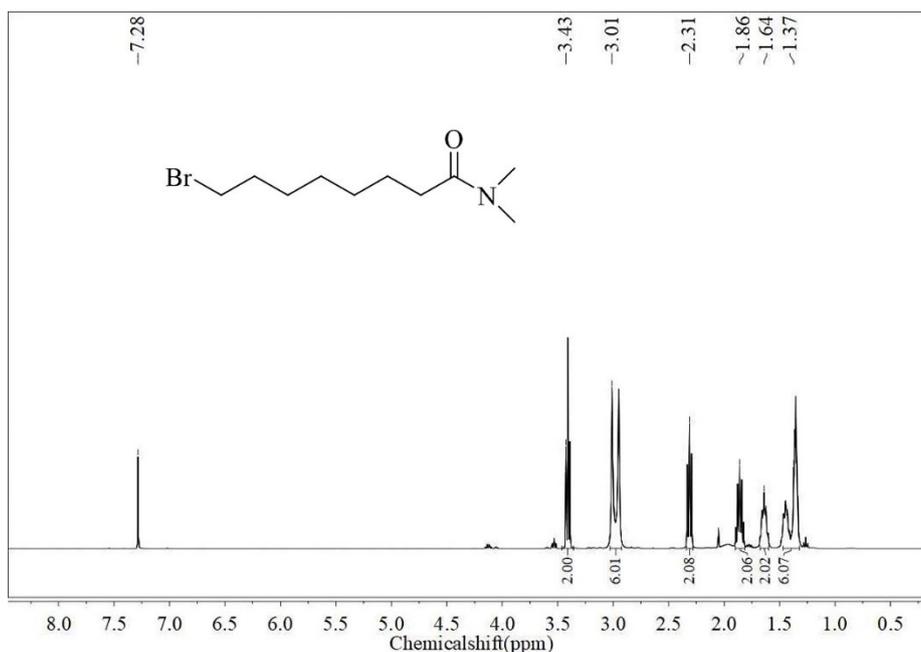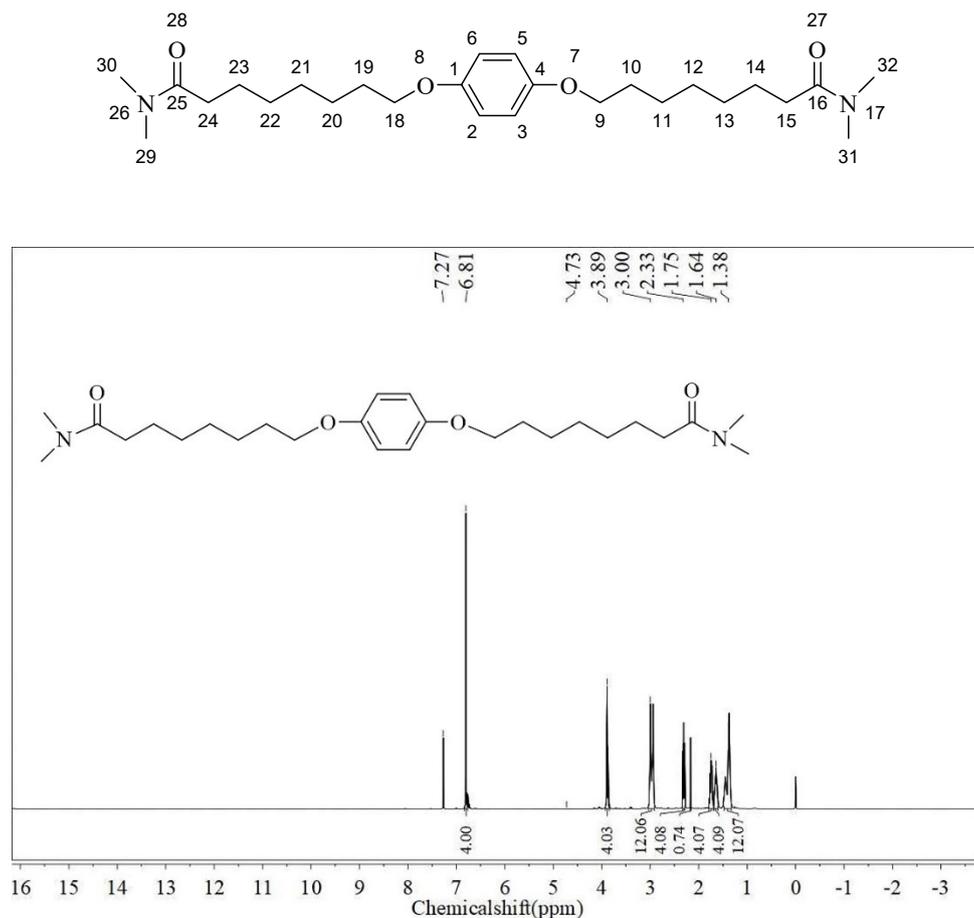
Figure S1. ^{1}H NMR of intermediate II

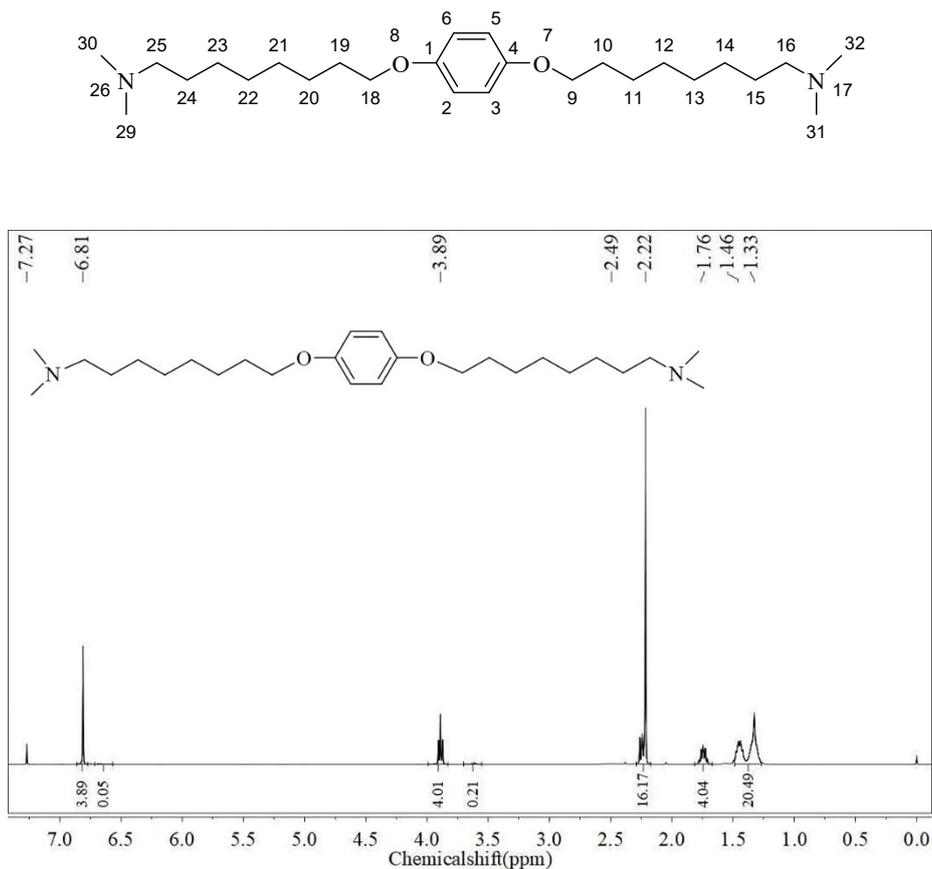### (3) *Synthesis of compound III*

Anhydrous potassium carbonate (26 g, 0.188 mol) was dissolved in DMF (200 mL) under a nitrogen atmosphere. After stirring for 10 min, hydroquinone (5.0 g, 0.045 mol) was added with stirring for another 10 min, then the intermediate **II** (25 g, 0.10 mol) was added followed by stirring at room temperature for 1 h and then stirred for another 10 h at 70 °C. After the reaction was finished, the insoluble matter in the mixture was filtered off and the filtrate was collected and diluted with deionized water (100 mL), followed by extraction with petroleum ether (100 mL×3) to obtain the product. The extracted organic phase was dried with anhydrous Na_2SO_4 and the petroleum ether was removed by evaporation. The product collected was then recrystallized from acetone, and compound **III** was received as a pale-yellow solid with a yield = 57.96 %. ^{1}H-NMR is shown in Figure S2 (400 MHz, CDCl$_3$, δ): 6.89 – 6.76 (s, C2-1H, C3-1H, C5-1H, C6-1H), 3.95 – 3.81 (s, C9-2H, C18-2H), 3.12 – 2.85 (d, C29-3H, C30-3H, C31-3H, C32-3H), 2.42 – 2.24 (s, C15-2H, C24-2H), 1.79 – 1.70 (s, C10-2H, C19-2H), 1.69 – 1.59 (s, C14-2H, C21-2H), 1.52 – 1.22 (s, C11-2H, C12-2H, C13-2H, C20-2H.C21-2H, C22-2H).

Figure S2. ^{1}H NMR of intermediate III

(4) *Synthesis of compound IV*

LiAlH$_4$ (2.50 g, 0.066 mol) and THF (300ml) were added to a three-necked flask fitted with a reflux condenser and the mixture was stirred for a few min. Then the temperature was raised to 60 °C and intermediate **III** (12 g, 0.027 mol) was added. The temperature was further raised to 72 °C and the mixture was stirred for 2 h. The mixture was then cooled to room temperature and deionized water (2.50 g) and 15 wt.% NaOH (2.50 g) were added dropwise. The mixture was stirred for 30 min, dried with anhydrous Na$_2$SO$_4$, filtered and evaporated to obtain compound **IV** as a colourless product with a yield = 86.77 %. ^{1}H-NMR is shown in Figure S3 (400 MHz, CDCl$_3$, δ): 6.86 – 6.77 (s, C2-H, C3-1H, C5-1H, C6-1H), 3.99 – 3.83 (s, C9-2H, C18-2H), 2.29 – 2.17 (s, C16-2H, C25-2H, C29-3H, C30-3H, C31-3H, C32-3H), 1.81 – 1.67 (s, C10-2H, C19-2H), 1.49 – 1.27 (d, C11-2H, C12-2H, C13-2H, C14-2H, C15-2H, C20-2H, C21-2H, C22-2H, C23-2H, C24-2H).

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Figure S3. ^{1}H NMR of intermediate VI

(5) Synthesis of N+-8P8-N (compound V)

The flask for reaction and anhydrous ethanol were frozen overnight. Intermediate **IV**, anhydrous ethanol (15mL) and methyl bromide (0.9 g, 0.0095 mol) were added to the flask. After 4 h stirring at room temperature, the reaction mixture was heated to 40 °C with stirring for 3 h, followed by stirring at 60 °C for another 3 h. After completion of the reaction, the ethanol in the mixture was removed using a rotary evaporator and the product was recrystallized from acetone (50 mL×2) and petroleum ether (50 mL×2) respectively to give the target product N+-8P8-N (compound **V**) as a white solid with a yield = 15.61 %.

(6) Characterization of N+-8P8-N surfactant

To confirm the chemical structure of synthesized N-8P8-N+, FT-IR, ^{1}HNMR and ESI-MS measurements were carried out and shown in Figure S4.
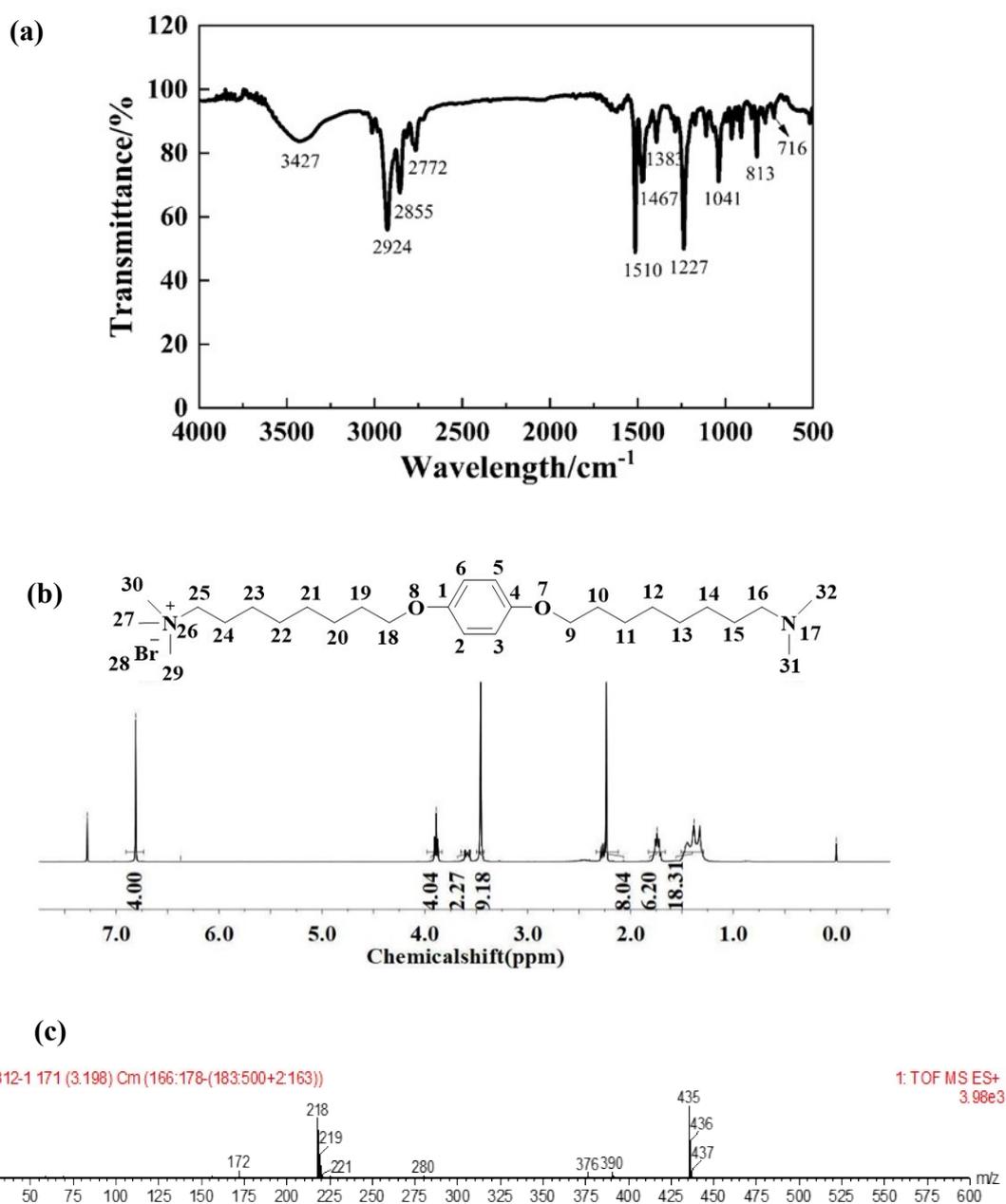
Figure S4. (a) FT-IR, (b) ^{1}HNMR and (c) ESI-MS spectra of synthesized N$^+$-8P8-N surfactant.

(i) <u>FT-IR characterization</u> The structure of N$^+$-8P8-N was investigated using a Fourier transform infrared (FT-IR) spectrometer (Nicolet 6700, USA). FT-IR spectra with baseline correction were acquired.

(ii) ^{1}H NMR characterization The structure of N$^+$-8P8-N was also characterized by ^{1}H NMR (Advance III, Bruker) with CDCl$_3$ as solvent.

(iii) ESI-MS characterization An ultra-performance liquid chromatography-tandem mass spectrometrometer (LCZ/2690XE/996, Waters, USA) was used to perform MS analysis for N$^+$-8P8-N.

As can be seen in Figure S4(a), the peak at 3427 cm^{-1} is the vibration of free tertiary amine; the strong peaks at 2924 cm^{-1} and 2855 cm^{-1} are stretching vibrations of methyl and methylene groups ν_{C-H}; the absorbance peaks at 1510 cm^{-1} are benzene skeleton vibrations; those at 1467 cm^{-1}, 1383 cm^{-1} and 1227 cm^{-1} are bending vibrations of methyl, methylene groups δ_{C-H} and aromatic ether ν_{C-O}. Other peaks are: 1041 cm^{-1}, vibration of ν_{C-N}; 813 cm^{-1}, fingerprint region of the disubstituted benzene ring; 722 cm^{-1}, characteristic absorption of long-chain saturated hydrocarbons.

The ^{1}H NMR data shown in Figure S4(b) indicates a total hydrogen number of 51, in good agreement with the molecular formula of N$^+$-8P8-N. 6.89 – 6.70 (s, C2-1H, C3-1H, C5-1H, C6-1H), 4.00 – 3.81 (s, C9-2H, C18-2H), 3.64 – 3.54 (m, C25-2H), 3.48 – 3.43 (s, C27-3H, C29-3H, C30-3H), 2.33 – 2.20 (s, C16-2H, C31-3H, C32-3H), 1.80 – 1.67 (s, C10-2H, C19-2H, C24-2H), 1.48 – 1.23 (s, C11-2H, C12-2H, C13-2H, C14-2H, C15-2H, C20-2H, C21-2H, C22-2H, C23-2H).

The ESI-MS spectrum shown in Figure S4(c) (positive ion mode) indicates an m/z of 435 = [M-Br]$^+$. Probably, the tertiary amine chain can accept a proton to endow the molecule with double charge (z = 2), resulting in a halved m/z = 218. The height of the peaks is not proportional to the content as shown by the purity measurement as shown in Table S1, where the cationic surfactant N$^+$-8P8-N was quantitatively titrated to have a purity of 96.6% by Hyamine 1622 with bromocresol green as indicator [1] in alkaline conditions to ensure the tertiary amine group is uncharged.

Table S1. Titration data of target surfactant N^+-8P8-N ([Hyamine 1622] = 2.023 mM, [SDS] = 1.994 mM, 0.73 mL of Hyamine 1622 solution required for blank test).

	1	2	3	Average
$V_{\text{hyamine 1622}}$/mL	5.81	5.82	5.80	5.81
V_{SDS}/mL	10	10	10	10
$V_{\text{isopropanol-water}}$/mL	4	4	4	4
C_{actual}/mM	2.415	2.411	2.420	2.415
Purity	96.6 %	96.4 %	96.8 %	96.6 %

Preparation of emulsions

(1) *Conventional emulsions* 3 mL of water or N^+-8P8-N aqueous solution was added into a 10 mL glass vessel of dimensions 20 mm (d) ×50 mm (h), followed by addition of 3 mL of *n*-decane and the mixture was homogenized using an Ultra-turrax homogenizer (IKA T18 basic, S18N-10G head) at 11,000 rpm for 2 min. The emulsion type was identified by the drop test as described below. The concentration of surfactant is expressed as mM with respect to the aqueous phase and the oil:water volume ratio was fixed at 1:1. Emulsion stability was monitored by taking photographs using a digital camera and optical micrographs using a VHX-1000 microscope system (Keyence Co.), respectively.

(2) *Pickering emulsions and oil-in-dispersion emulsions* A certain mass of silica nanoparticles or alumina nanoparticles was weighed into a 25 mL glass vessel of dimensions 25 mm (d) ×65 mm (h), followed by addition of 7 mL water or N^+-8P8-N aqueous solution and the particles were ultrasonically dispersed using an ultrasound probe (JYD-650, Shanghai) of tip diameter 0.6 cm at an output of 60 W for 60 s. The concentration of particles and surfactant is expressed as wt.% and mM, respectively with respect to the aqueous phase. Then 7 mL of *n*-decane was added and the mixture was homogenized as described above to form emulsions. Similarly the oil:water volume ratio was fixed at 1:1 and the emulsion type and stability were identified and monitored as described above.

Identification of emulsion type

The dilution method (drop test) was used to identify the type of emulsion prepared. 1-2 drops of emulsion were added respectively into either 10 mL of the aqueous solution /dispersion used for preparing the emulsion or 10 mL of n-decane followed by gentle mixing. If the emulsion droplets dispersed well in the aqueous solution/dispersion but did not disperse in oil, the emulsion is regarded as O/W, and conversely the emulsion formed was regarded as water-in-oil (W/O).

Demulsification/re-emulsification cycles

(1) *pH trigger* An initial O/W emulsion was prepared at a certain surfactant concentration without or with particles as described above using pure water (pH = 6.8). The pH of the aqueous phase was decreased by adding HCl solution at a concentration of 2 M (for conventional emulsions) or 0.2 M (for Pickering emulsions and oil-in-dispersion emulsions). The emulsions were demulsified by hand shaking or stirring at low speed. Each time, once demulsification happened the upper oil layer was carefully removed and fresh n-decane was added for the next emulsification. To increase the aqueous pH to alkaline, concentrated NaOH solution at 2 M (for conventional emulsions) or 0.2 M (for Pickering emulsions and oil-in-dispersion emulsions) was added dropwise followed by thorough mixing. The pH was measured using a digital pH meter (FE220, Mettler Toledo) at room temperature (20-25 °C). After homogenization, a stable emulsion was formed and the above operation was repeated. In this way the surfactant structure is switched between surface-active and surface-inactive alternately (Scheme 1), and accordingly demulsification/re-emulsification was recycled.

(2) *CO_2/N_2 trigger* With n-decane as oil phase and the oil:water volume ratio set at 1:1 (10 mL/10 mL), an initial stable O/W emulsion was prepared in the same way as described above for the pH trigger. CO_2 was then bubbled into the emulsion through a needle at room temperature at a controlled rate to achieve demulsification. Similarly the upper oil phase was carefully removed and fresh n-decane was added for the next emulsification. Then N_2 was bubbled into the oil-water mixture in a similar way, followed by homogenization to produce an emulsion again. If the re-formed

emulsion is stable, the demulsification/re-emulsification process was repeated.

Measurements

(1) ***Surface tension*** The surface tension of N^+-8P8-N aqueous solutions was measured by the du Noüy ring method using a home-built instrument[24] at 25 ± 0.2 °C. A stock solution of 20 mM was prepared using pure water or an aqueous solution of HCl at pH = 2.0, respectively which was then diluted using either pure water or aqueous HCl to different concentrations. The pH of the solutions was measured using a digital pH meter (FE220, Mettler Toledo) at room temperature (20-25 °C). Before measurement, the surfactant solution was transferred to a clean petri dish with diameter of 60 mm and allowed to stand for 24 h at 25 ± 0.1 °C (air thermostat). The surface tensions were measured at least three times and the average value is reported.

(2) ***Zeta potential*** A mass of silica or alumina nanoparticles was accurately weighed into a 25 mL sample bottles, then N^+-8P8-N aqueous solution (10 mL) of different concentrations was added and dispersed using an ultrasonic disperser for 1 min. The bottles were then closed and fixed on a rotary mixer to overturn for 24 h to reach equilibrium. After that 3 mL of each dispersion was transferred to a cuvette, and the zeta potential of nanoparticles was measured using a ZetaPALS instrument (Brookhaven) at 25 °C. For each sample, the measurement was repeated at least three times and the final zeta potential was calculated using the Helmholtz-Smoluckowski equation.

(3) ***Adsorbed amount*** The adsorption isotherm of N^+-8P8-N at the silica-water interface was measured by depletion.[26] A series of surfactant solutions containing dispersed silica nanoparticles was subjected to an ultrasonic disperser for 1 min, then transferred to a clean petri dish of diameter 60 mm and placed in the thermostat at 25 °C overnight to reach adsorption equilibrium. The surface tensions of the dispersion were measured by the du Noüy ring method analogous to the measurement of solutions without particles.

(4) ***Concentration of N^+-8P8-N in aqueous phase*** N^+-8P8-N aqueous solutions of different concentrations were prepared and 3 mL was placed into a quartz cuvette and the absorbance of the solution at 200-800 nm was scanned to find the wavelength

at maximum absorption (λ_{max}). After that, the absorbance of all the prepared solutions at λ_{max} was measured to obtain an absorbance-concentration calibration curve. Then the absorbance of N⁺-8P8-N aqueous solutions after demulsification was measured and compared with that without emulsification or the calibration curve. The aqueous solution remains transparent and any decrease in absorbance suggests a reduction in N⁺-8P8-N concentration or migration of N⁺-8P8-N molecules to the oil phase.
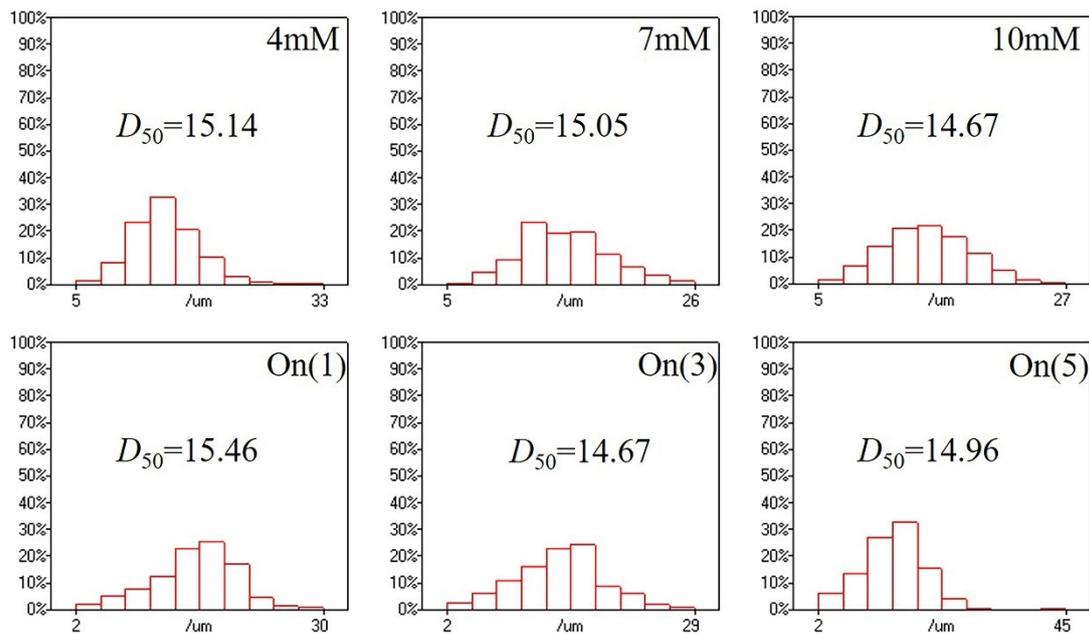
Figure S5. Droplet size distribution of (upper) *n-decane*-in-water conventional emulsions stabilized by N^+-8P8-N dissolved in pure water (pH = 6.8) at different concentrations (given) and (lower) *n-decane*-in-water conventional emulsions stabilized by 4 mM N^+-8P8-N undergoing alternate demulsification (off, pH = 2.9) and re-emulsification (on, pH = 10.7) with fresh oil by homogenization (H).
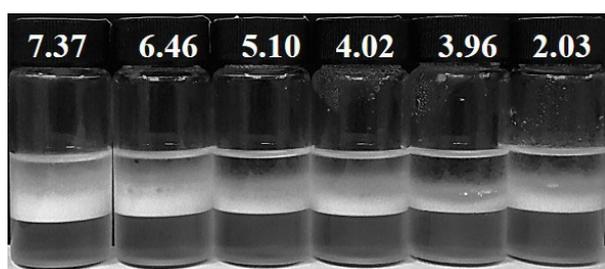
Figure S6. Digital photos of *n*-decane-in-water (7 mL/7 mL) emulsions stabilized solely by 4 mM N^+-8P8-N at different pH as shown, taken 6 h after preparation at 25 °C.
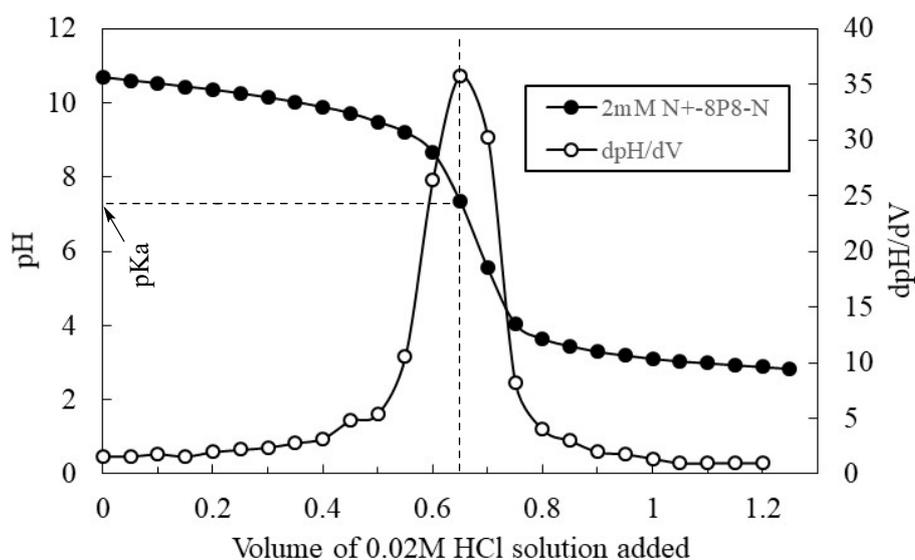
Figure S7. pH titration curve of N$^+$-8P8-N solution (2 mM) and corresponding dpH/dV-V curve (25 °C).
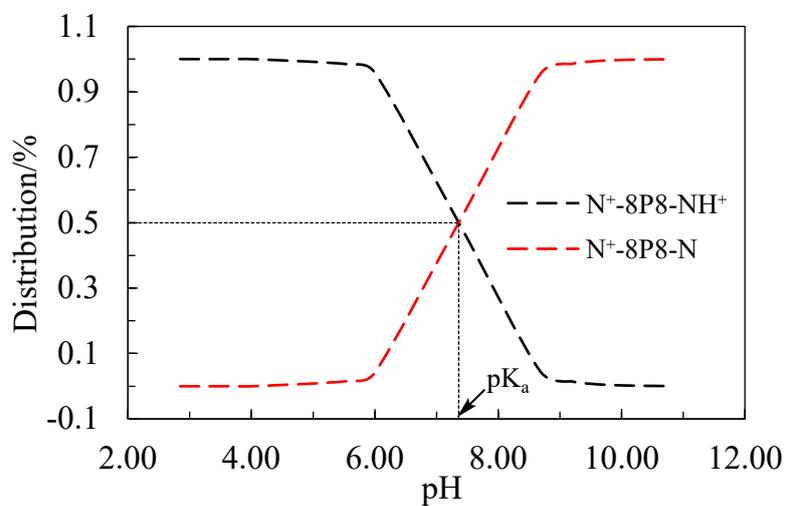
Figure S8. Fraction of N$^+$-8P8-N and N$^+$-8P8-NH$^+$ in solution (2 mM) as a function of pH derived from the pH titration curve at 25 °C; from D.-F. Liu, Y.-X. Suo, J. Tan, H.-S. Lu, *Soft Matter,* 2017, **13**, 3783-3788.
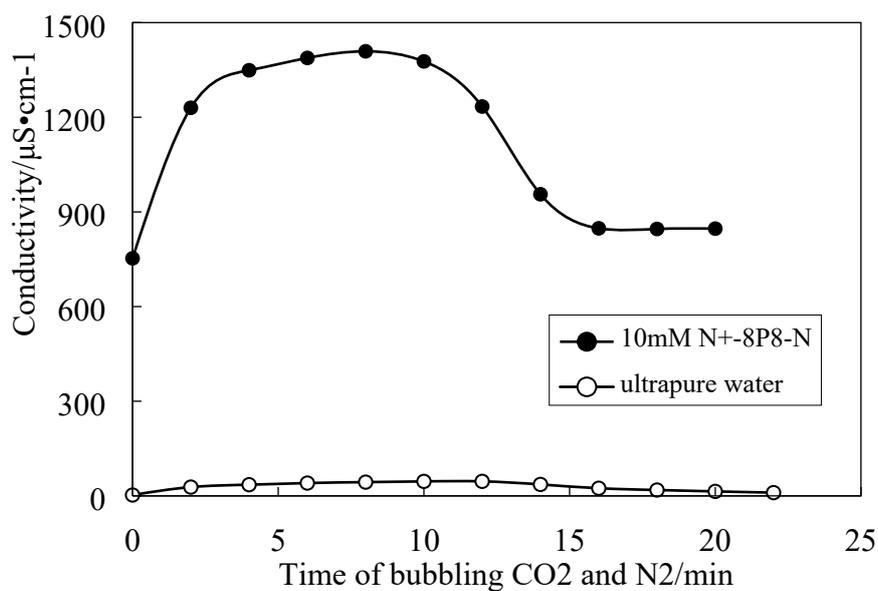
Figure S9. Variation of conductivity of the N^+-8P8-N aqueous solution (10 mM) upon bubbling CO_2 or N_2, respectively, at a flow rate of 10 mL/min (25°C).
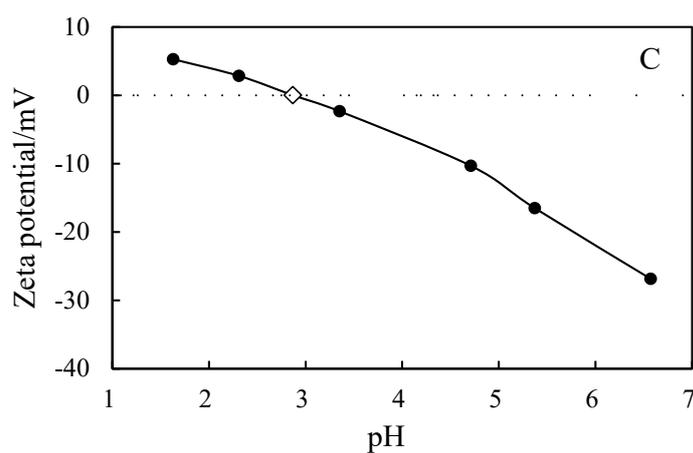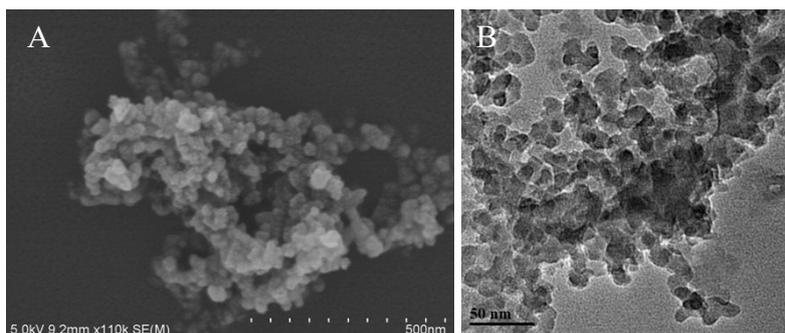
Figure S10. (A) SEM and (B) TEM images of silica nanoparticles, (C) zeta potential of 0.1 wt.% silica nanoparticles dispersed in water of different pH at 25 °C.
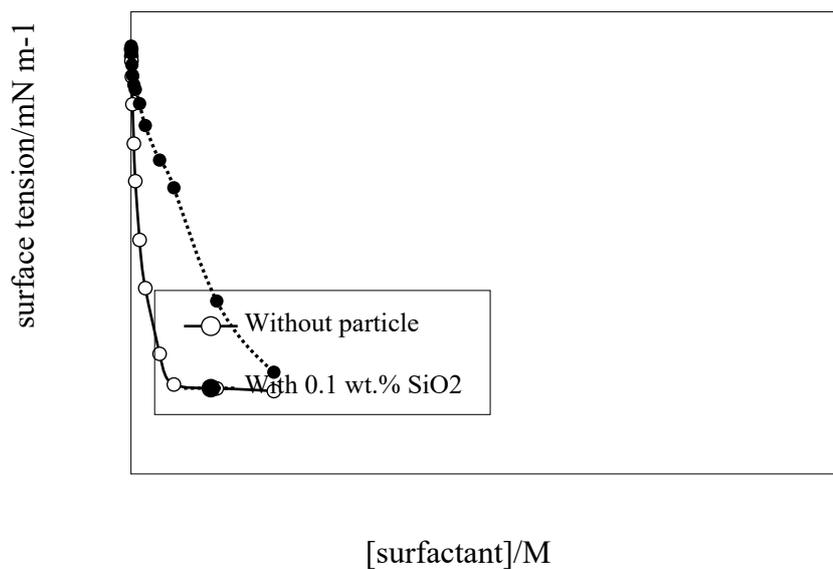
Figure S11. Surface tension of aqueous solutions of N^+-8P8-N in pure water with or without 0.1 wt.% silica nanoparticles as a function of surfactant concentration at 25 °C.
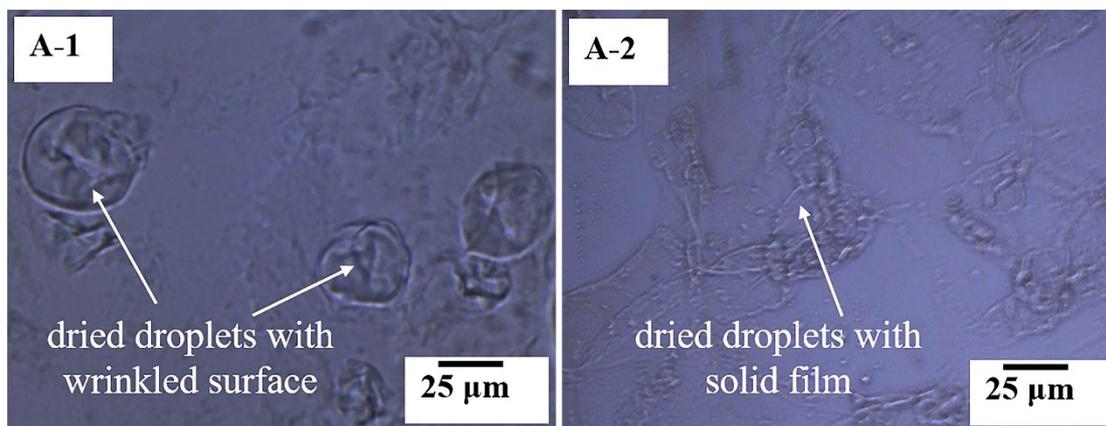

Figure S12. Optical micrographs of O/W Pickering emulsion stabilized by 0.1 wt.% silica nanoparticles and 0.1 mM N^+-8P8-N after drying.
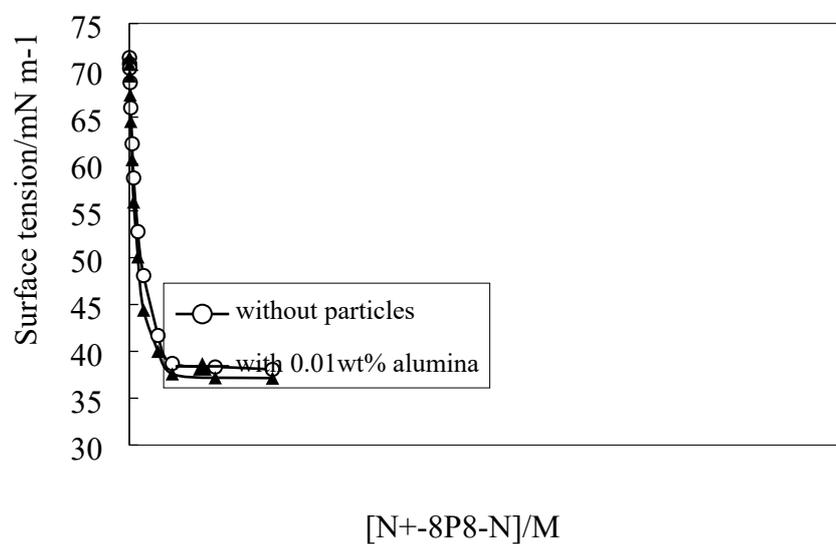
Figure S13. Digital photos of *n*-decane-in-water (7 mL/7 mL) Pickering emulsions stabilized by 0.1 wt.% silica nanoparticles and 0.1 mM N$^+$-8P8-N at different pH at 25 °C, taken 24 h after preparation.
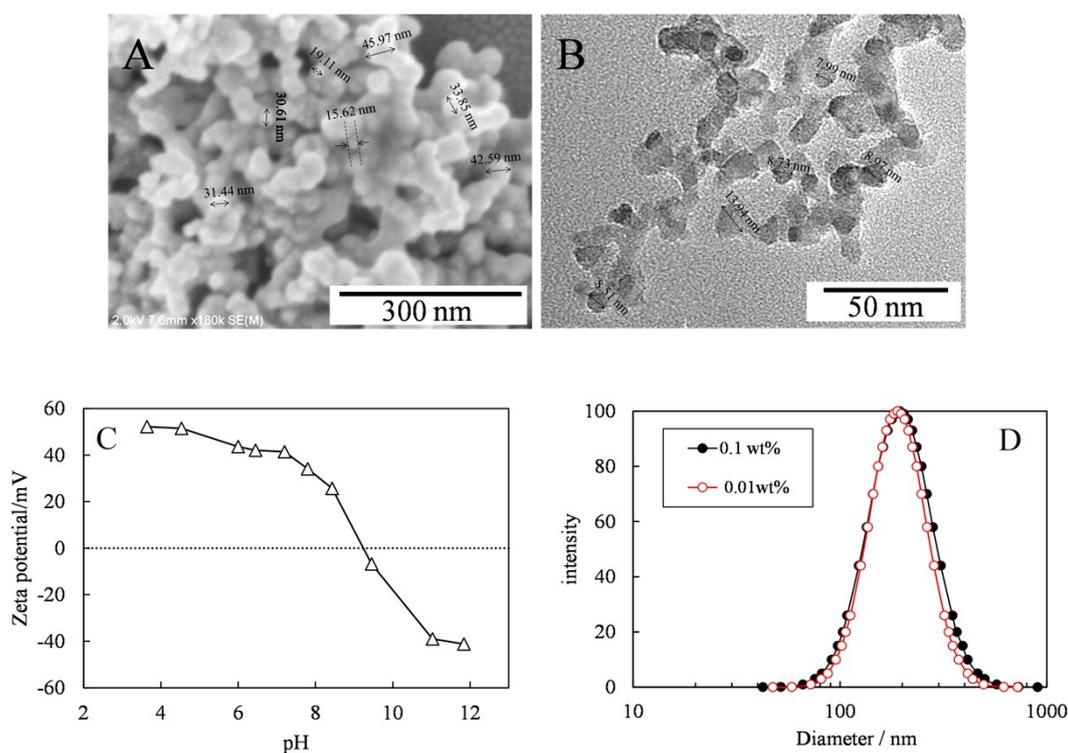
Figure S14. (A) SEM and (B) TEM images of alumina nanoparticles, (C) zeta potential of 0.1 wt.% alumina nanoparticles dispersed in water of different pH, (D) size distribution of alumina nanoparticles dispersed in neutral water at different concentrations as shown at 25 °C.
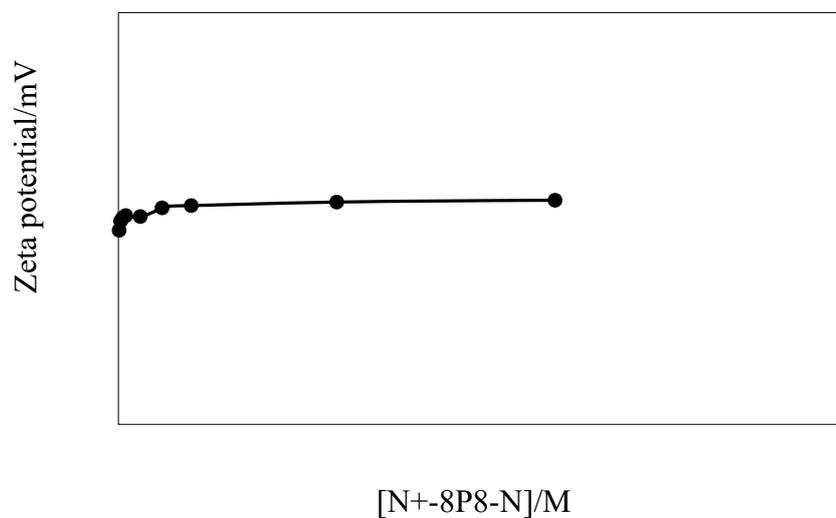
Figure S15. Zeta potential of 0.01 wt.% alumina nanoparticles dispersed in different concentrations of N^+-8P8-N at 25 °C.


Figure S16. Surface tension of N^+-8P8-N aqueous solutions with or without 0.01 wt.% alumina nanoparticles at 25 °C.
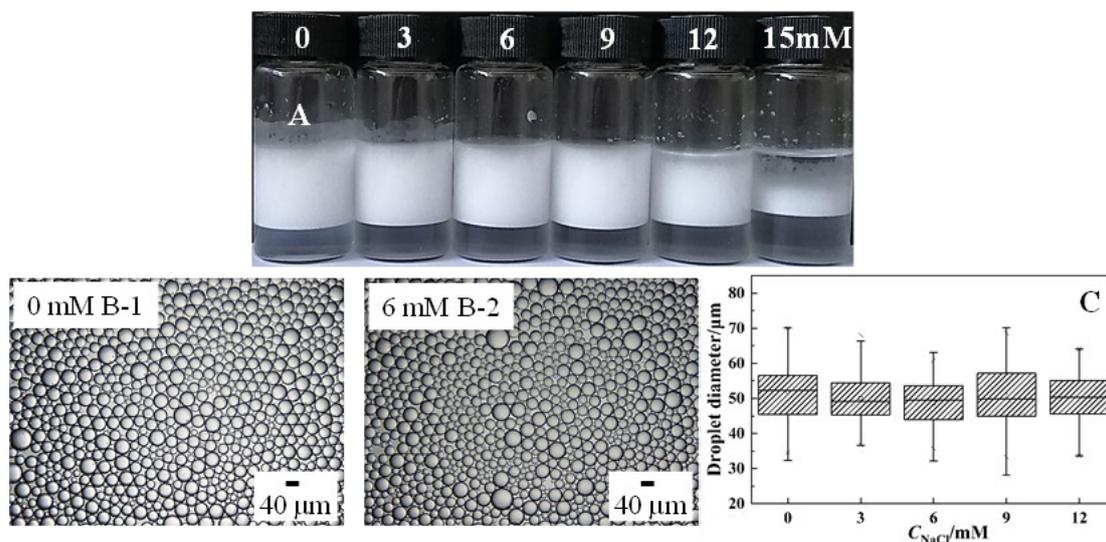
Figure S17. Digital photos of *n*-decane-in-water (7 mL/7 mL) oil-in-dispersion emulsions stabilized by 0.01 wt.% alumina nanoparticles and 0.06 mM N^+-8P8-N at different pH, taken 24 h after preparation at 25 °C.
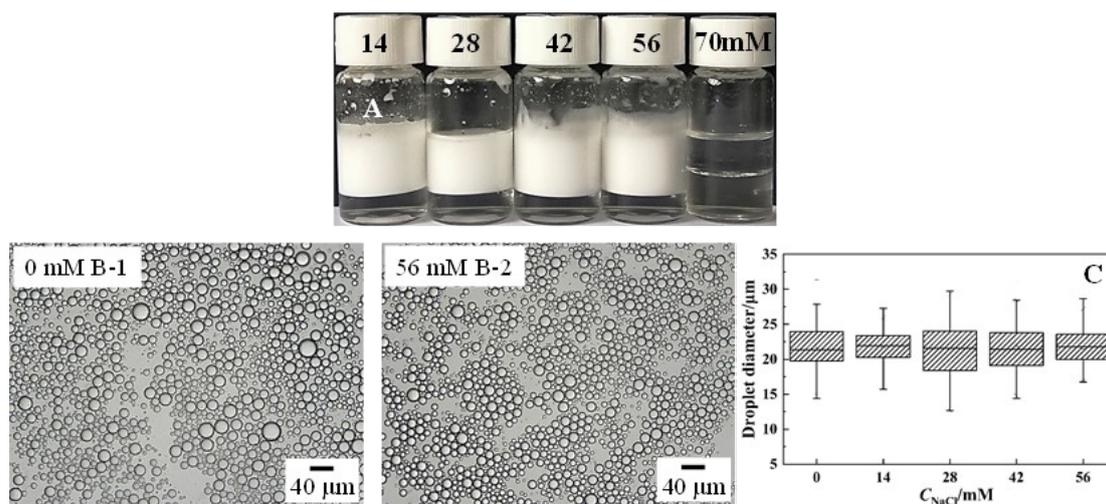

Figure S18. (A) Digital photos, (B) micrographs and (C) droplet size distribution of decane-in-water conventional emulsions (7 mL/7 mL) stabilized solely by 5 mM N^+-8P8-N in the presence of NaCl of different concentration (mM) as shown, taken 24 h after preparation at 25 °C.
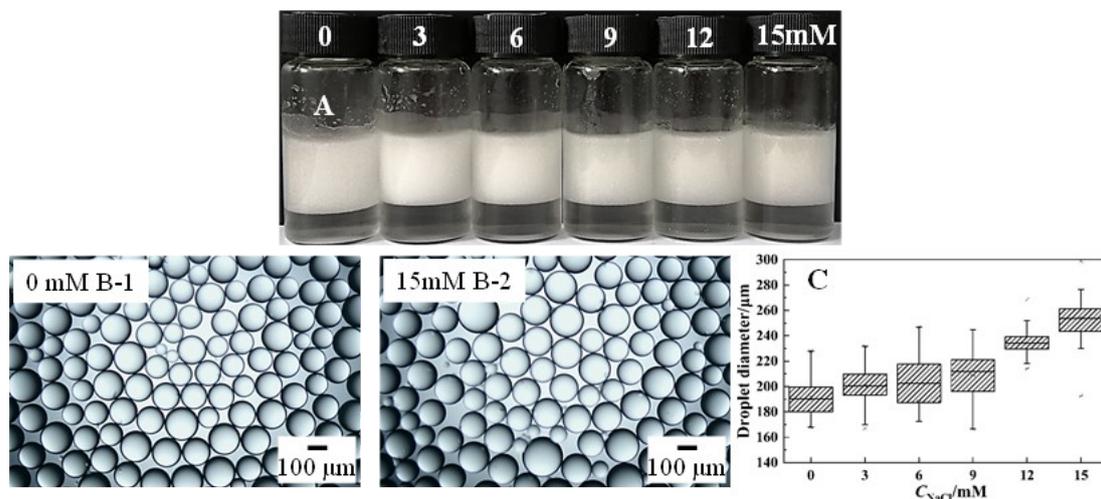
Figure S19. (A) Digital photos, (B) micrographs and (C) droplet size distribution of decane-in-water Pickering emulsions (7 mL/7 mL) stabilized by 0.1 wt.% silica nanoparticles and 0.1 mM N$^+$-8P8-N in the presence of NaCl of different concentration (mM) as shown, taken 24 h after preparation at 25 °C.

Figure S20. (A) Digital photos, (B) micrographs and (C) droplet size distribution of decane-in-dispersion emulsions (7 mL/7 mL) stabilized by 0.01 wt.% alumina nanoparticles and 0.06 mM N$^+$-8P8-N in the presence of NaCl of different concentration (mM) as shown, taken 24 h after preparation 25 °C.
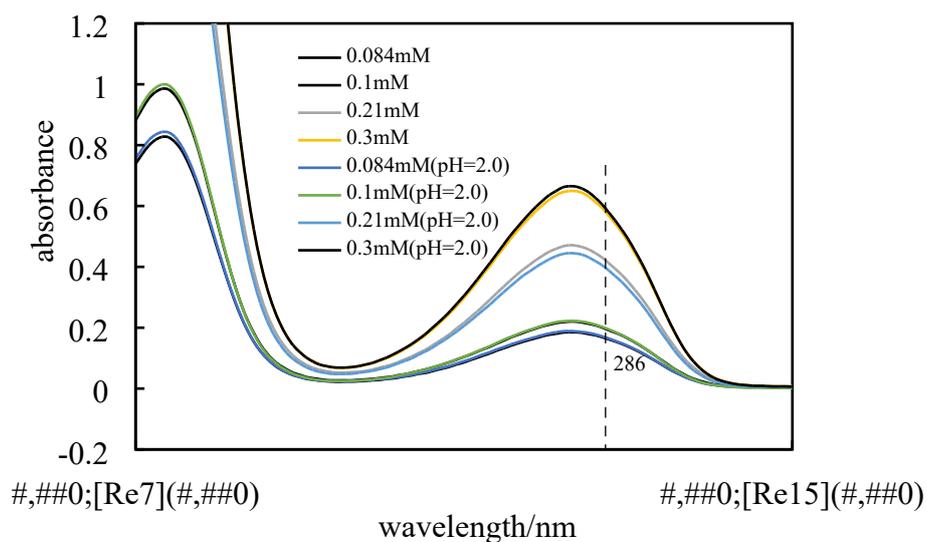
Figure S21. Absorbance-wavelength scan of aqueous N$^+$-8P8-N solutions of different concentration in either neutral or acidic (pH = 2) conditions at room temperature.

[1] G.F. Longman, The Analysis of Detergents and Detergents Products, Wiley, New York, 1975, p.241.