Electronic Supplementary Information (ESI) for

Tandem triggering wormlike micelles using CO_2 and redox

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Experimental section

Materials

Selenium powder, sodium borohydride, benzyl bromide, chlorosulfuric acid, sodium bicarbonate, hydrazine hydrate, 30 wt% H_2O_2 and all other organic solvents used in this study were analytical-grade products from Shanghai Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was dried by CaH_2 and distilled under normal pressure prior to use. 11-bromoundecanol and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine (TMEDA) were purchased from Adamas-beta and used as received. Water was triply distilled by a quartz water purification system.

Synthesis of selenium-containing anionic surfactant

The anionic surfactant, sodium benzylselanyl undecyl sulfate (BSeAS), was prepared by a simple 3-step process as shown in Fig. S1.

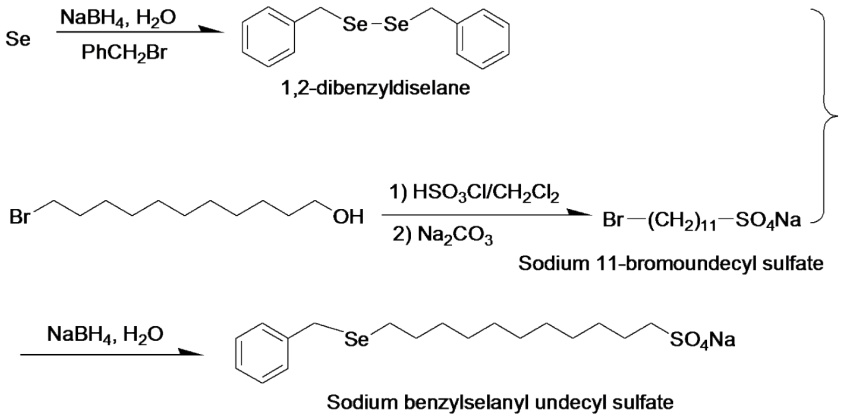

Figure S1. Synthesis pathway for sodium benzylselanyl undecyl sulfate (BSeAS).

(1) 1,2-dibenzyldiselane (DBDSe)

Under N_2 atmosphere, 9.00 g Se power was added into 75 mL deionized water at room temperature, and the mixture was stirred for 15 min. Sodium borohydride (9.43g) in 75 mL of deionized water was slowly added into Se power suspension at 0 °C. After the initial vigorous reaction had subsided (20min), one additional equiv of Se powder (9.00 g) was added. The reaction was continuously carried out 20 min at 70 °C and a brownish red solution was obtained. At room temperature a solution of 39.35 g benzyl bromide in 285 mL refined THF was injected into and the mixture was stirred for *ca*. 18 h at 50 °C. The crude product was extracted with dichloromethane, and then the solid was recrystallized from the ethyl acetate. DBDSe (28.82 g, yield 73.38 %) was obtained as yellow needle-like crystals.

(2) Sodium 11-bromoundecyl sulfate (BrAS)

12.4g（0.11mol) chlorosulfuric acid was slowly dropwise added 170 mL dichloromethane solution of 25.123g(0.1mol) 11-bromoundecanol under mechanical strring, and the temperature was maintains at 25~30 ^oC. The resulting mixture was aged for 30min and then added into 140 mL aqueous solution of 30.695g Na_2CO_3. The solvent was removed under reduced pressure to give BrAS as white solid (23.256g, 66.36%).

^{1} H NMR (400 MHz, D_2O, Fig. S2), /ppm: 1.25~1.37 (m, 14H), 1.58~1.60 (m, 2H), 1.75~1.81 (m, 2H), 3.37~3.40 (t, J=6.8 HZ, 2H), 3.92~3.96 (t, J=6.6 HZ, 2H). ESI-MS (Fig. S3): Calcd: 329.0 (M-Na^+). Found: m/z = 329.0.

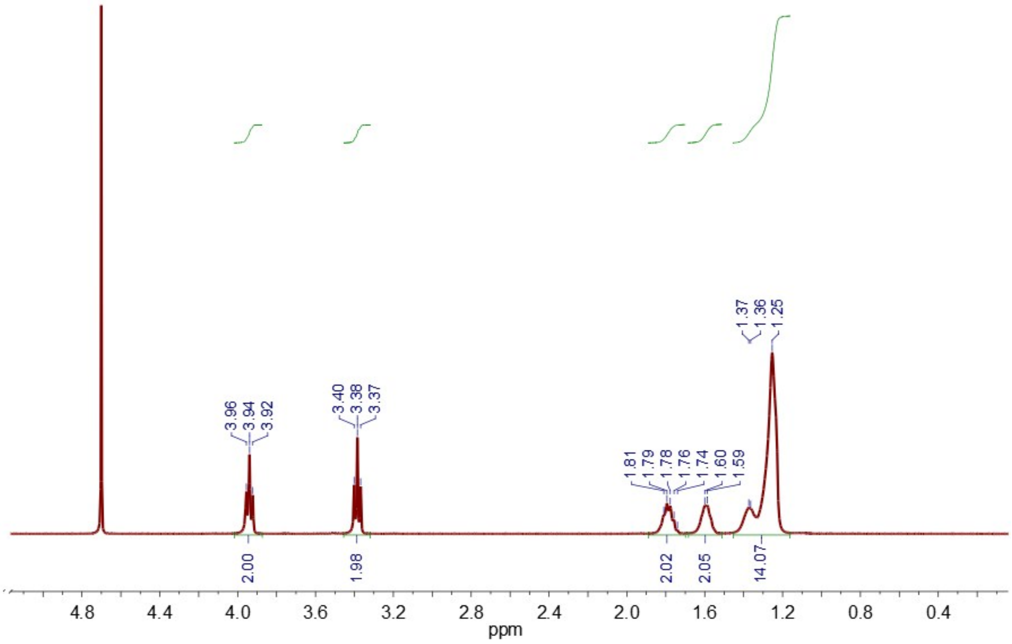

Figure S2. ^{1}H NMR spectra of BrAS using D_2O as solvent.

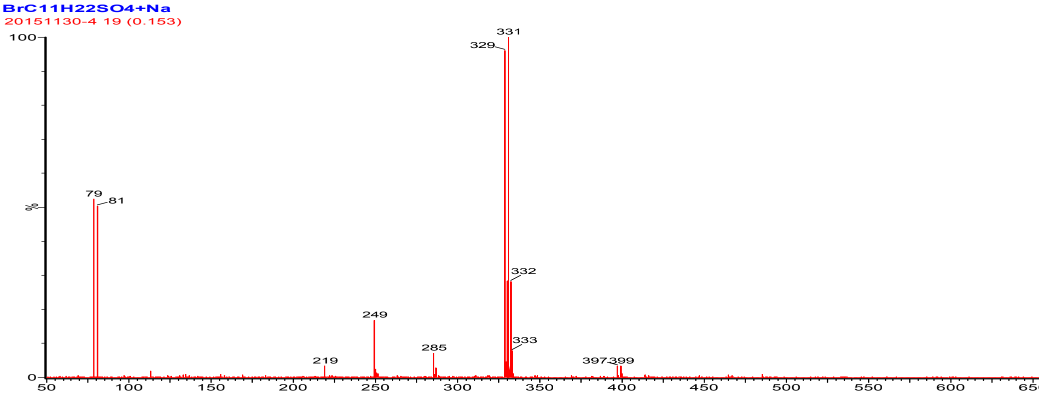

Figure S3. ESI-MS spectra of BrAS.

(3) Sodium benzylselanyl undecyl sulfate (BSeAS)

Under N_2 flow and ice bath，80 mL aqueous solution of 4.49 g $NaBH_4$ was dropwise added into 120 mL

THF solution of 5.75 g DBDSe in 1 h, and a milky dispersion was obtained. 80 mL aqueous solution of 12.00 g BrAS was added into the dispersion above. The reaction was first carried out at room temperature for 0.5 h, and then heated to 50 °C ca. 15 h. The solvent was removed under reduced pressure to give white solid. The solid was washed with petroleum ether and then recrystallized from the deionic water. BSeAS (9.51g， 64.3%) was obtained.

^{1} H NMR (400 MHz, D_2O, Fig. S4), /ppm: 1.06 (m, 14H), 1.36~1.38 (m, 2H), 1.48 (s, 2H), 2.21~2.24 (t, J=7.0 Hz, 2H), 3.48 (s, 2H), 3.85~3.87 (t, J=5.4 Hz, 2H), 6.90~7.00 (m, 5H).

^{13}C NMR (400 MHz, D_2O, Fig. S5), /ppm: 22.58, 25.28, 28.42~28.98, 46.54, 51.35, 69.20, 128.71~130.24.

ESI-MS (Fig. S6): Calcd: 421.1 (M-Na^+). Found: m/z = 421.0.

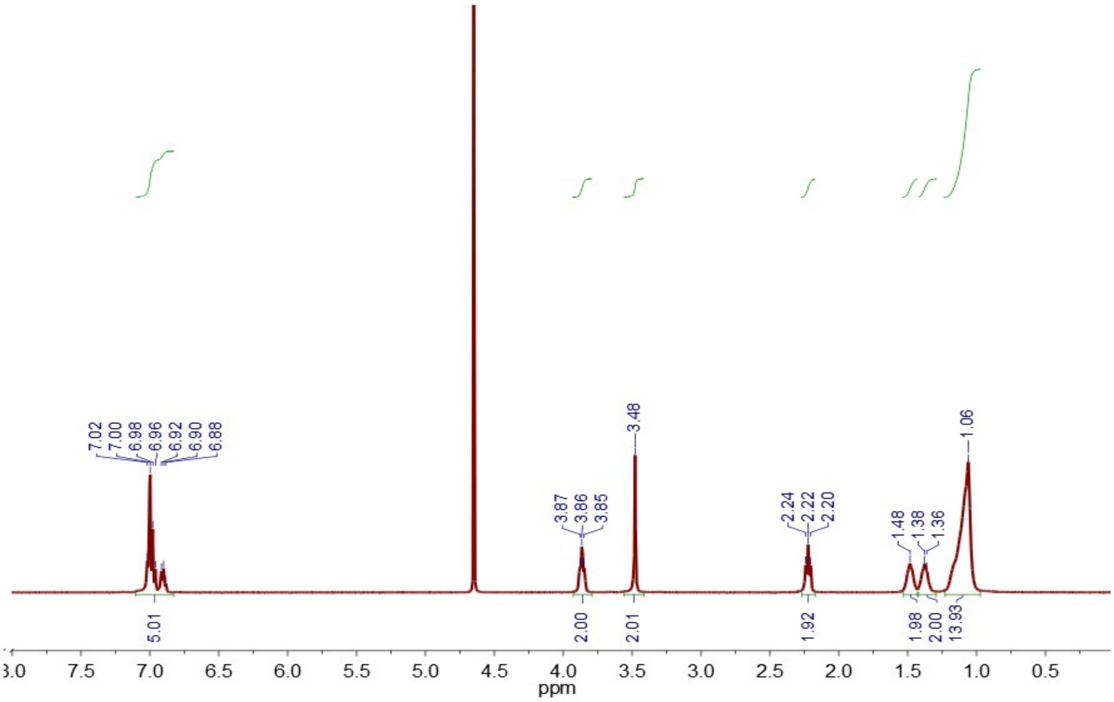

Figure S4. ^{1}H NMR spectra of BSeAS using D_2O as solvent.

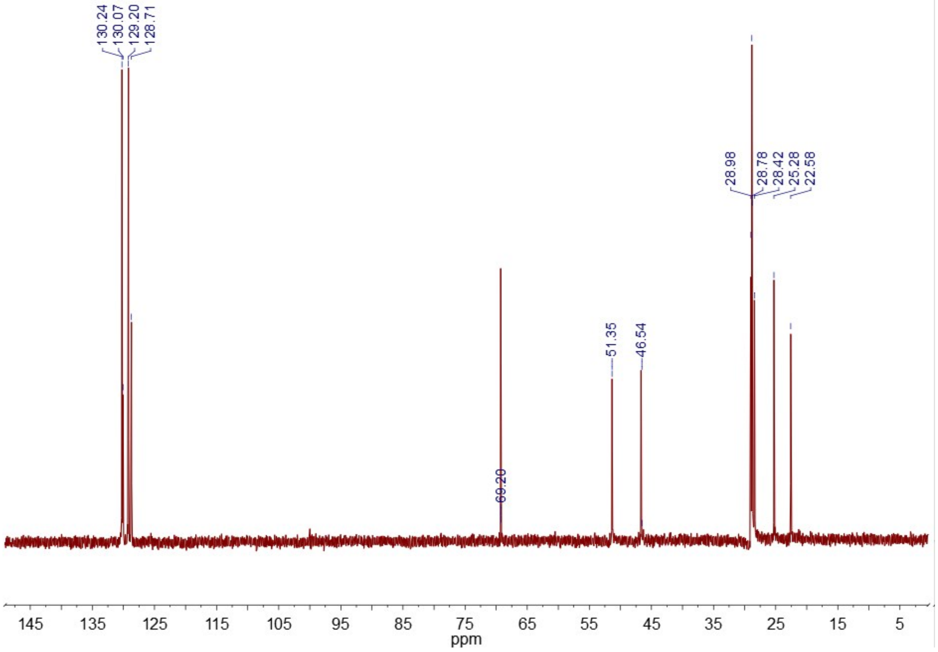

Figure S5. ^{13}C NMR spectra of BSeAS using D_2O as solvent.

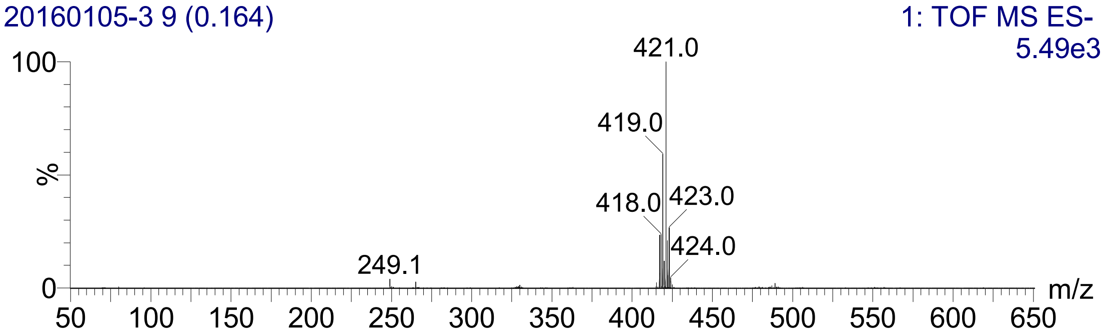

Figure S6. ESI-MS spectra of BSeAS.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz at room temperature. ^{77}Se NMR spectra were recorded on an Agilent DD2 600 spectrometer at 600 MHz at room temperature. Chemical shifts are expressed in ppm downfield from TMS as internal standard. ESI-MS spectra were obtained with the Bruker Daltonics Data Analysis 3.2 system.

Sample preparation

200 mmol BSeAS, 100 mmol TMEDA and 1 L distilled water were introduced into a glass bottle sealed with rubber septa, followed by magnetic agitation for several minutes (referred to as “BSeAS-TMEDA”), other samples were obtained by diluting with distilled water. All the sample are fixed at the same molar ratio of BSeAS /TMEDA, 2:1, otherwise specifically stated. The concentration of mixture solution is marked as the concentration of TMEDA. CO_2 was bubbled into BSeAS-TMEDA mixture solution at ambient temperature with a fixed flow rate of 0.1 L/min under the pressure of 0.1 MPa, leading to a transparent viscoelastic fluid (referred to as “BSeAS-TMEDA-CO_2”). After that, the sample was kept in a sealed vessel to avoid contacting with air. To efficiently remove CO_2, N_2 was bubbled into the SDS-TMPDA-CO_2 solution at 55 °C until equilibrium with the same flow rate as CO_2, resulting in a low viscosity water-like solution (referred to as “BSeAS-TMEDA -CO_2-N_2”). H_2O_2 (1.1 equimolar of BSeAS) was added into BSeAS-TMEDA-CO_2 at room temperature, resulting in a water-like fluid (referred to as “BSeAS-TMEDA -CO_2-Ox”) in less than 30 min. The reversible process can be achieved by adding designed amount of $N_2H_4{\cdot}H_2O$ (1.0 equimolar of H_2O_2) at room temperature for 12 h. All the samples obtained were kept at 25 °C for about 24 h prior to the measurements.

Rheology

Rheological measurements were carried out on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with concentric cylinder geometry CC17 (ISO3219). Samples were equilibrated at 25 °C for no less than 20 min prior to the experiments. Dynamic frequency spectra were performed in the linear viscoelastic regime, previously determined from dynamic stress sweep measurements. All the experiments were carried out in the stress-controlled mode, and CANNON standard oil was used to calibrate the instrument before the measurements. The temperature was set to 25 ± 0.01 °C with a Peltier temperature control device, and a solvent trap was used to minimize solvent evaporation during the measurements.

Cryo-TEM observation

Cryo-TEM observation of the solutions was performed in a controlled environment vitrification system. The chamber temperature was 25−28 °C, and the relative humidity was kept close to saturation to prevent evaporation during the preparation. 5 μL of solutions pre-heated at 25 °C was placed on a carbon-coated holey film supported by a copper grid, and gently blotted with a piece of filter paper to obtain a thin liquid film (20–400 nm) on the grid. The grid was quenched rapidly with liquid ethane at −180 °C and then transferred into liquid nitrogen (−196 °C) for storage. The vitrified specimen stored in liquid nitrogen was then transferred to a JEM2010 cryo-microscope using a Gatan 626 cryo-holder and its workstation. The acceleration voltage was 120 kV, and the working temperature was kept below −170 °C. The images were recorded digitally with a charge-coupled device camera (Gatan 832) under low-dose conditions with an under-focus of approximate 3 μm.

pH measurement

The pH of solutions with bubbling CO$_2$ was monitored at 25 °C by a Sartorius basic pH-meter PB-10 (± 0.01) calibrated with standard buffer solutions. The CO$_2$ gas flow rate was fixed at 0.1 L·min^{-1}. The variation of pH of pure water under bubbling CO$_2$ at 25 °C was also recorded as a reference.

Conductivity measurement

The conductivity of solutions with bubbling CO$_2$ was monitored by an FE30 conductometer (Mettler Toledo, USA) at 25 °C, and the average values were calculated from three repeats. The CO$_2$ gas flow rate was fixed at 0.1 L·min^{-1}. The conductivity of pure water under bubbling CO$_2$ at 25 °C was also determined as a reference.

Surface tension measurement

The surface tension (*γ*) of the systems were conducted on a drop volume tensionmeter at 25 ± 0.1°C. The outer radius of the glass capillary was 0.58 mm. In the procedure for γ measurements, a sufficient aging time is necessary for the pendant drop surface to reach an equilibrium state. Finally, the drop volume was corrected by the Harkins–Brown method.

Dynamic light scattering (DLS)

DLS measurements were performed on a ALV/DLS/SLS-5022F (HOSIC LIMITED, Germany) with a 90° back scattering angle and He–Ne laser (λ= 633 nm). Samples were filtered with a 0.2-µm filter of mixed cellulose acetate to remove any interfering dust particles.

Additional results

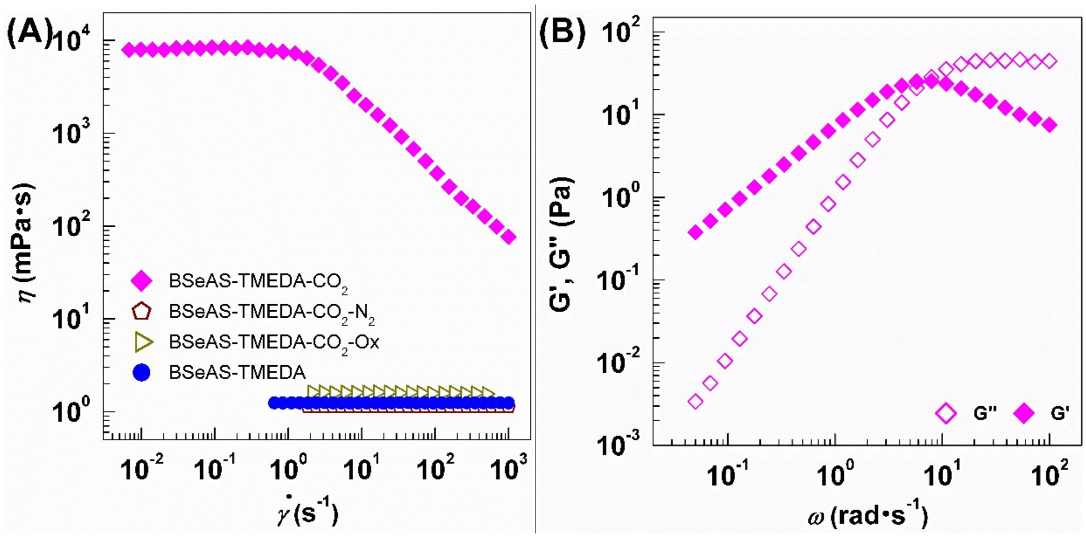

Figure S7. (A) Steady rheology, and (B) dynamic rheology for 100 mM BSeAS-TMEDA (2:1 molar ratio; the concentration refers to that of TMEDA).

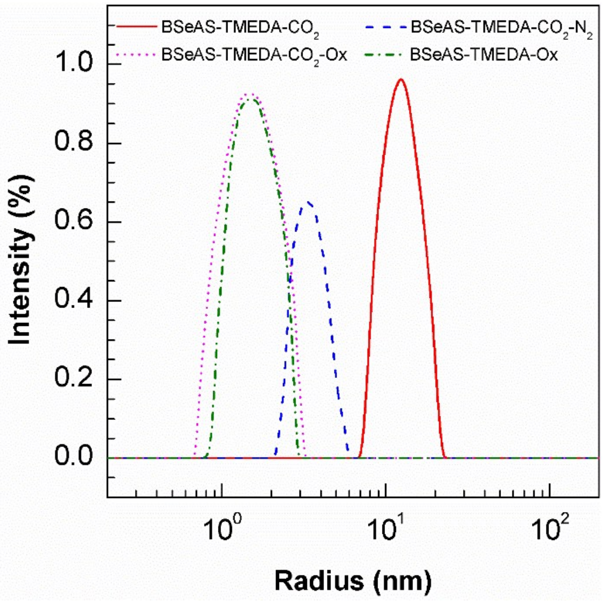

Figure S8. Size distribution of BSeAS-TMEDA-CO_2, BSeAS-TMEDA-CO_2-N_2, BSeAS-TMEDA-CO_2-Ox, and BSeAS-TMEDA-Ox.

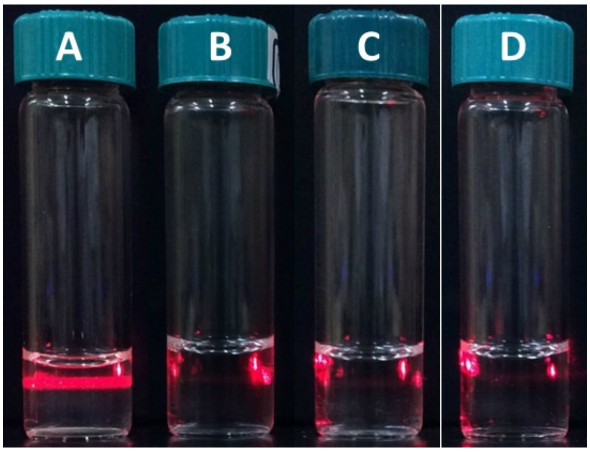

Figure S9. Tyndall phenomenon of (A) BSeAS-TMEDA-CO_2, (B) BSeAS-TMEDA, (C) BSeAS-TMEDA-CO_2-Ox, and (D) BSeAS-TMEDA-Ox.

When a laser pointer was used to illuminate these samples, typical Tyndall phenomena (Fig. S7) were clearly detected for BSeAS-TMEDA-CO_2, indicate of the presence large aggregates, but the red beam is more feeble in other three samples, implying smaller aggregates.[1]

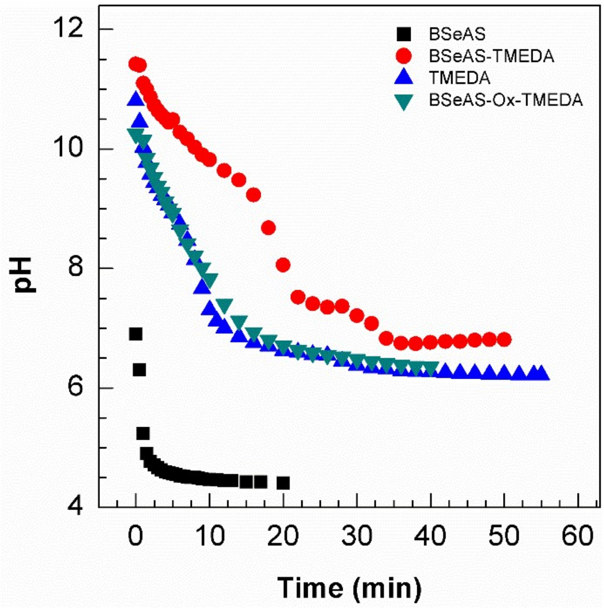

Figure S10. The variation of pH values of aqueous solution with bubbling of CO_2 at 25 °C.

With bubbling of CO_2, all the pH values decreases dramatically in the initial stage, and then tend to an equilibrium. For BSeAS-TMEDA, BSeAS-Ox-TMEDA and TMEDA, the pH values decrease from basic (> 10.0) to weak acidic (~7.0), which is mainly ascribed to the neutralization of TMEDA with H_2CO_3. While the pH of BSeAS decreases from 7.0 to 4.6 resulted from the dissociation of H_2CO_3. Such a deduction is further confirmed by the variation of conductivity.

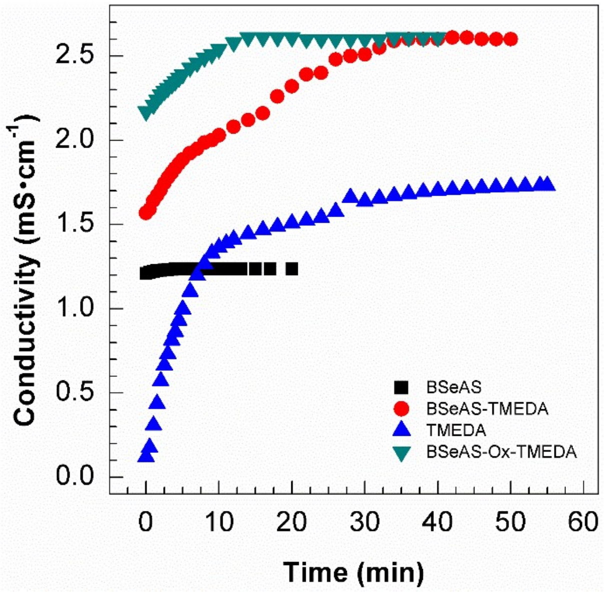

Figure S11. The variation of conductivity of aqueous solution with bubbling of CO_2 at 25 °C.

With bubbling of CO_2, all the conductivities show a rise except for BSeAS, implying the production of a large amount of charge species, i.e., the protonation of TMEDA.[2]

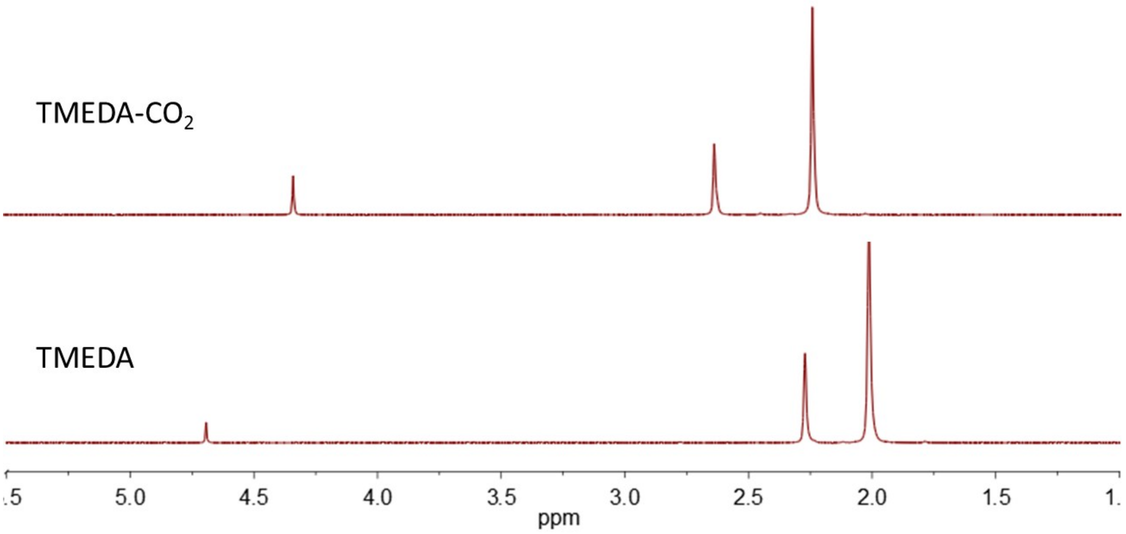

Figure S12. ^{1}H NMR spectra of TMEDA in the presence and absence of CO_2. D_2O is used as solvent.

When TMEDA is exposed to CO_2, the peaks assigned to the protons of methyl and methylene show obvious downfield shifts in ^{1}H NMR spectra, from 2.01 and 2.27 to 2.37 and 2.81, respectively. This means that the protonation of tertiary amine, resulting in increasing in environmental polarity.[2,3]

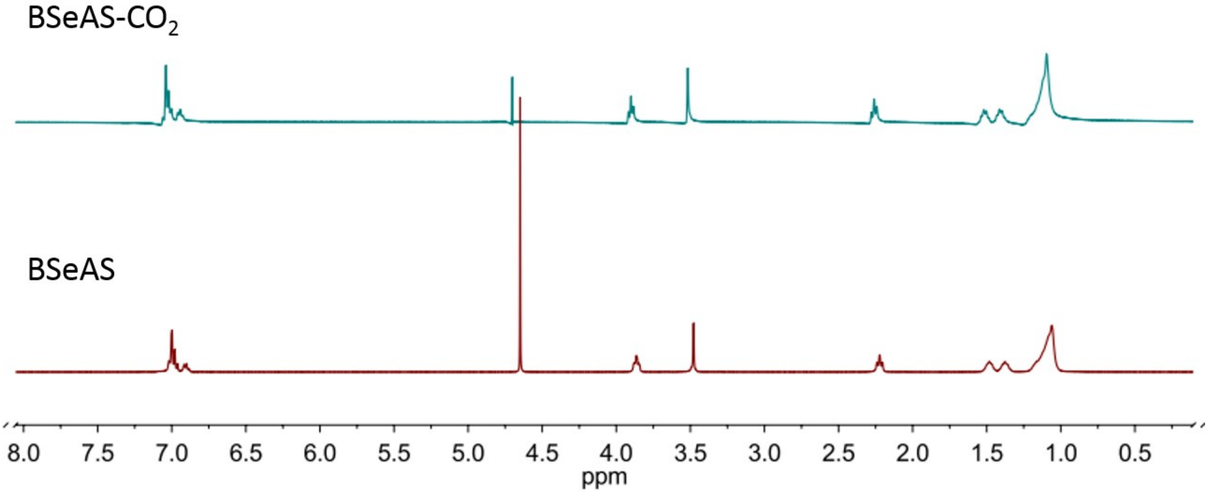

Figure S13. ^{1}H NMR spectra of BSeAS in the presence and absence of CO_2 using D_2O as solvent.

From Fig. S11 one can see that the bubbling of CO_2 does not cause the chemical shifts of BSeAS to change. It susggests that BSeAS is not CO_2-sensitive.

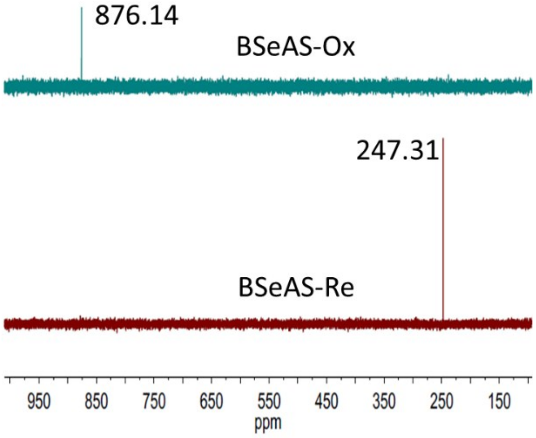

Figure S14. ^{77}Se NMR spectra of BSeAS in the reduced and oxidized forms using D_2O as solvent.

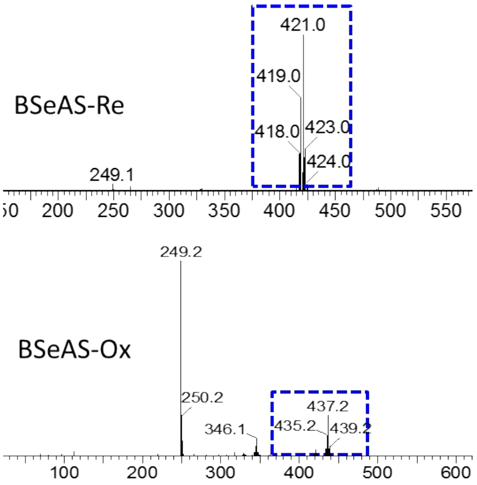

Figure S15. ESI-MS spectra of BSeAS in the reduced and oxidized forms using methanol as solvent.

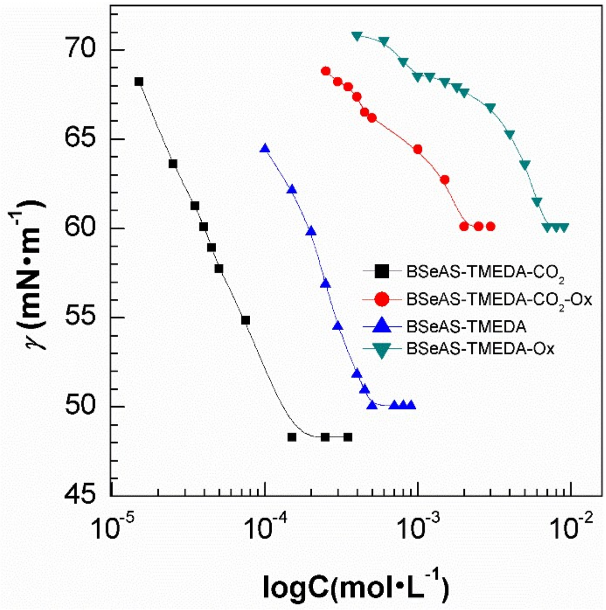

Figure S16. Variation in surface tension with surfactant concentration at 25 °C.

Exhibited in Figure S12 is the variation of surface tension against surfactants concentration in pure water at 25 °C. The surface tension decreases with increasing surfactant concentration, and then reaches a clear break point which is taken as the critical micelles concentration (*cmc*). However, note that is there are two break points in BSeAS-TMEDA-Ox and BSeAS-TMEDA-CO_2-Ox, which is generally observed in bola-type surfactants.[4]

The amount of adsorbed surfactant (Γ) at the air–water interface can be calculated using the Gibbs adsorption isotherm:[5]

$$\Gamma = -\frac{1}{\mathrm{n}RT}\left(\frac{\partial \gamma}{\partial \ln C}\right) \tag{1}$$

where R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), T is the absolute temperature (K), C is the surfactant concentration ($mol \cdot L^{-1}$), and $\partial\gamma / \partial \ln C$ refers to the slope below the *cmc* in the surface tension plots. The value of n that stands for the number of species at the interface was taken as 2 for BSeAS-TMEDA and BSeAS-TMEDA-Ox,[6] and 1 for BSeAS-TMEDA-CO_2 and BSeAS-TMEDA-CO_2-Ox because it can be considered a net zero charge.[7] The area occupied (A) by a surfactant molecule at the air–solution interface was obtained from the saturated adsorption as follows:

$$A = \frac{1}{N \cdot \Gamma_{cmc}} \tag{2}$$

where N is Avogadro's number, and Γ_{cmc} is the maximum surface excess concentration at *cmc*.

Table S1. Values of surface properties parameters of BSeAS-TMEDA under different conditions at 25 °C.

Surfactant	cmc ($mmol \cdot L^{-1}$)	γ_{cmc} ($mN \cdot m^{-1}$)	$10^6\Gamma_{max}$ ($mol \cdot m^{-2}$)	A_{cmc} ($nm^2 \cdot molecule^{-1}$)
BSeAS-TMEDA-CO_2	0.15	48.31	7.11	0.23
BSeAS-TMEDA-CO_2-Ox	2.04	60.10	1.81	0.92
BSeAS-TMEDA	0.49	50.21	7.29	0.23
BSeAS-TMEDA-Ox	6.99	60.14	4.02	0.41

As listed in Table S1, after oxidization with H_2O_2, the cmc exhibit obvious increase for either BSeAS-TMEDA-CO_2-Ox or BSeAS-TMEDA-Ox, and the γ_{cmc} also show a rise from 48.31 and 50.21 $mN \cdot m^{-1}$ to 60.10 and 60.14 $mN \cdot m^{-1}$, respectively. Such high equilibrium γ_{cmc} makes BSeAS-TMEDA-CO_2-Ox and BSeAS-TMEDA-Ox be only amphiphiles, not typical surfactant. More importantly, compared with reduced forms, the oxidized systems have a larger A_{cmc}, being agreement with that reported for bola-type surfactants.[4]

References

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