Supporting information (SI)

Switching wormlike micelles of selenium-containing surfactant using redox reaction**

Yongmin Zhang,* Weiwei Kong,a Cheng Wang,a Pengyun An,a Yun Fang,a Zhirong Qin,c Yujun Feng,b Xuefeng Liu*a

1 EXPERIMENTAL SECTION

1.1 Materials

Selenium powder, sodium borohydride, benzyl bromide, phosphorus tribromide, 33 wt% dimethylamine, 30% H2O2 and all other organic solvents used in this study were analytical-grade products from Shanghai Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was dried by CaH2 and distilled under normal pressure prior to use. 11-bromoundecanol, 1,3-propane sultone, ascorbic acid was purchased from Aldrich and used as received. Water was triply distilled by a quartz water purification system.

1.2 Synthesis of selenium-containing sulfobetaine surfactant (BSeUSBe)

The selenium-containing zwitterionic surfactant, 3-(11-Benzylselanyl-undecyl)-dimethyl ammonium propane sulfonate (BSeUSBe), was prepared by a 5-step process (Scheme S1) following a previously-reported procedure.

Scheme S1. Synthesis pathway for 3-(11-Benzylselanyl-undecyl)-dimethyl ammonium propane sulfonate (BSeUSBe).

1,2-dibenzyl diselane (DBDSe): Sodium borohydride (9.43g) in 75 mL of deionized water was added with magnetic stirring to 9.00g of Se suspended in 75 mL of deionized water at room temperature. After the initial vigorous reaction had subsided (30
min), one additional equiv of Se powder (9.00 g) was added. The mixture was continuous stirred for 20 min at 70 °C until Se powder was completely disappeared and the solution turned brownish red. After that a solution of 39.35 g benzyl bromide in 285 mL refined THF was injected into it under N₂ flow and the mixture was stirred for ca. 18 h at 50 °C. A yellow needle-like crystals, 1,2-dibenzylidiselenane (33.28 g, yield 85%), was collected by the recrystallization with ethyl acetate-hexane. IR (neat): $\nu = 2926.8, 2851.5, 1585.6, 1393.9, 1243.6, 1113.4, 1058.9 \text{ cm}^{-1}$; $^1$H NMR (400 MHz, CD$_3$Cl), $\delta$/ppm: 3.87 (s, 4H), 7.26~7.36 (m, 10H).

**Figure S1.** $^1$H NMR spectrum of 1,2-dibenzylidiselenane (DBDSe).

11-(benzylselanyl)undecan-1-ol (BSeUOH): 13.61 g DBDSe was dissolved in 100 mL refined THF and then added into 40 mL solution of 3.80 g sodium borohydride with magnetic stirring under the ice bath N₂ flow. After about 30 min 20.00 g 11-bromoundecanol in 100 mL THF solution was added. The reaction was performed at 50 °C for ca. 15 h. The product was extracted with CH$_2$Cl$_2$ and then was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$) gave BSeUOH (22.5 g, yield 80%) as white solid. IR (neat): $\nu = 2926.8, 2851.5, 1585.6, 1393.9, 1243.6, 1113.4, 1058.9 \text{ cm}^{-1}$; $^1$H NMR (400 MHz, CD$_3$OD), $\delta$/ppm: 1.27~1.32 (m, 14H), 1.49~1.62 (m, 4H), 2.46 (t, $J = 8.00$ Hz, 2H), 3.54 (t, $J = 6.40$ Hz, 2H), 3.76 (t, $J = 6.40$ Hz, 2H), 7.15~7.29 (m, 5H).

**Figure S2.** $^1$H NMR spectrum of 11-(benzylselanyl)undecan-1-ol (BSeUOH).

Benzyl(11-bromoundecyl)selane (BSeUBr): 0.85 mL phosphorus tribromide was added into 30 mL solution of 2.00 g BSeUOH. After stirring for 2 h at room temperature, the reaction was quenched with ice water. The mixture was extracted with CH$_2$Cl$_2$ and then was purified by flash column chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) gave BSeUBr.
(2.83 g, yield 70%) as yellow oil. IR (neat): ơ = 2926.8, 2851.5, 1585.6, 1393.9, 1243.6, 1113.4, 1058.9 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂), δ/ppm (Fig.1): 1.28 (d, 14H), 1.60~1.72 (m, 2H), 1.84~1.92 (m, 2H), 2.51 (t, ơ = 7.60 Hz, 2H), 3.43 (t, ơ = 6.80 Hz, 2H), 3.80 (t, ơ = 6.00 Hz, 2H), 7.2~7.3 (m, 5H).

**Figure S3.** ¹H NMR spectrum of benzyl(11-bromoundecyl)selane (BSeUBr).

**11-(benzylselanyl)-N,N-dimethylundecan-1-amine (BSeDMUA):** Under N₂ flow, 6.80 g BSeUBr was dissolved in 100 mL, and then added into 13.80 g 33 wt% dimethylamine aqueous solution. The mixture was stirred for ca. 20 h at room temperature. The solvent was removed under reduced pressure and 200 mL was added. The product was extracted with CH₂Cl₂ and then was purified by flash column chromatography (silica gel, CH₃OH) gave BSeDMUA (5.64 g, yield 91%) as orange oil. IR (neat): ơ = 2926.8, 2851.5, 1585.6, 1393.9, 1243.6, 1113.4, 1058.9 cm⁻¹; ¹H NMR (400 MHz, CD₃CN), δ/ppm: 1.26~1.40 (m, 16H), 1.56~1.63 (m, 2H), 2.12 (s, 6H), 2.18 (t, ơ = 7.60 Hz, 2H), 2.48 (t, ơ = 7.60 Hz, 2H), 3.77 (t, ơ = 6.00 Hz, 2H), 7.19~7.29 (m, 5H). ¹³C NMR (100 MHz, CDCl₃), δ/ppm: 24.12, 26.93, 27.53, 27.82, 29.13, 29.49~29.63, 29.95, 30.29, 45.54, 59.99, 126.54, 128.41, 128.79, 139.64.

**Figure S4.** ¹H NMR spectrum of 11-(benzylselanyl)-N,N-dimethylundecan-1-amine (BSeDMUA).
Figure S5. $^{13}$C NMR spectrum of 11-(benzylselanyl)-N,N-dimethylundecan-1-amine (BSeDMUA).

3-(11-Benzylselanyl-undecyl)-dimethyl ammonium propane sulfonate (BSeUSBe): 20mL acetone solution of 3.80 g 1,3-propane sultone was added into 40 mL solution of 5.70 g BSeDMUA with magnetic stirring. After refluxing for ca. 15 h, the resulting suspension was filtered, and the solid was washed with acetone (3 × 10 mL), and then the solid was recrystallized from the mixture of methanol-acetone. BSeUSBe(7.16 g, yield 94%) was obtained as a white solid. IR (neat): $\nu$ = 2926.8, 2851.5, 1585.6, 1393.9, 1243.6, 1113.4, 1058.9 cm$^{-1}$; $^1$H NMR (400 MHz, D$_2$O), $\delta$/ppm: 1.26 (d, 14H), 1.53~1.58 (m, 2H), 1.67 (s, 2H), 2.15~2.22 (m, 2H), 2.42 (t, $J = 7.20$ Hz, 2H), 2.94 (t, $J = 7.20$ Hz, 2H), 3.08 (s, 6H), 3.20~3.24 (m, 2H), 3.43~3.47 (m, 2H), 3.68 (s, 2H), 7.13~7.21 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$/ppm: 19.45, 22.72, 24.17, 26.35, 26.95, 29.08~29.40, 29.89, 30.24, 47.89, 50.75, 63.31, 64.39, 126.56, 128.42, 128.76, 139.60. ESI HRMS: Calcd: 492.2 (M + H$^+$). Found: m/z = 492.3.

Figure S6. $^1$H NMR spectrum of3-(11-Benzylselanyl-undecyl)-dimethyl ammonium propane sulfonate (BSeUSBe).
1.3 Characterization

$^1$H NMR spectra were recorded on a Bruker AV400 NMR spectrometer at 400 MHz. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the internal standard protons of tetramethylsilane (TMS). IR spectra were taken on a Nicolet MX-1E Infrared spectrophotometer (KBr pellet) and ESI HRMS spectra were obtained with the Bruker Daltonics Data Analysis 3.2 system.

1.4 Rheology

Rheological measurements were performed on a Physica MCR 302 (Anton Paar, Austria) rotational rheometer equipped with CC27 (ISO3219) concentric cylinder geometry with a measuring bob radius of 13.33 mm and a measuring cup radius of 14.46 mm. Samples were equilibrated at 20 °C for no less than 20 min prior to the experiments. Dynamic frequency spectra were conducted in the linear viscoelastic region, as determined from prior dynamic stress sweep measurements. All measurements were carried out in the stress-controlled mode, and CANNON standard oil was used to calibrate the instrument before the measurements. The temperature was controlled by a Peltier device, and a solvent trap was used to minimize water evaporation during the measurements.
1.5 Freeze-Fracture transmission electron microscopy

The morphology of organized assemblies was studied by transmission electron microscopy (TEM, JEOL Model JEM-2100). The freeze-fracture techniques were used for TEM sample preparation. Fracturing and replication were carried out with a freeze-fracture apparatus (Leica, EM BAF060) on a nitrogen-cooled support. The procedure is composed of the following main steps: sample preparation, freezing of the specimen, fracturing about 30 min at high vacuum of $10^{-5}$ Pa from $-115$ to $-95 \, ^{\circ}\text{C}$, replication of the fracture face with Pt–C vapor, and finally transmission electron microscopic investigation of the replicas.

1.6 UV-vis absorbance measurements

The absorbance of the BSeUSBe solutions before and after oxidation was measured on a double-beam UV-4802 UV-vis spectrophotometer (Unico, USA) at a temperature of 20 °C, which was controlled by a circulating water bath, over the wavelength range 190–600 nm. Pure water with Nile red was used as a reference.

1.7 Dynamic light scattering

DLS measurements were performed on a ALV/DLS/SLS-5022F (HOSIC LIMITED, Germany) with a 90° back scattering angle and He–Ne laser ($\lambda= 633$ nm). Samples were filtered with a 0.45 μm filter of mixed cellulose acetate to remove any interfering dust particles. To obtain the apparent hydrodynamic radius ($R_{\text{h,app}}$), the intensity autocorrelation functions were analyzed using CONTIN.

1.8 Determination of the critical micellar concentration by fluorescence spectroscopy

The critical micellar concentration ($cmc$) of was measured using a Varian Cary Eclipse spectrometer (Varian Inc. USA). The temperature of the cell holder was controlled by a Neslab circulating water bath. The fluorescence emission spectra were recorded from 350 to 500 nm. The excitation wavelength was set at 335 nm, and the excitation and emission slit widths were set to 10 and 2.5 nm, respectively. First, a concentrated stocked solution was prepared with pyrene-saturated distilled water, and then a series of solutions were prepared by diluting determined amounts of concentrated solutions with pyrene-saturated distilled water. All the measurements were performed at 20 °C.

1.9 Measurement of GPx activity taking TNB as a substrate

The GPx catalytic activity was monitored using 3-Carboxy-4-nitrobenzenethiol (TNB) as a glutathione alternative. The reaction was carried out at 20 °C in 1000 μL of phosphate buffer, containing EDTA, TNB, and GPx mimic. After preincubation for 5 min, the reaction was initiated by the addition of $H_2O_2$. The initial reduction rate was detected by UV absorption at 410 nm.

2.5 Small angle X-ray scattering (SAXS)

X-ray scattering measurements were performed using a SAXSessMC2 high flux small angle X-ray scattering instrument (Anton Paar, Austria, Cu-Kα, $\lambda= 0.154$ nm), equipped with a Kratky block-collimation system and using an image plate (IP) as the detector. The X-ray generator was operated at 40 kV and 50 mA. A standard temperature control unit (Anton-Paar TCS 120) connected to the SAXSess instrument was used to control the temperature and keep it at the desired level. Samples were transferred into standard quartz capillaries with a diameter of 1 mm. Both SAXS and WAXS scattering profiles were recorded simultaneously. An exposure time of 2 h was long enough to give a good signal-to-noise ratio. The scattering curve of pure water in the same type of capillary was recorded as a background. All of the data were normalized to the same incident primary beam intensity and corrected for background scattering from the capillary and water, according to the scattering of water in the
2 ADDITIONAL RESULTS

Figure S9. Oscillatory shear measurements of 50 mM BSeUSBe-SDS brine solution.

Figure S10. The apparent viscosity decay curves of 50 mM BSeUSBe-SDS brine solution with time after addition of H$_2$O$_2$. 
Figure S11. Snapshot of 50 mM single BSeUSBe or SDS brine solution before and after addition of H$_2$O$_2$.

Figure S12. Size distribution of 50 mM single-component BSeUSBe or SDS brine solution before and after oxidation.

Figure S13. Size distribution of 50 mM redox-responsive BSeUSBe-SDS brine solution.
Just as shown in Fig. 1, the scattering behavior of BSeUsBe-SDS is obvious modified upon addition of H$_2$O$_2$, and then after adding VC, the scattering behavior of BSeUsBe-SDS-Re can perfectly coincide with that of BSeUsBe-SDS. These SAXS results fully confirm the reversible redox-responsive behavior of the current system.

Furthermore, for BSeUsBe-SDS-Ox, BSeUsBe-SDS and BSeUsBe-SDS-Re, the low q scattering intensity and the calculated form factor P (q) reach zero q following q$^0$, q$^{-1}$ and q$^{-1}$ behavior, respectively. This means that the aggregates structures are spheroid and 1D rodlike\(^1\), respectively, i.e., redox-induced micellar structures transition.

However, the scattering behavior of BSeUsBe-SDS-Ox shows the spheroid core-shell type micelles, but the real-space pair-distance distribution function p (r) (Fig. 2) exhibits a dissymmetrical bell-shaped curve, indicating not typical spherical micelles\(^1\). Under the aid of SAXS engineer from Anton Paar, the micellar structures are confirmed to be vesicle, and the maximum radius is about 9 nm obtained from Fig. 2, which is far below that observed from FF-TEM and DLS (~100 nm).

The significant difference is mainly resulted from the sensitivity of the SAXS equipment (q$_{\text{min}}$=0.08 nm$^{-1}$, corresponding ~37 nm), while the vesicle presents in BSeUsBe-SDS-Ox is about 100 nm, beyond the maximum detection limits. Besides, the SAXS result is statistical, and all the micellar structures detected by equipment will have a contribution to the results.
Figure S16. ESI-MS spectra of BSeUSBe before and after oxidation.

Figure S17. Critical micelles concentration of BSeUSBe before and after oxidation.
Figure S18. Critical micelles concentration of BSeUSBe-SDS before and after oxidation.

Figure S19. 2D NOESY NMR spectra of BSeUSBe-SDS after oxidation.
Figure S20. $^1$H NMR spectra of single BSeUSBe, SDS and the mixture before oxidation.

Figure S21. $^1$H NMR spectra of single BSeUSBe-Ox, SDS and the mixture after oxidation.
Figure S22. UV absorbance at 410 nm vs time during the catalytic reduction of H$_2$O$_2$ using 3-Carboxy-4-nitrobenzenethiol (TNB) as reducing substrate.

Reference