Supporting Information

Aggregate evolution in aqueous solutions of a Gemini surfactant derived from Dehydroabietic Acid

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1. Synthesis

The detailed synthetic process, which is shown in Fig. 1, is described as follows.

1.1 Synthesis of 1-bromo-2-(2-bromoethoxy)ethane. Diethylene glycol (15.0 g, 0.141 mol) was added into a three-necked flask. PBr₃ (30.6 g, 0.113 mol) was added dropwise over a period of 1 hour at 0 °C. Then, the mixture was reacted at 50-60 °C for 12 hours. After cooling, the reaction mixture was diluted with CH_2Cl_2 . The organic layer was successively washed with water, NaHCO₃ solution and water. After drying with anhydrous Na₂SO₄, the resulting CH_2Cl_2 solution was evaporated under reduced pressure, and the crude product was purified on a silica gel column (300-400 mesh) using petroleum ether as the eluent. 1-Bromo-2-(2-bromoethoxy)ethane was obtained as a colorless liquid. Yield: 82.3%.

1.2 Synthesis of compound **2**. Purified dehydroabietic acid (40.0 g, 0.133 mol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added into a three-necked flask. Thionyl chloride (20.6 g, 0.173 mol) was added dropwise at 50 °C. Acidic gas was generated during this process, and it was adsorbed by a saturated NaOH solution. After the addition, the mixture was stirred at 72 °C for 2.5 hours. After cooling, the reaction mixture was evaporated under reduced pressure to remove the excessive thionyl chloride and obtain dehydroabietic chloride. The obtained dehydroabietic chloride (43.4 g, 0.136 mol) was dissolved into CH_2Cl_2 and added dropwise into a three-necked flask filled with 3-dimethylaminopropyl amine (15.3 g, 0.15 mol) and excessive

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trimethylamine at -5 °C. After the addition, the reaction continued for another 1.5 hours. The reaction mixture was then washed with alkaline water three times and extracted with CH₂Cl₂ two times. The extractions were combined and dried using anhydrous Na₂SO₄. The remaining solvent and triethylamine in the extracts were removed under reduced pressure. The residue was purified on a silica gel column (300-400 mesh) using petroleum ether/ethyl acetate (1:1) as the eluent. Compound **2** was obtained as yellow, viscous liquid after the removal of the solvent. Yield: 80.0%. **1.3** Synthesis of R-(EO)-E-R. 1-Bromo-2-(2-bromoethoxy)ethane (10.0 g, 0.043 mol), compound **2** (38.0 g, 0.099 mol) and 100 mL anhydrous ethanol were added into a single-necked flask. The mixtures were stirred at 80 °C for 72 hours. After cooling, the ethanol was removed under reduced pressure. The residue was recrystallized with ethanol and ethyl acetate three times. The final product was obtained as a white solid after being dried under vacuum at 50 °C. Yield: 59.5%.



Fig. S1. ¹H NMR spectrum of dehydroabietic acid (DMSO)



¹H NMR (400 MHz, DMSO) δ 12.15 (s, 1H, COOH), 7.16 (d, 1H, C14-1H), 6.98 (d, 1H, C13-1H), 6.85 (s, 1H, C11-1H), 2.88 – 2.68 (m, 3H, C8-2H, C15-1H), 2.30 (d, 1H, C4-1H), 2.03 (dd, 1H, C2-1H), 1.76 – 1.56 (m, 5H, C5-2H, C6-2H, C7-1H), 1.43 – 1.30 (m, 2H, C4-1H, C7-1H), 1.17





¹H NMR (400 MHz, DMSO) δ 7.71 (t, 1H, N21-1H), 7.16 (d, 1H, C14-1H), 6.96 (d, 1H, C13-1H), 6.83 (s, 1H, C11-1H), 3.19 - 2.93 (m, 2H, C23-2H), 2.87 - 2.61 (m, 3H, C8-2H, C15-1H), 2.26 (d, 1H, C4-1H), 2.18 (t, 2H, C25-2H), 2.10 (s, 6H, C27-3H, C28-3H), 2.02 (d, 1H, C2-1H), 1.76 – 1.57 (m, 4H, C5-2H, C6-2H), 1.52 (m, 2H, C24-2H), 1.43 – 1.21 (m, 3H, C4-1H, C7-2H), 1.16 (s, 3H, C19-3H), 1.14 (s, 3H, C18-3H), 1.13 (s, 6H, C16-3H, C17-3H).

(d, 6H, C16-3H, C17-3H), 1.15 (s, 3H, C19-3H), 1.13 (s, 3H, C18-3H).



Fig. S3. ¹H NMR spectrum of R-(EO)-E-R (DMSO)

¹H NMR (400 MHz, DMSO) δ 7.81 (t, 2H, N21-1H, N37-1H), 7.17 (d, 2H, C14-1H, C51-1H), 6.98 (d, 2H, C13-1H, C50-1H), 6.84 (s, 2H, C11-1H, C48-1H), 3.87 (s, 4H, C29-2H, C31-2H), 3.59 (s, 4H, C27-2H, C32-2H), 3.32 – 3.26 (m, 4H, C25-2H, C34-2H), 3.15 – 3.09 (m, 4H, C23-2H, C36-2H), 3.08 (s, 12H, C28-3H, C59-3H, C60-3H, C61-3H), 2.84 – 2.73 (m, 6H, C8-2H, C45-2H, C15-1H, C52-1H), 2.29 (d, 2H, C4-1H, C41-1H), 2.03 (d, 2H, C2-1H, C39-1H), 1.82 – 1.60 (m, 12H, C5-2H, C6-2H, C42-2H, C43-2H, C24-2H, C35-2H), 1.49 – 1.28 (m, 6H, C4-1H, C41-1H, C7-2H, C44-2H), 1.17 (s, 6H, C19-3H, C56-3H), 1.16 (s, 6H, C18-3H, C55-3H), 1.15 (s, 12H, C16-3H, C17-3H, C53-3H, C54-3H).



Fig. S4. HRMS spectrum of R-(EO)-E-R

HRMS (ESI): m/z calcd for C₅₄H₈₈N₄O₃²⁺ (M-2Br)²⁺ : 420.34227, found 420.34247. Elemental analysis: Calc. (%) for C₅₄H₈₈Br₂N₄O₃: C, 64.79; H, 8.86; N, 5.60. Found (%): C, 64.42; H, 9.17; N, 5.66.

2. The electrical conductivity of R-(EO)-E-R, 12-5-12 and 12-6-12



Fig. S5. Electrical conductivity curves of R-(EO)-E-R, 12-5-12 and 12-6-12 (25 °C)

3. The aggregation number of R-(EO)-E-R



Fig. S6. Variations in aggregation number of R-(EO)-E-R with the concentrations of CPC (25 °C) **4.** The thermodynamic performance of R-(EO)-E-R



Fig. S7. Heat flow of R-(EO)-E-R as a function of time at 25 °C



Fig. S8. Variations of the electrical conductivity with the R-(EO)-E-R concentration at 25 °C

5. The Rheological properties of R-(EO)-E-R solutions



Fig. S9. Variations of G' and G'' with shear frequency ω of R-(EO)-E-R aqueous solutions at different concentrations



Fig. S10. Cole-Cole plots of R-(EO)-E-R at different concentrations

6. The molecular simulation diagram of R-(EO)-E-R



Fig. S11. The 3D model of R-(EO)-E-R molecule optimized by Gaussian(white for H, ash for C, red for O, blue for N and claret for Br)