

Formation of asymmetric belt-like aggregates from a bio-based surfactant derived from dehydroabiatic acid

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1 Synthesis

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

1.1 Synthesis of compound 1. Purified dehydroabiatic acid (12 g, 0.04 mol) and a catalytic amount of DMAP was added into a 250 mL three-necked flask. Thionyl chloride (7.1 g, 0.06 mol) was added dropwise at 35°C. The acidic gas generated during reaction was absorbed by saturated NaOH solution. After the reaction was completed, dehydroabiatic chloride was obtained by removing excessive thionyl chloride under reduced pressure. The raw dehydroabiatic chloride dissolved in DCM was then added dropwise into a flask containing tert-Butyl (10-aminodecyl) carbamate (13 g, 0.048 mol) dissolved in DCM and excessive triethylamine at -10°C within 4 h. After the reaction was completed, the reaction mixture was washed by alkaline water (pH=12) three times. The remaining organic layer was separated and dried using anhydrous Na₂SO₄. After suction filtration, the remaining solvent in the filtrate was removed under reduced pressure. The residue was then purified on a silica gel column (300-400 mesh) using ethyl acetate as eluent. Compound 1 is obtained as a yellow, viscous liquid. Y=83.8%.

1.2 Synthesis of compound 2. 10 mL concentrated HCl was added dropwise into a flask filled with compound 1 dissolved in ethyl acetate at room temperature within 30 min. After the reaction was completed, saturated NaOH solution was added until the reaction mixture reached pH=12. The mixture was extracted with ethyl acetate twice. The extracts were combined and washed by alkaline water (pH=12) three times and then dried using anhydrous Na₂SO₄. After suction filtration, the solvent in the filtrate was removed under reduced pressure. Compound 2 was obtained as a yellow, viscous liquid.

1.3 Synthesis of compound 3. Formic acid solution (88%, 6.0 g, 0.115 mol) and formaldehyde solution (37%, 9.33 g, 0.115 mol) was added in sequence into a three-necked flask filled with compound 2 (17.4g, 0.0383 mol) which was dissolved in ethanol at room temperature. The

reaction mixture was stirred at 80°C for 8 h. After the reaction was completed, saturated NaOH solution was added until the reaction mixture reached pH=12. The mixture was extracted with ethyl acetate twice. The extracts were then combined and dried using anhydrous Na₂SO₄. After suction filtration, the solvent in the filtrate was removed under reduced pressure. Compound 3 was obtained as a light yellow, viscous liquid. Y=72.5%.

1.4 Synthesis of the compound R-10-AO. Compound 3 (14.0 g, 0.0289 mol), citric acid (catalytic amount) and EDTA-2Na (catalytic amount) was added into a three-necked flask filled with 200 mL ethanol. H₂O₂(30%, 10 g, 0.0868 mol) was added dropwise at 50°C. The mixture was stirred at 85°C for 5 h. When the reaction was finished, the solvent in the reaction mixture was removed under reduced pressure. The residue was then purified on a silica gel column (300-400 mesh) using ethyl acetate/methanol (5:1) as the eluent. R-10-AO was obtained as a light yellow, viscous liquid after removing solvent and being dried under vacuum at 40 °C. Y=88.4%

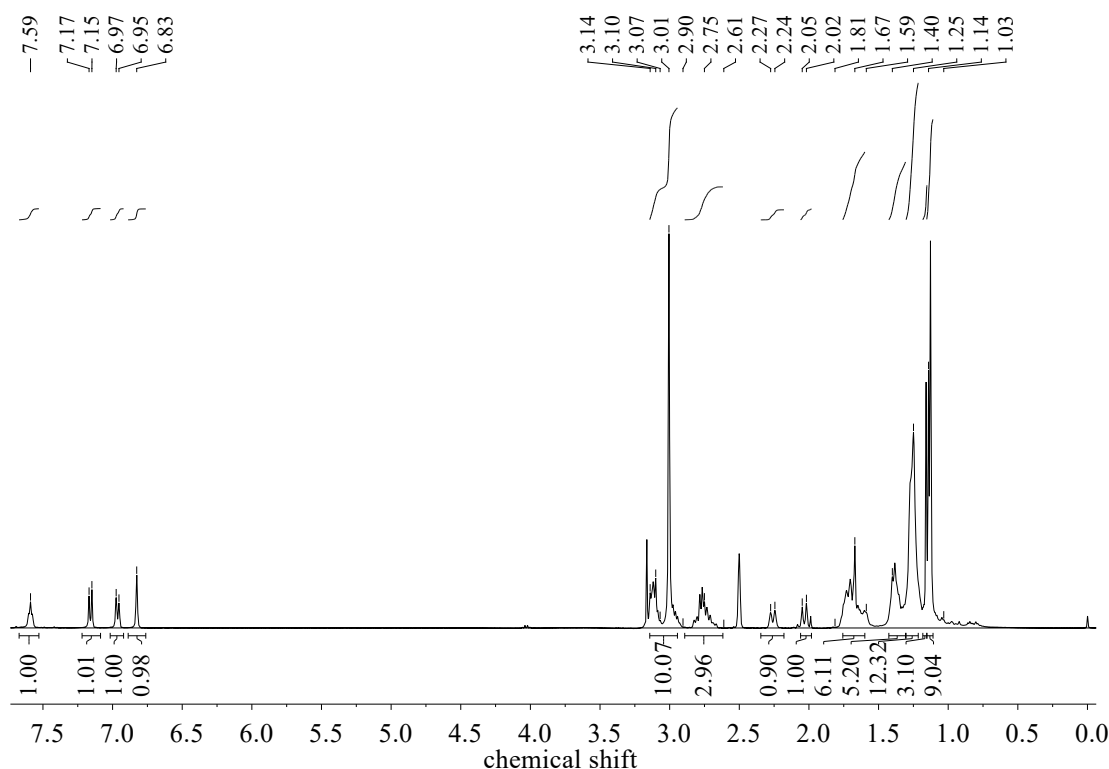
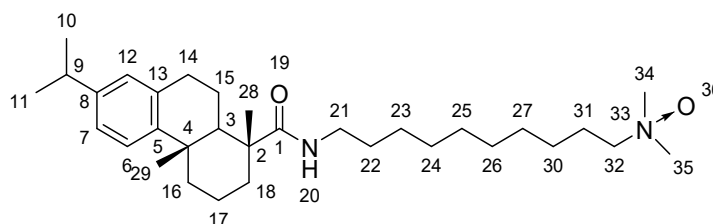


Figure S1 ¹H NMR spectrum of R-10-AO (in DMSO-d₆)



^1H NMR (400 MHz, DMSO) δ 7.59 (t, 1H, N20-1H) , 7.16 (d, 1H, C6-1H) , 7.03-6.92 (d, 1H, C7-1H) , 6.84 (s, 1H, C12-1H) , 3.14-2.90 (m, 10H, C32-2H, C21-2H, C34-3H, C35-3H) , 2.85-2.64 (m, 3H, C14-2H, C9-1H) , 2.26 (d, 1H, C16-1H) , 2.04 (d, 1H, C3-1H) , 1.77- 1.57 (m, 6H, C31-2H, C22-2H, C18-1H, C15-1H) , 1.59-1.40 (m, 5H, C17-2H, C15-1H, C18-1H, C16-1H) , 1.25 (m, 12H, C23-2H, C24-2H, C25-2H, C26-2H, C27-2H, C30-2H) , 1.16 (s, 3H, C29-3H) , 1.14 (d, 9H, C11-3H, C10-3H, C28-3H) . Elemental analysis. Calcd for $\text{C}_{32}\text{H}_{54}\text{N}_2\text{O}_2$: C, 77.06; H, 10.91; N, 5.62. Found: C, 76.93; H, 10.63; N, 5.51.

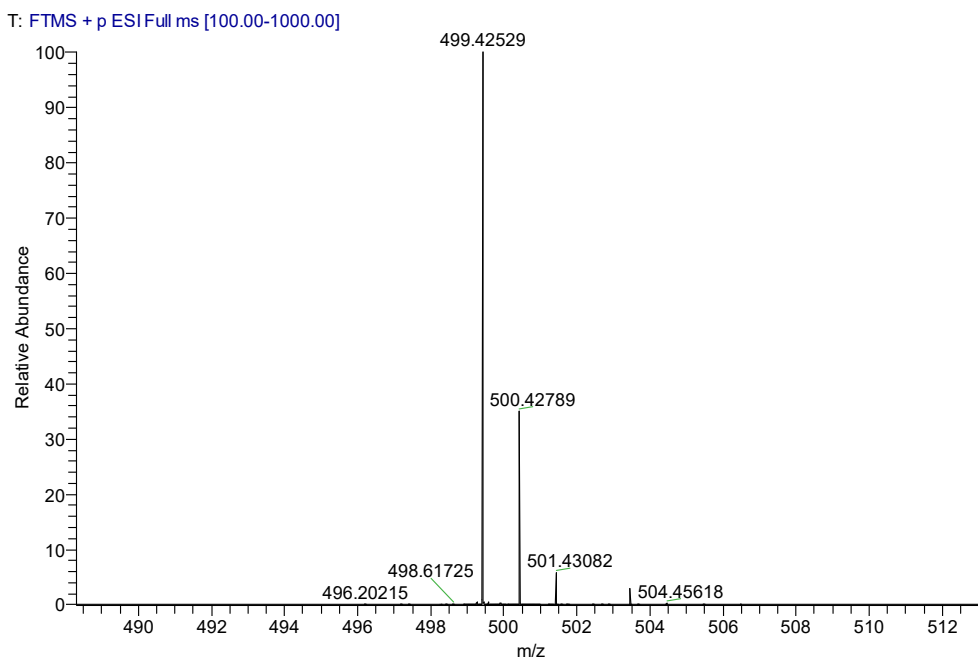


Figure S2 MS spectrum of R-10-AO

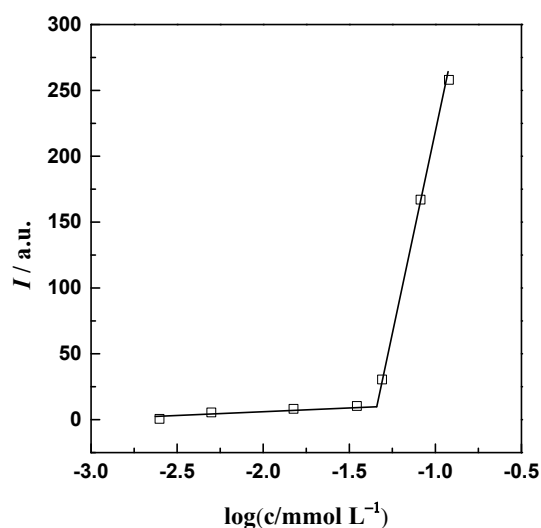


Figure S3 Intensity of Nile Red fluorescence for R-10-AO aqueous solutions with concentrations at 25 °C

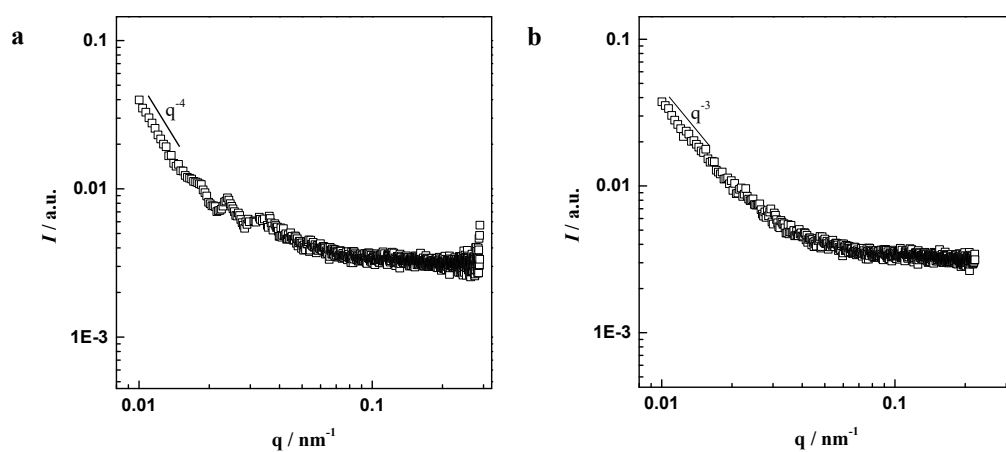


Figure S4 SAXS result (plots of scattering intensity I versus scattering vector q) measured at 25 °C for (a) 1 mM and (b) 2.5 mM R-10-AO solution.

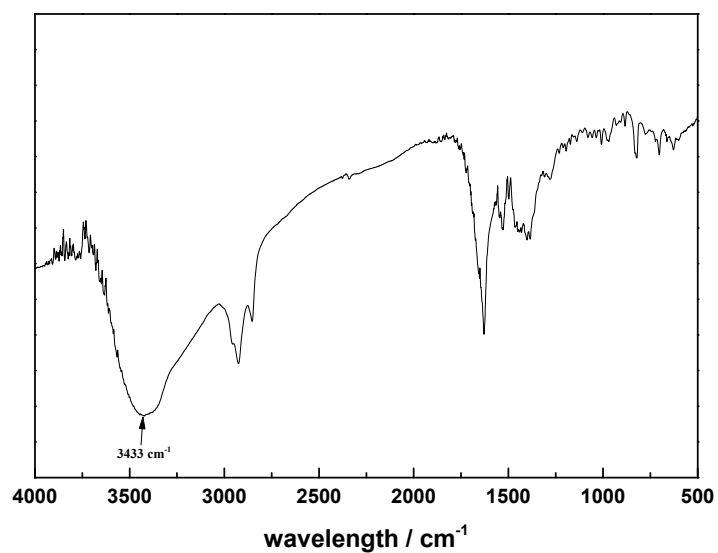


Figure S5 FT-IR spectrum of R-10-AO.

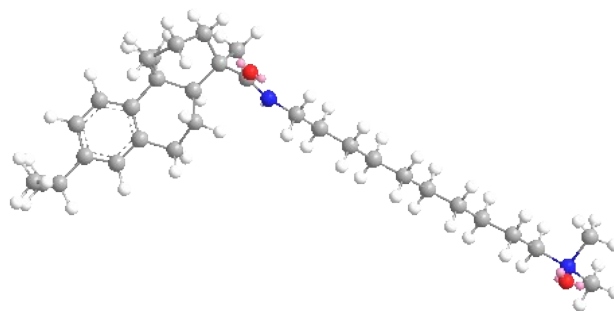


Figure S6 Optimised molecular configuration of R-10-AO