Electronic Supplementary Information for

Memorized chiral arrangement of gemini surfactant assemblies in nanometric hybrid organic-silica helices

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Experimental

Materials

1-Bromohexadecane, D-(–)-tartaric acid, and methyl orange (MO) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received. *N*,*N*,*N'*,*N'*-tetramethyl-ethylenediamine, acetonitrile (super dehydrated), L-(+)- and DL-tartaric acid, silver carbonate, and sodium bromide were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. Tetraethyl orthosilicate (TEOS) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA) and used as received. Other chemicals were also used without further purification. Millipore deionized water was used throughout this work.

Structure confirmation

Gemini surfactants with bromide and L- and D-tartrate counterions (16-2-16 2Br⁻ and Land D-tartrate, respectively) were synthesized according to a previously published method.¹⁴ The chemical structures of the synthesized gemini surfactants were confirmed by Fourier transform infrared spectroscopy (FTIR) measurements with a JASCO FT/IR-6300 FTIR spectrometer equipped with a JASCO ATR Pro450-S, proton nuclear magnetic resonance spectroscopy (¹H NMR) measurements with a Varian Unity/INOVA 400-MHz Fourier transform NMR spectrometer, and elemental analysis with an Elementar vario MICRO cube elemental analyser.

N,N'-Dihexadecyl-*N,N,N',N'*-tetramethylethylene diammonium dibromide (16-2-16 2Br⁻): White solid; FTIR (ATR): 2918, 2870, 2850, 1463, 1424, and 722 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.87 (6 H, t, *J* = 6.8 Hz, C*H*₃CH₂ × 2), 1.26 (48 H, s, CH₃(C*H*₂)₁₂ × 2), 1.39–1.41 (4 H, m, CH₃(CH₂)₁₂C*H*₂ × 2), 1.82 (4 H, m, CH₃(CH₂)₁₃C*H*₂ × 2), 3.24 (12 H, s, N⁺(C*H*₃)₂ × 2), 3.45–3.49 (4 H, m, CH₃(CH₂)₁₄C*H*₂ × 2), 4.01 (4 H, s, N⁺(C*H*₂)₂N⁺); EA (%): (Found: C, 62.69; H, 11.77; N, 3.80. Calculated for C₃₈H₈₂Br₂N₂: C, 62.79; H, 11.37; N, 3.81).

N,N'-Dihexadecyl-*N,N,N',N'*-tetramethylethylene diammonium L-tartrate (16-2-16 L-tartrate): White solid; FTIR (ATR): 3380, 2952, 2917, 2850, 1605, 1469, 1348, and 718 cm⁻¹; ¹H NMR (400 MHz, CD₃OD): δ 0.89 (6 H, t, *J* = 6.9 Hz, CH₃CH₂ × 2), 1.28 (48 H, s, CH₃(CH₂)₁₂ × 2), 1.40–1.41 (4 H, m, CH₃(CH₂)₁₂CH₂ × 2), 1.81–1.85 (4 H, m, CH₃(CH₂)₁₃CH₂ × 2), 3.20 (12 H, s, N⁺(CH₃)₂ × 2), 3.41 (4 H, m, CH₃(CH₂)₁₄CH₂ × 2), 3.92 (4 H, s, N⁺(CH₂)₂N⁺), 4.28 (2 H, s, (CH)₂); EA (%): (Found: C, 67.96; H, 11.89; N, 3.64. Calculated for C₄₂H₈₆N₂O₂·1.5H₂O: C, 67.97; H, 12.09; N, 3.78).

N,N'-Dihexadecyl-*N,N,N',N'*-tetramethylethylene diammonium D-tartrate (16-2-16 D-tartrate): White solid; FTIR (ATR): 3386, 2955, 2917, 2850, 1604, 1469, 1348, and 718 cm⁻¹; ¹H NMR (400 MHz, CD₃OD): δ 0.89 (6 H, t, *J* = 6.8 Hz, CH₃CH₂ × 2), 1.28 (48 H, s, CH₃(CH₂)₁₂ × 2), 1.40–1.41 (4 H, m, CH₃(CH₂)₁₂CH₂ × 2), 1.79–1.85 (4 H, m, CH₃(CH₂)₁₃CH₂ × 2), 3.20 (12 H, s, N⁺(CH₃)₂ × 2), 3.41 (4 H, m, CH₃(CH₂)₁₄CH₂ × 2), 3.92 (4 H, s, N⁺(CH₂)₂N⁺), 4.28 (2 H, s, (CH)₂); EA (%): (Found: C, 68.42; H, 11.94; N, 3.67. Calculated for C₄₂H₈₆N₂O₂·1.2H₂O: C, 68.47; H, 12.09; N, 3.80).

Sonication

An ultrasonic homogenizer (Branson Sonifier II model 250, Danbury, CT, USA) equipped with a 3.2 mm microtip was used for the dispersion of gemini surfactant–silica composites (maximum power 50 W, frequency 20 kHz). The samples (2 mL) were sonicated for 10 s (20% amplitude, 0.5 s pulse, 0.5 s pause) with cooling in an ice bath to prevent increase of the sample temperature.

Transmission electron microscopy observations

Transmission electron microscopy (TEM) observations were made with a JEOL JEM-1400Plus transmission electron microscope. Aqueous solutions of 16-2-16 L-tartrate (0.5 mM) aged for 24 h at 20 °C, 16-2-16 $2Br^-$ (0.5 mM) aged for 5 days at 20 °C, and the composite (0.3 or 0.5 mg mL⁻¹) in water at pH 3.0 prepared from the 16-2-16 L-tartrate aqueous solution were spotted onto carbon-coated copper grids. The samples were air-dried at room temperature by blotting excess solution using filter paper. The samples of bare 16-2-16 L-tartrate and $2Br^-$ were post-stained with 1 wt% aqueous uranyl acetate or osmium tetroxide using a Filgen osmium plasma coater OPC60A.

Zeta potential measurements

The zeta potentials of the gemini surfactant–silica composite and its calcine were measured at 20 °C with a Malvern Zetasizer Nano ZS.

Elemental analysis

The amount of gemini surfactant in the composites was estimated by elemental analysis. The freeze-dried composites were further dried at 120 °C for 3 h before analysis.

¹H NMR spectroscopy measurements

The chemical structure of the gemini surfactant in the composite was confirmed by ¹H NMR measurement. The gemini surfactant was extracted with hot methanol (55 °C) from the freeze-dried composite and then dried in a vacuum. The resulting solid was dissolved in deuterated methanol containing 0.03% tetramethylsilane (TMS) as an internal reference and measured at room temperature.

Differential scanning calorimetry measurements

The gel-to-liquid-crystalline phase transition temperatures (T_c 's) and transition enthalpies (ΔH 's) of the gemini surfactants in water before and after compositing were measured by differential scanning calorimetry (DSC) measurements with a Seoko Sii Exstar DSC7020 calorimeter. Encapsulated in a silver capsule, 15 μ L of aqueous solutions of the bare gemini surfactants (5.0 mM) and an aqueous dispersion of the composite (14.6 mg mL⁻¹) were scanned using a heating rate of 2.0 °C min⁻¹ from room temperature to 80 °C.

Ultraviolet-visible absorption and circular dichroism spectral measurements

Aqueous dispersions of the gemini surfactant–silica composites (5 mg mL⁻¹, pH 3.0) were added to MO aqueous solutions (0.04 mM, pH 3.0) and then subjected to ultraviolet–visible (UV–vis) absorption and circular dichroism (CD) spectral measurements using a JASCO J-820 spectropolarimeter equipped with a JASCO PTC-423L temperature controller. The samples in a 1.0 cm path length quartz cell were incubated in a sample holder for 5 min at 20 °C.

Calculation of the volume per cent of the interwall space in the silica matrix

The volume per cent of ~31 wt% 16-2-16 $2Br^{-}$ in the composite was calculated to be ~46 vol% from the densities of silica = 2.2 g cm⁻³ and the gemini surfactant = 1.05 g cm⁻³.¹⁵ From the values of the distance between the silica walls (around 6.5 nm) and the thickness of the silica walls (around 3.5 nm),¹⁵ the volume per cent of the interwall space was calculated to be 52 vol%, which almost corresponds to the volume per cent of the 16-2-16 Br⁻ molecules in the composite (~46 vol%).

Supplementary figures



Fig. S1 Zeta potential diagrams of gemini surfactant–silica composites in water at pH 3.0 before and after calcination at 600 °C for 3 h (temperature = 20 °C).

The 16-2-16 2Br⁻-silica composite showed good dispersibility in water at pH 3.0 (13 mV). Conversely, after removal of the residual gemini surfactant by calcination at 600 °C for 3 h, the calcine did not completely disperse at pH 3.0 because its hydroxyl groups were removed and it has no charge at this pH (0 mV).



Fig. S2 ¹H NMR spectrum of (a) the extract from the gemini surfactant–silica composite prepared from 16-2-16 L-tartrate washed with 100 mM sodium bromide aqueous solution and pure water and (b) the original 16-2-16 L-tartrate (400 MHz, CD_3OD , room temperature, TMS). The peak corresponding to the protons on the asymmetric carbons of the tartrate counterions of 16-2-16 L-tartrate appears at around 4.28 ppm.



Fig. S3 UV–vis absorption spectra of MO (0.04 mM) in water at pH 3.0 and 5.0 (temperature = 20 °C, path length = 1.0 cm).



Fig. S4 (a) UV–vis absorption and (b) CD spectra of MO (0.04 mM) in the presence of 0.06 mg mL⁻¹ composites containing gemini surfactant with L-tartrate and Br⁻ as counterions prepared from 16-2-16 L-tartrate in water at pH 3.0 (temperature = 20 °C, path length = 1.0 cm). The spectra are normalized to 0.04 mM MO. The composites contain around 29 wt% 16-2-16 L-tartrate and 31 wt% 16-2-16 2Br⁻, respectively.



Fig. S5 (a) UV-vis absorption and (b) CD spectra of MO (0.04 mM) in the presence of various concentrations of composite washed with methanol in water at pH 3.0 ([composite] = $0-0.20 \text{ mg mL}^{-1}$, temperature = 20 °C, path length = 1.0 cm). The spectra are normalized to 0.04 mM MO. The washed composite contains less than 1 wt% gemini surfactant.



Fig. S6 (a) UV–vis absorption and (b) CD spectra of MO (0.04 mM) in the presence of 0.06 mg mL⁻¹ composites prepared from 16-2-16 L-tartrate in water at pH 10.0 and 3.0 and alone in water at pH 10.0 (temperature = 20 °C, path length = 1.0 cm). The spectra are normalized to 0.04 mM MO.



Fig. S7 (a) Chemical structure of totally anionic cyanine (left) and porphyrin dyes (right) used in this study. (b) UV–vis absorption (top) and CD spectra (bottom) of cyanine (left) and porphyrin dyes (right) in the presence and absence of 0.06 mg mL⁻¹ composites prepared from 16-2-16 L-tartrate in water at pH 3.0 and alone in methanol ([cyanine] = 0.02 mM, [porphyrin] = 0.01 mM, temperature = 20 °C, path length = 1.0 cm). The spectra are normalized to 0.02 mM cyanine dye (left) and 0.01 mM porphyrin dye (right).



Fig. S8 (a) Chemical structure of crystal violet (left) and methylene blue (right). (b) UV–vis absorption (top) and CD spectra (bottom) of crystal violet (left) and methylene blue (right) in the presence and absence of 0.06 mg mL⁻¹ composites prepared from 16-2-16 L-tartrate in water at pH 3.0 and alone in methanol ([dye] = 0.02 mM, temperature = 20 °C, path length = 1.0 cm). The spectra are normalized to 0.02 mM dyes.



Fig. S9 (a) UV–vis absorption and (b) CD spectra of MO (0.04 mM) in the presence of 0.025 mM 16-2-16 L-tartrate and 0.06 mg mL⁻¹ 16-2-16 2Br⁻-silica composite (containing 0.025 mM 16-2-16 2Br⁻) prepared from 16-2-16 L-tartrate in water (pH = 5.8 for 16-2-16 L-tartrate and 3.0 for the composite, temperature = 20 °C, path length = 1.0 cm). The pH of the 16-2-16 L-tartrate aqueous solution was not adjusted to prevent ion exchange of the tartrate counterions with chloride anions.



Fig. S10 TEM images of 16-2-16 L-tartrate assemblies in water (a) without and (b) containing MO post-stained with (a) 1 wt% aqueous uranyl acetate or (b) osmium tetroxide and unstained composite prepared from 16-2-16 L-tartrate (c) without and (d) containing MO. (a) and (c) were taken from Fig. 1a and b, respectively. The samples for (b) and (d) were prepared from aqueous mixtures of (b) 0.5 mM 16-2-16 L-tartrate and 0.8 mM MO and (d) 0.3 mg mL⁻¹ composite (containing 0.125 mM 16-2-16 2Br⁻) and 0.2 mM MO.