Supplementary Information

Chirality induction on non-chiral dye-linked polysilsesquioxane in nanohelical structures

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Experimental

Materials

4,4'-Bis(triethoxysilyl)-1,1'-biphenyl (BS-BP) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA) and used as received. The cationic gemini surfactant with enantiomeric tartrate counterion (16-2-16 tartrate) was previously synthesized[1a] and used without further purification. Other chemicals were also used without further purification.

Structure confirmation

The chemical structures of the 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 (^{1}H NMR) measurements with a Varian Unity/INOVA 400-MHz Fourier transform NMR spectrometer and elemental analysis (EA) with an Elementar vario MICRO cube elemental analyser.

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}; ^{1}H NMR (400 MHz, CD_3OD): δ 0.89 (6 H, t, J = 6.9 Hz, $CH_3CH_2 \times 2$), 1.28 (48 H, s, $CH_3(CH_2)_{12} \times 2$), 1.40–1.41 (4 H, m, $CH_3(CH_2)_{12}CH_2 \times 2$), 1.81–1.85 (4 H, m, $CH_3(CH_2)_{13}CH_2 \times 2$), 3.20 (12 H, s, $N^+(CH_3)_2 \times 2$), 3.41 (4 H, m, $CH_3(CH_2)_{14}CH_2 \times 2$), 3.92 (4 H, s, $N^+(CH_2)_2N^+$), 4.28 (2 H, s, $(CH)_2$) ppm; EA: (Found: C, 67.96; H, 11.89; N, 3.64%. Calculated for $C_{42}H_{86}N_2O_2 \cdot 1.5H_2O$: 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}; ^{1}H NMR (400 MHz, CD_3OD): δ 0.89 (6 H, t, J = 6.8 Hz, $CH_3CH_2 \times 2$), 1.28 (48 H, s, $CH_3(CH_2)_{12} \times 2$), 1.40–1.41 (4 H, m, $CH_3(CH_2)_{12}CH_2 \times 2$), 1.79–1.85 (4 H, m, $CH_3(CH_2)_{13}CH_2 \times 2$), 3.20 (12 H, s, $N^+(CH_3)_2 \times 2$), 3.41 (4 H, m, $CH_3(CH_2)_{14}CH_2 \times 2$), 3.92 (4 H, s, $N^+(CH_2)_2N^+$), 4.28 (2 H, s, $(CH)_2$) ppm; EA: (Found: C, 68.42; H, 11.94; N, 3.67%. Calculated for $C_{42}H_{86}N_2O_2 \cdot 1.2H_2O$: C, 68.47; H, 12.09; N, 3.80%).

Differential scanning calorimetry measurements

The gel–sol transition temperature (T_{gel}) and transition enthalpy (ΔH) of 16-2-16 L-tartrate in a pyridine-water mixture (19:1 v/v) were measured using differential scanning calorimetry (DSC) measurement with a Seiko Sii Exstar DSC7020 calorimeter. Encapsulated in a silver capsule, 15 μL of the dispersion of 16-2-16 L-tartrate (20 mM) was scanned at a heating rate of 2.0 °C min^{-1} from 20 °C to 80 °C.

Low-voltage scanning transmission electron microscopy and scanning electron microscopy

Low-voltage scanning transmission electron microscopy (LV-STEM) and scanning transmission electron microscopy (SEM) observations were made with a HITACHI SU8000 scanning electron microscope. 16-2-16 tartrate (5.0 mM) in a pyridine-water mixture (19:1 v/v) aged for 24 h at 20 °C, biphenyl-linked polysilsesquioxane (BP–PSQ) containing 16-2-16 tartrate in the pyridine-water mixture, and washed and sonicated BP–PSQ in ethanol were spotted onto carbon-coated copper grids. The samples were air-dried at ambient temperature (25 °C) by blotting excess solution using filter paper. The sample of 16-2-16 tartrate for LV-STEM observation was post-stained and the sample of BP–PSQ containing 16-2-16 tartrate for SEM observation was coated with osmium tetroxide using a Filgen osmium plasma coater OPC60A.

Sonication

An ultrasonic homogenizer (Branson Sonifier II model 250, Danbury, CT, USA) equipped with a 3.2 mm microtip was used for BP–PSQ dispersed in ethanol (maximum power 50 W, frequency 20 kHz). The samples (2 mL) were sonicated for 3 min (20% amplitude, 0.5 s pulse, 0.5 s pause).

Powder X-ray diffraction analysis

X-ray diffraction (XRD) pattern of BP–PSQ were recorded on an X-ray diffractometer (SmartLab 9kW, Rigaku Corp.) using Cu Kα radiation with $\lambda = 0.15418$ nm operating at 45 kV and 200 mA. Freeze-dried BP–PSQ was mounted on a glass plate and scanned from 2 to 160° 2θ at a rate of 4° min^{-1}.

Simulation of molecular structure

Simulation of molecular structure of BP–PSQ was performed using a molecular modeling system (HyperChem, Hypercube Inc.). The molecular structure was optimized by the MM+ force field.

Ultraviolet–visible absorption and electronic circular dichroism spectral measurements

Ultraviolet–visible (UV–vis) absorption and electronic circular dichroism (ECD) spectral measurements of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) and BS-BP (0.05 mM) in ethanol were performed 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 a given temperature, and UV–vis absorption and ECD spectra were measured.

Fluorescence spectral measurement

Fluorescence spectral measurement of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) and BS-BP (0.05 mM) in ethanol was performed using a JASCO FP-6600 spectrofluorometer equipped with a JASCO EHC-573T temperature controller. The samples in a triangular quartz cell (1 × 1 cm) were incubated in a sample holder for 5 min at 20 °C, and fluorescence spectra were measured by the front-face method.

Circularly polarized luminescence spectral measurement

Circularly polarized luminescence (CPL) spectral measurement of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) dispersed in ethanol was performed using a JASCO CPL-200 spectrofluoropolarimeter 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, and CPL spectra were measured. Curve fitting of the obtained spectra was carried out using Voigt functions.

Fluorescence lifetime measurement

Time–resolved fluorescence lifetimes (τ) of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) and BS-BP (0.05 mM) in ethanol were measured using a fluorescence lifetime measurement system (Quantaurus-Tau C11367-01, Hamamatsu Photonics K.K.) at ambient temperature (25 °C). The detector was set to each emission maximum wavelength. The both samples were excited at 320 nm.

Fluorescence quantum yield measurement

BP–PSQ and BS-BP in ethanol were diluted to absorbance about 0.1 at each absorption maximum wavelength, and subjected to fluorescence quantum yield (ϕ) measurement using an absolute photoluminescence quantum yield measurement system (C9920-02, Hamamatsu Photonics K.K.) with a solution measurement jig (A10104-01, Hamamatsu Photonics K.K.) at ambient temperature (25 °C).

Infrared and vibrational circular dichroism spectral measurements

Infrared (IR) and vibrational circular dichroism (VCD) spectral measurements of freeze-dried BP–PSQ was performed using a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench. In this optical bench, the light beam was focused on the sample by a BaF_2 lens (191 mm focal length), passing an optical filter, a BaF_2 wire grid polarizer (Specac), and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1 mm focal length) onto a 1 × 1 mm^2 HgCdTe (ThermoNicolet, MCTA*

E6032) detector. The sample disks were prepared by mixing freeze-dried BP–PSQ with KBr powder and pressing at a pressure of 10 ton/cm^2 in vacuo. IR absorption and VCD spectra were recorded at a resolution of 4 cm^{-1}, by coadding 50 scans and 24000 scans (8h acquisition time), respectively. Since the sample preparation may induce molecular orientation, the KBr disks of powdered materials were placed on a rotating sample holder and the VCD spectra were obtained with the KBr disks rotated at four angles around the light beam axis (0°, 45°, 90° and 135°). The VCD spectra of the two enantiomers of freeze-dried BP-PSQ were obtained by averaging the four spectra. Baseline corrections of the VCD spectra were performed by subtracting the raw VCD spectra of a KBr disk without BP-PSQ powders. The photoelastic modulator was adjusted for a maximum efficiency in the mid-IR region at 1400 cm^{-1}. Calculations were performed via the standard ThermoNicolet software, using Happ and Genzel apodization, de-Haseth phase-correction and a zero-filling factor of one.

Supplementary figures

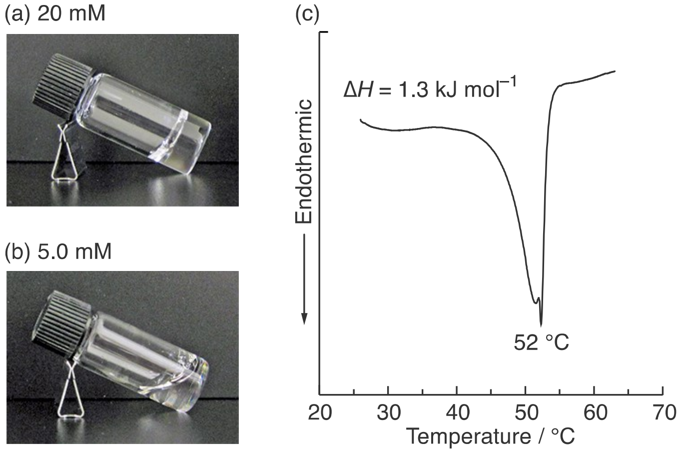

Fig. S1 Photographs of 16-2-16 L-tartrate in a pyridine–water mixture (19:1 v/v) at ambient temperature (25 °C); [16-2-16 L-tartrate] = (a) 20 and (b) 5.0 mM. (c) DSC thermogram of the heating process of 16-2-16 L-tartrate (20 mM) in a pyridine–water mixture (19:1 v/v); heating rate = 2 °C min^{-1}.

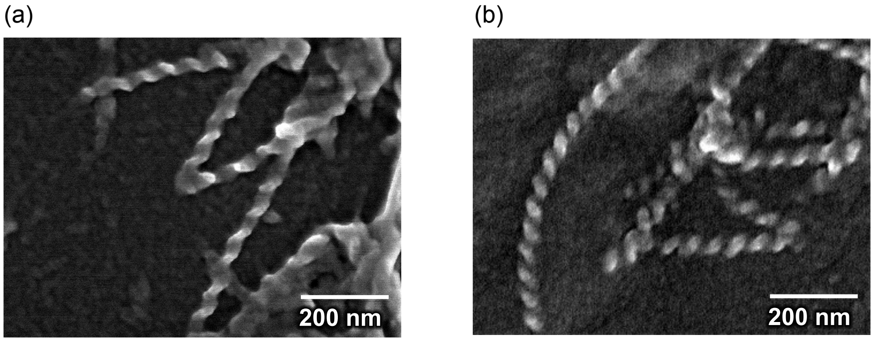

Fig. S2 SEM images of BP–PSQ containing 16-2-16 (a) L- and (b) D-tartrate before washing and sonication.

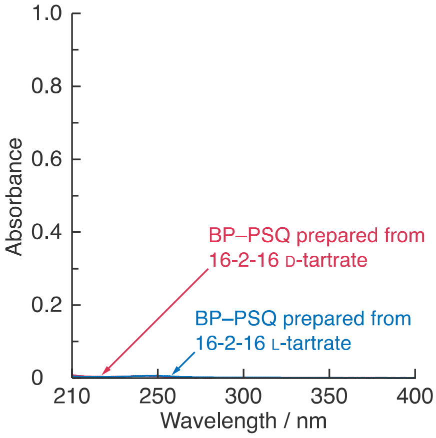

Fig. S3 UV-vis absorption spectra of last washing solution (methanol) for BP–PSQ prepared from 16-2-16 L- and D-tartrate at 20 °C; path length = 1.0 cm.

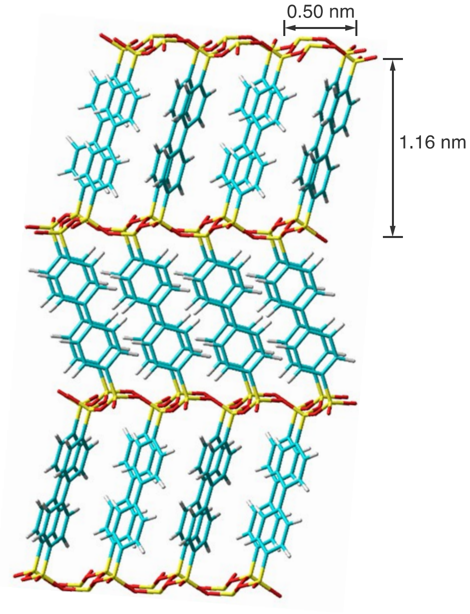

Fig. S4 Simulated model of the molecular structure of BP–PSQ.

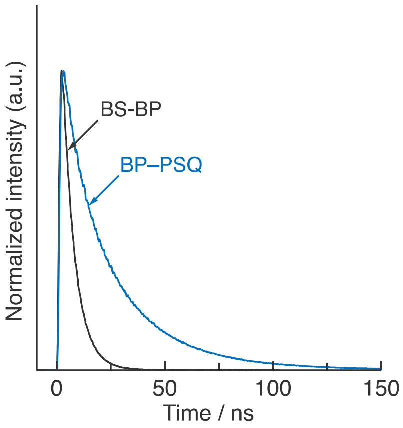

Fig. S5 Fluorescence decay profiles of BP–PSQ prepared from 16-2-16 L-tartrate and BS-BP in ethanol monitored at 384 and 312 nm, respectively; ambient temperature (25 °C), excitation wavelength = 320 nm.

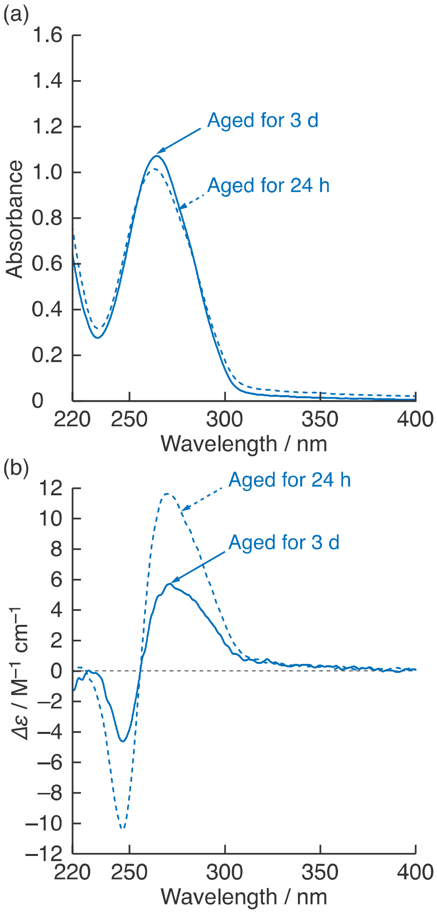

Fig. S6 (a) UV-vis absorption and (b) ECD spectra of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) prepared from 16-2-16 L-tartrate with different aging time of 24 h and 3 d during the sol–gel process in ethanol at 20 °C; path length = 1.0 cm.

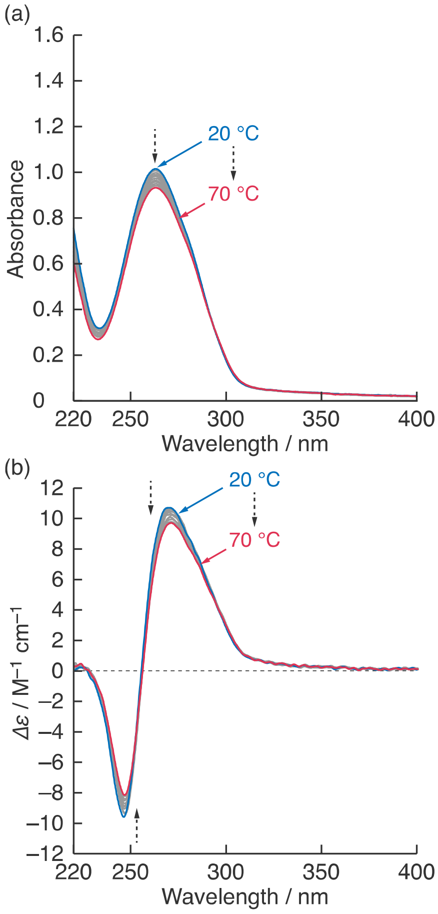

Fig. S7 (a) UV-vis absorption and (b) ECD spectra of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) prepared from 16-2-16 L-tartrate in ethanol at different temperature (20–70 °C); path length = 1.0 cm.

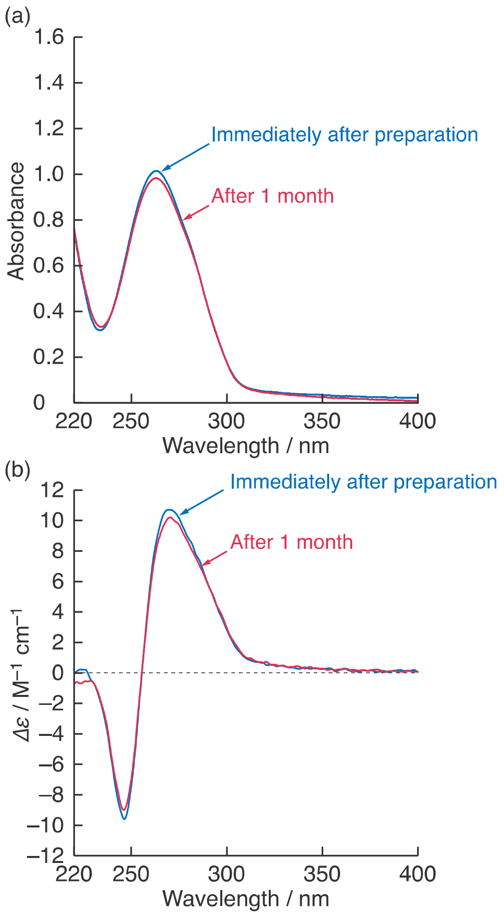

Fig. S8 (a) UV-vis absorption and (b) ECD spectra of BP–PSQ (0.05 mM as biphenyl-bis(silsesquioxane) unit) prepared from 16-2-16 L-tartrate in ethanol at 20 °C immediately after the sample preparation and after standing at 20 °C in the dark for 1 month from the preparation; path length = 1.0 cm.