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In situ helicity inversion of self-assembled nano helices

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Methods

Synthesis, 16-2-16 L-tartrate amphiphiles was obtained by ion exchange from complex of bromide counter anion after *in situ* formation of silver salt with tartrate in methanol solution. The cationic surfactant with bromide counter-anion as starting compound was synthesized from bromoalkane with tetramethylethylenediamine. The L-tartaric acid was mixed with silver carbonate (1 equiv.) to prepare silver L-tartrate in methanol and the mixture was stirred for 1 h at 25 ˚C. 16-2-16 bromide was added to the solution of silver L-tartrate and stirred for 30 min at 40 ˚C and filtered on Celite to obtain a colorless solution. After evaporation of methanol, the product was dissolved in a mixture of Chloroform/methanol (9/1, v/v), made precipitate with acetone, filtered, and dried.

Typical example of 16-2-16 L-tartrate *^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C, δ ppm)*: 4.23 (2H, s), 3.92 (4H, dm), 3.30 (4H, m), 3.10 (12H, d) 1.64 (4H, m), 1.22 (50H, m), 0.81 (6H, t) *^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C, δ ppm)*: 178.01, 66.10, 51.30, 32.47, 30.70, 30.53, 30.26, 30.20, 30.02, 29.90, 26.75, 23.23, 14.60

Ion exchange method

The 16-2-16 L-tartrate powder was solubilized in water at 50 °C (10 mM), then was cooled down to 21 ˚C. While cooling, the clear and fluid solution became increasingly opaque and viscous, then became gel with *P* tubular structures within an hour. On this gel, D-tartaric acid solutions with various equivalences of D-tartrate (1 eq, 2 eq, 4 eq, and 20 eq) were poured through. Due to the porosity of the gel network, excess liquid passed through the gel, and was collected through the hole at the bottom of the container. This gel was then rinsed with a large amount of milli-Q water to remove the excess tartaric acid, and the final concentration was adjusted to 10 mM. All this procedure from the addition of acid and rinsing took a few minutes and was performed at 21 ˚C.

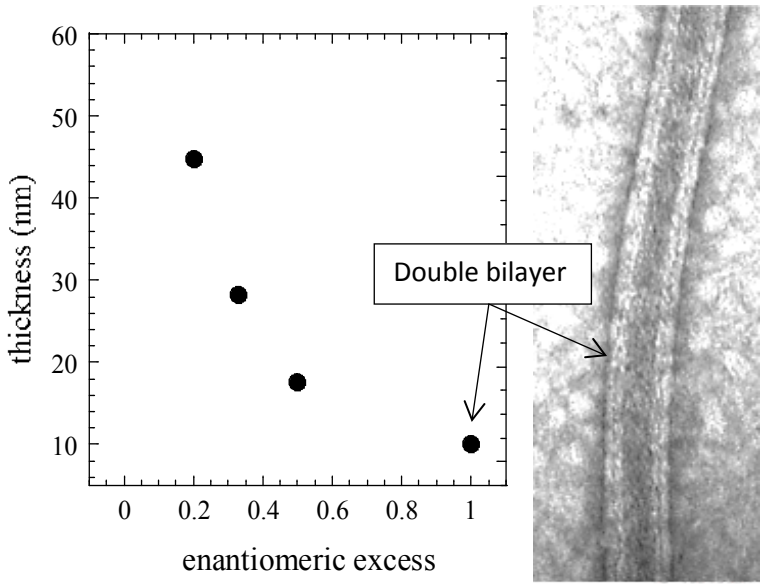
SAXS The experiments were performed on a Rigaku Nanoviewer (Micro-souce generator, MicroMax 007, 800 W rotating anode coupled with a Confocal Maxflux Mirror). The X-ray diffraction patterns were collected on an intensified CCD (Chip Charge-coupled Device) with a sample to detector distance of 422 mm, at exposure times of 30-45 min. The samples were prepared in Millipore water, at a concentration of 100 mM for 16-2-16 L-tartrate and D-tartaric acid solution were filtered through the gel network such a way that final ee's are 0, -0.33, -0.60, and -0.90. These samples were washed by water and removed the water immediately. Gels were put between two Mylar windows with spacer of 1 mm. The temperature of the samples was regulated at 20 ˚C unless indicated differently.

CD The circular dichroism measurement was performed on a JASCO J-815 CD spectrometer with data pitch of 0.1 nm, scanning speed of 100 nm/min, and quartz cuvette with optical path length of 0.1 mm for nucleoamphiphiles and 1 mm for 16-2-16 tartrate amphipihles were used. The spectra were measured for 10 mM gels.

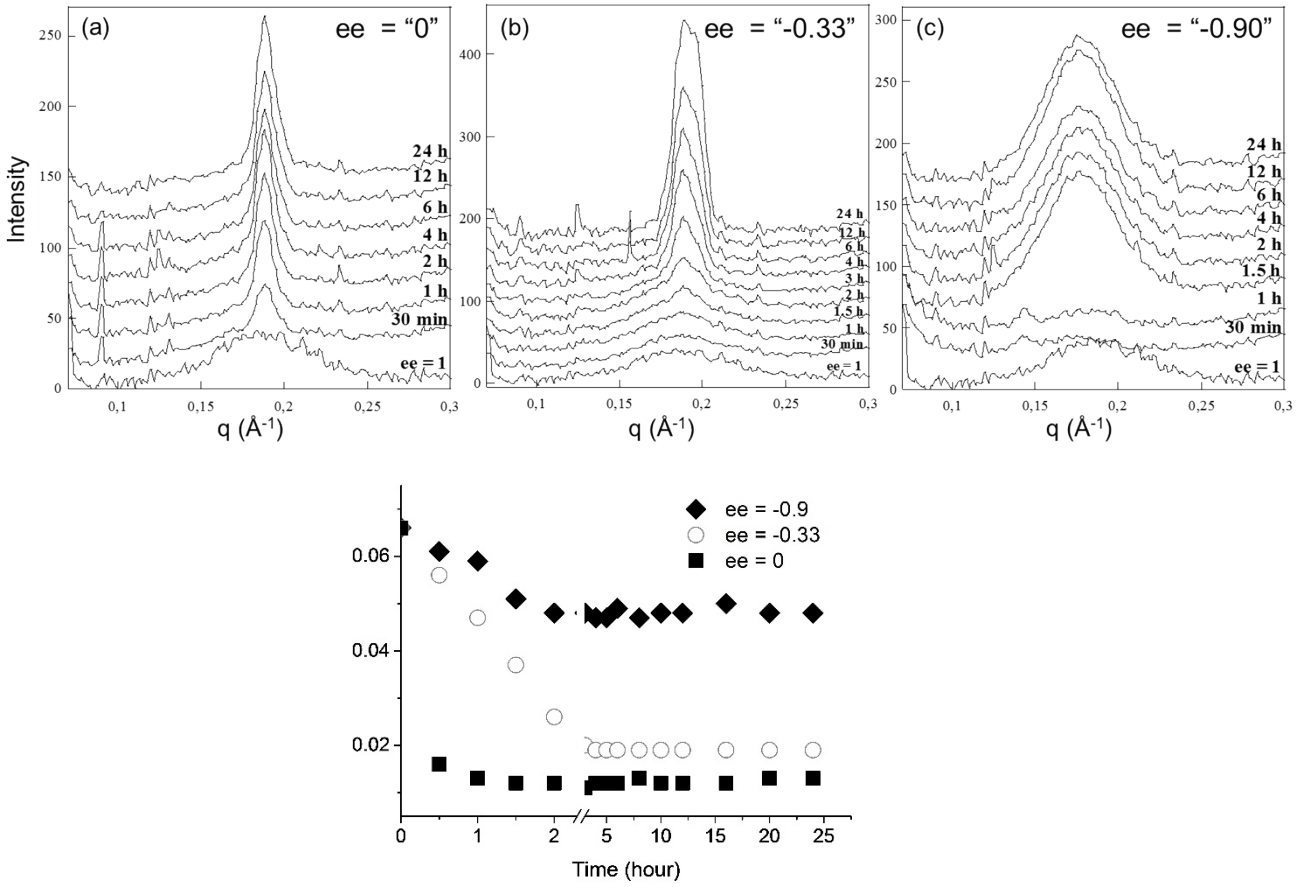
TEM A small drop of 16-2-16 tartrate samples in water was deposited on 400-mesh carbon-coated copper grid. After a few minutes, the excess liquid was blotted with filter paper. These air-dried specimens were stained by applying a small drop of a 0.2 wt% uranylacetate aqueous solution and removed the excess solution with a filter paper. The samples were then metallized by platinum (at an

angle 10 °) using vacuum chamber (Balzers). The replication was done for 20 sec. TEM observation were performed using a Philips EM 120 electron microscope operating at 120 kV and the images were collected by 2k × 2k Gatan ssCCD camera.

ROA. ROA spectra were recorded at ambient temperature on a ChiralRAMAN spectrometer (BioTools, Inc), equipped with a Millennia PRO 2sJ (Spectra-Physics) diode-pumped solid-state laser (Nd:YV04) operating at 532 nm. This spectrometer employs backscattering geometry and scattered circular polarization (SCP) setup as designed by W. Hug.[i] The ROA spectra are presented as intensity differences (I_R-I_L), with I_R and I_L denoting the Raman scattered intensities with right- and left-circular polarization states, respectively. After addition of D-tartaric acid and rinsing with water, the gel (10 mM) was filled into ROA fused silica microcell (4 × 3 × 10 mm , BioTools, Inc). The power of the laser was 500 mW (~ 200 mW at the sample). Each presented spectrum is an average over about 1 h of spectra of 15 min acquisition time, corresponding to 704 scans. The exposure time was 1 s to prevent saturation of the CCD detector. ROA spectra were collected in the range 2500-100 cm^{-1} with spectral resolution of about 7 cm^{-1}. All measured spectra were exported into the Origin 7.5 software package for data treatment and figure preparation. After removing the artifact spikes (false CCD detector signal, coming from cosmic rays), the ROA spectra were averaged, smoothed (adjacent average over 5 points), and baseline corrected.



The membrane thickness (number of bilayers ~ thickness/5 nm) of chiral fiber of 16-2-16 tartrate increase with decreasing ee. The TEM image shows the tubules (ee=1) formed with double bilayers



SAXS intensities as a function of time for ee = "0", "-0.33", "-0.9", and FWHM of the SAXS peak at q ~ 0.185 Å^{-1} with ee from 1 to 0, 1 to -0.33, 1 to -0.60 and 1 to -0.90

[i] a) W. Hug, G. Hangartner, *J. Raman Spectrosc.* **1999**, *30*, 841-852. b) W. Hug, *Appl. Spectrosc*. **2003**, *57*, 1-13.