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Supporting Information for

Switching Chirality in the Assemblies of Bio-based Amphiphiles Solely by Varying their Alkyl Chain Length

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Contents

1. Materials

D-Sorbitol (purity ⩾ 99%), n-Octylamine (99%), 1-Aminodecane (98%), 1-Dodecylamine (98%), 1-Hexadecylamine (90%), D_2O (99.9%), $CDCl_3$ (99.8%) were purchased from Acros and used without any further purification. Pyrene was purchased from Aldrich and recrystallized from ethanol before used. Acetyl bromide (purity > 98%), D-(-)-Tartaric acid (D-TA) (99%) and L-(-)-Tartaric acid (L-TA) (99%) were provided by Alfa Aesar China (Shanghai) Co., Ltd. Methanol (A. R. grade), ethanol (A. R. grade), 1,4-dioxane (A. R. grade), dichloromethane (A. R. grade), aetone (A. R. grade) were obtained from Sinopharm Chemical Reagent Co., Ltd.

2. Synthesis and characterization of sorbitol-alkylamides SAAS-C_m (m = 8, 10, 12, 16)

Synthesis

The procedures to prepare intermediate 1,6-dibromosorbitol **(1)** was similar to that reported.[1] In the experiments, acetyl bromide (1.1 mL; 13.6 mmol) was added dropwise to a suspension of D-sorbitol (1.11 g; 6.1 mmol) in 1,4-dioxane (16 mL) solution in ice bath. Then the mixture was stirred at 18 °C for 48 h. After the reaction, the product was extracted with dichloromethane and dried by anhydrous $MgSO_4$, and the intermediate **(1)** was obtained after removing of the solvent. The yield of the 1,6-dibromosorbitol **(1)** was 85%.

The procedures for preparation of SAAS-C_m are discussed taking SAAS-C_{12} as the example. In the experiment, 0.01 mol (3.08 g) of 1,6-dibromosorbitol **(1)** was added into methanol solution containing 0.022 moles of 1-dodecylamine. The mixture was stirred at 35 °C for 48 h. Then the mixture was concentrated in vacuum to afford residue which was recrystallized with ethanol/acetone for three times, giving the product as bright yellow powder in 73% yield. The procedures to prepare SAAS-C_8, SAAS-C_{10} and SAAS-C_{16} were similar, and the main difference was that the corresponding alkylamines were used, respectively. The product of SAAS-C_8 is white powder in 57% yield; SAAS-C_{10} is bright yellow powder in 62% yield; SAAS-C_{16} is white powder in 58% yield, respectively.

Characterizations

^{1}H NMR spectra for variations in chemical shifts were obtained on a proton frequency of 600.13 MHz spectrometer in D_2O at 25 °C. ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer in $CDCl_3$. MS spectra were determined with BEFLEX III for MALDI-TOF mass spectrometer.

(2S, 3R, 4R, 5R) -1, 6-bis(octylamino)hexane-2,3,4,5-tetraol (SAAS-C_8): ^{1}H-NMR (600 MHz, D_2O): δ = 0.76-0.78 (t, J = 6.0 Hz, 6H, -CH_3), 1.19-1.21 (m, 24H,), 1.23-1.29 (m, J = *12.0, 6.0* Hz, 4H), 1.54-1.59 (m, 4H), 2.88-2.91 (m, J = 6.0 Hz, 4H); ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 40.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 27.6, 25.5, 22.6, 14.1; MALDI-TOF-MS $(M+Na)^+$: Calcd. for $C_{22}H_{48}N_2O_4$: 404.3. Found: 427.6.

(2S, 3R, 4R, 5R) -1, 6-bis(decylamino)hexane-2,3,4,5-tetraol (SAAS-C_{10}): ^{1}H-NMR (600 MHz, D_2O): δ = 0.77-0.79 (t, J = 6.0 Hz, 6H), 1.20-1.22 (m, 32H), 1.24-1.30 (m, J = *12.0, 6.0* Hz, 4H), 1.56-1.60 (m, 4H), 2.89-2.92 (m, J = 6.0 Hz, 4H); ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 40.2, 31.8, 29.5, 29.4, 29.3, 29.0, 27.5, 26.6, 14.1; MALDI-TOF-MS $(M+H)^+$: Calcd. for $C_{26}H_{55}N_2O_4$: 460.4. Found: 461.5.

(2S, 3R, 4R, 5R)-1,6-bis(dodecylamino)hexane-2,3,4,5-tetraol (SAAS-C_{12},): ^{1}H-NMR (600 MHz, D_2O): δ = 0.77-0.79 (t, J = 6.0 Hz, 6H), 1.20-1.22 (m, 44H), 1.23-1.30 (m, 4H), 1.54-1.59 (m, J = *12.0, 6.0* Hz, 4H), 2.89-2.91 (m, J = *12.0, 6.0* Hz, 4H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ = 58.3, 41.2, 31.9, 29.67, 29.66, 29.56, 29.38, 29.3, 26.8, 22.7, 14.1; MALDI-TOF-MS $(M+H)^+$: Calcd. for $C_{30}H_{64}N_2O_4$: 516.4. Found: 517.6.

(2S, 3R, 4R, 5R)-1,6-bis(hexadecylamino)hexane-2,3,4,5-tetraol (SAAS-C_{16},): ^{1}H-NMR (600 MHz, D_2O): δ = 0.82-0.83 (t, J = 6.0 Hz, 6H), 1.09-1.20 (m, 56H), 1.75-1.78 (m, 4H), 3.11-3.13

(d, J = 5.0, 2H), 3.41(s, -OH), 3.56-3.57 (m, 2H), 3.79 (m, 1H), 3.88 (m, 1H); ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 58.4, 41.5, 31.9, 31.8, 29.72, 29.68, 29.47, 29.6, 29.38, 27.2, 25.8, 22.7, 14.1; MALDI-TOF-MS $(M+H)^+$: Calcd. for $C_{38}H_{80}N_2O_4$: 628.6. Found: 629.7, 611.5.

3. Characterizations of the self-assembly behaviors of SAAS-C_m

Fluorescence spectroscopy study with pyrene as the probe: Pyrene was employed as fluorescence probes at the concentration of 1 μM and the sample solutions were stirred at room temperature overnight before measurement. Steady-state fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorometer using a xenon lamp as the excitation source at ambient temperature. The emission spectra scanned for Pyrene from 350 to 550 nm using a 335 nm excitation wavelength. The width of emission slit was 2.5 nm. The ratio of the intensities of the third (384 nm) to the first (373 nm) vibronic peak (I_1/I_3) in the emission spectra are sensitive to the environment polarity, which are frequently used for the determination of aggregate polarity and critical micelle concentration (cmc),[2] as showed in Fig. S1.

Transmission electron microscopy (TEM) charaterization: TEM micrographs were obtained with a JEM-1011 transmission electron microscope (working voltage of 100 kV) by the negative-staining method with uranyl acetate solution (1%) as the staining agent.

Small Angel X-ray Scattering (SAXS): The apparatus and procedures for the SAXS study were similar to that used previously.[3] Briefly, the experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility (BSRF) at 25 °C. The data were collected using a CCD detector (MAR) with maximum resolution of 3450×3450 pixels. The wavelength of X-ray was 1.54 Å, and the distance of the sample to detector was 1.57 m. In a typical experiment, the sample was added into the sample cell, and the X-ray scattering data were recorded. The 2-D SAXS images were obtained from the detector and then transformed into the profiles of intensity vs wavevector (q) by the software FiT2D. The pair-distance distribution function $p(r)$ was obtained from SAXS data using Gnom application software.[4] The indirect Fourier transform (IFT) is a model independent method to obtain information on the scattering object by generating a pair distance distribution function $p(r)$ of a scattering particle. The obtained $p(r)$ is shown in Fig. S2.

Atomic Force Microscopy (AFM) Imaging. The AFM images were obtained on a Dimension Fast Scan (Bruker) using Scan Asyst mode under ambient conditions. Standard silicon AFM probes (FASTSCAN-B) with cantilever spring constants of 4 N/m and resonance frequencies around 400 kHz were used for the scan. The AFM samples were prepared by dropping solutions onto a mica sheet.

Circular dichroism spectroscopy (CD): All circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. Samples were scanned from 550 to 180 nm at a rate of 1000 nm min^{-1}. The CD spectra of SAAS-C_m with tartaric acid (TA) enantiomer and various ee values of enantiomeric mixtures in desired concentration were recorded.

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H NMR spectra for variations in chemical shifts were obtained on a proton frequency of 600.13 MHz spectrometer in D_2O at 25 °C. For assuring complete recovery of magnetization vector, a small pulse flip-angle 30 ° was used rather than 90 ° in the conventional single pulse sequence.

4. Results

Fig. S1 shows variation of intensity ratio I_1/I_3 with SAAS-C_m concentration in aqueous solution. The critical micelle concentration (cmc) values of SAAS-C_8, SAAS-C_{10}, SAAS-C_{12}, and SAAS-C_{16} obtained from the curves are 2.2 mM, 1.0 mM, 0.04 mM, and 0.03 mM, respectively. The I_1/I_3 ratios decreased quickly after the cmc, indicating the formation of hydrophobic microdomains.

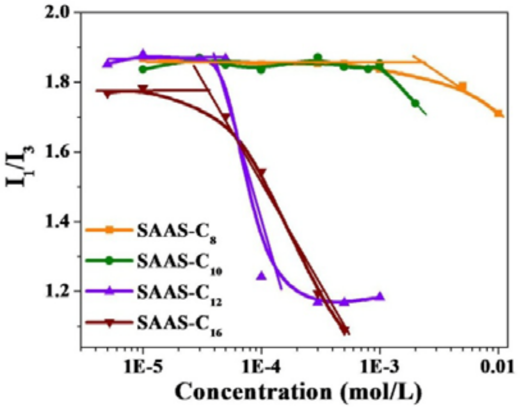

Fig. S1. The I_1/I_3 plots as a function of concentration for SAAS-C_m systems at 25 °C.

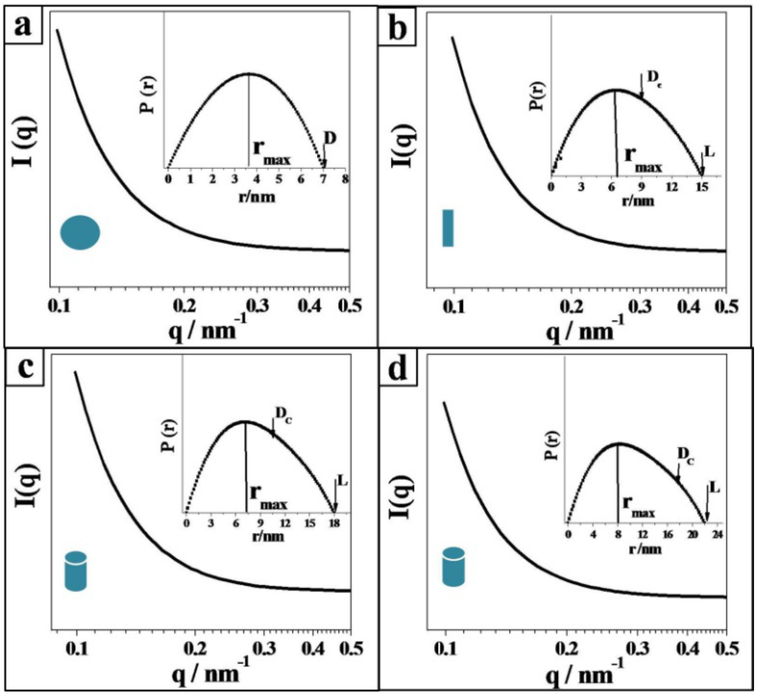

Fig. S2. The pair-distance distribution function *p*(*r*) obtained from SAXS curves of the nanostructures formed in SAAS-C_m (m= 8, 10, 12, 16) aqueous solutions. a) SAAS-C_8, 5.0 mmol/L; b) SAAS-C_{10}, 5.0 mmol/L; c) SAAS-C_{12}, 1.0 mmol/L; d) SAAS-C_{16}, 0.5 mmol/L.

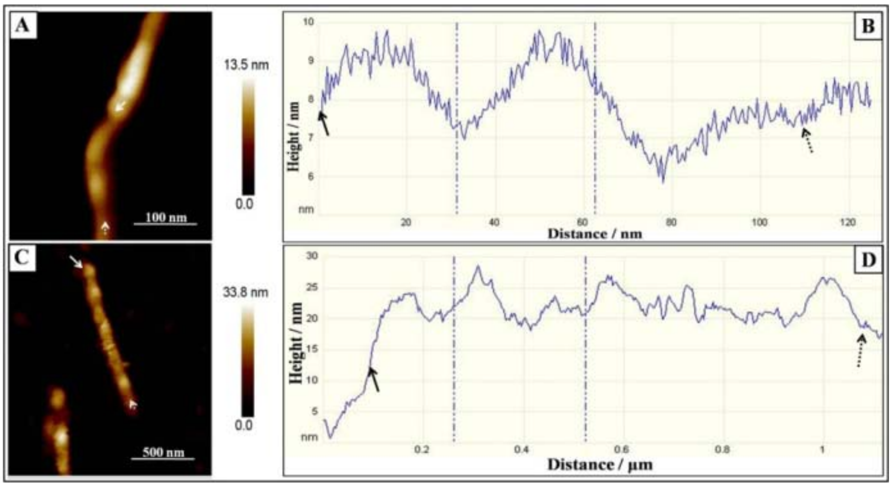

Fig. S3. AFM images and the height profile along the line connecting the arrows in assemblies: SAAS-C_{12} (A, B), 0.5 mmol/L; SAAS-C_{16} (C , D), 0.3 mmol/L.

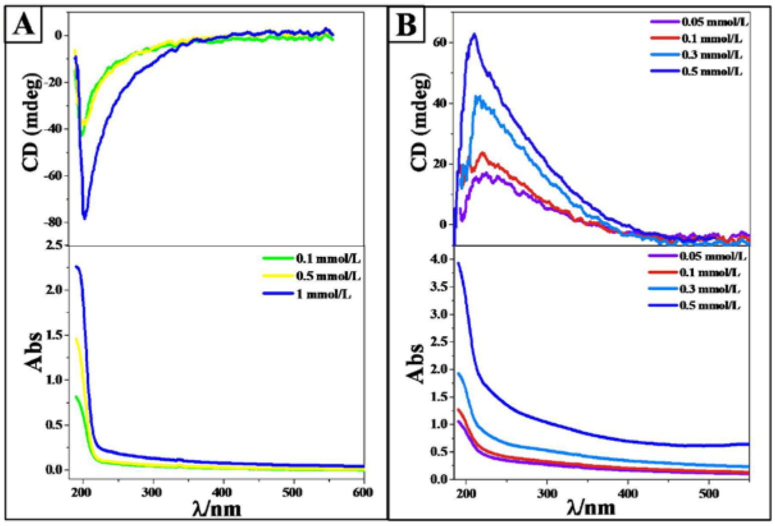

Fig. S4. Variable CD and UV-vis spectra of SAAS-C_{12} (A) and SAAS-C_{16} (B) in aqueous solution with different concentrations.

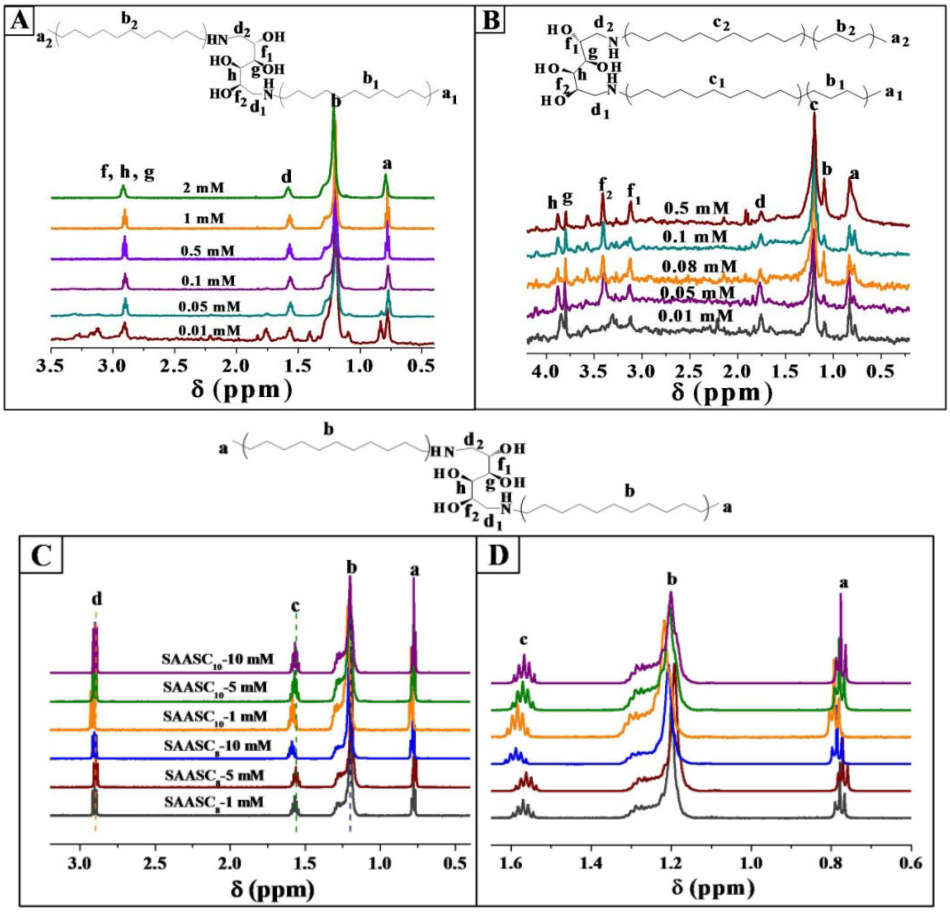

Fig. S5. Variations in chemical shifts for protons of SAAS-C_m as a function of the concentration in the self-assembly at 25 °C: (A): SAAS-C_{12}; (B): SAAS-C_{16}; (C): SAAS-C_8 and SAAS-C_{10}; (D) the corresponding enlargement of protons for SAAS-C_8 and SAAS-C_{10} in high field.

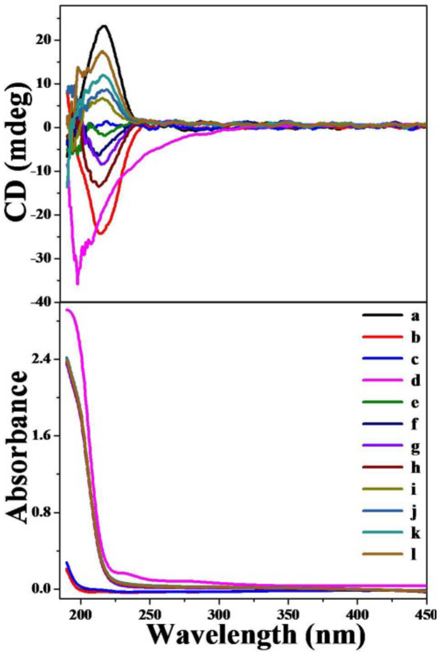

Fig. S6. The CD and corresponding UV-vis spectra of tartaric acid enantiomers (L-TA/D-TA) with concentration of 0.1 M. (a) L-TA, 0.1 M; (b) D-TA, 0.1 M; (c) racemic mixture of 0.1M; (d) 0% ee; (e) 20% ee; (f) 30% ee; (g) 50%; (h) 75%; (i) -20%; (j) -30%; (k) -50%; (l) -75%.

Table S1. Chemical Shifts δ_{obsd} (ppm) for protons of SAAS-C_m in high field before (H_1) and after cmc (H_2) in D_2O, and the cmc values obtained by fluorescence spectroscopy

	δ_{obsd} (ppm)		δ_{obsd}		δ_{obsd}		cmc
SAAS-C_m	H_{a1}	H_{a2}	H_{b1}	H_{b2}	H_{c1}	H_{c2}	(mM)
SAAS-C_8	0.779	0.785	1.198	1.191	1.571	1.588	~ 2.2
SAAS-C_{10}	0.791	0.775	1.217	1.200	1.585	1.566	~1.0
SAAS-C_{12}	0.776	0.790	1.195	1.212	1.568	1.582	0.04
SAAS-C_{16}	0.774	0.817	1.196	1.198	1.764	1.748	0.03

5. References

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