Electronic Supplementary Information for

Controlled topologies and self-assemblies of oligomeric supra-amphiphiles

Lijuan Shi,*[a] Nan Sun[b] and Liqiang Zheng[b]

[a] *Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China*

[b] *Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China*

1. Experimental Section

Materials. Adipic acid (99%) was purchased from J&K Chemical Company. Dodecylamine (99%) was the product of Sigma-Aldrich. Ultrapure water was used throughout the whole experiments.

Sample preparation. Desired amounts of adipic acid and dodecylamine were mixed in ultrapure water. The samples were mixed sufficiently and aged at 25°C for 1 month before further examination.

The concentrated sodium hydroxide and hydrochloric acid solutions were added to adjust the pH values of the samples. Then, the samples were sealed and kept at 25 °C for 24 h prior to the measurements.

In the CO_2-N_2 circulation test, CO_2 was bubbled into DA-AA mixed solutions at 25°C with a fixed flow rate of 0.1 L·min^{-1} until pH was decreased to 5.9. After that, the samples were kept in a sealed vessel to avoid contact with air. To remove CO_2 efficiently, N_2 was bubbled into the solution at 70 °C until pH returned back to about 8.6. All the samples were thermostatically incubated at 25 °C for one week prior to further examination.

Characterization

Freeze fracture transmission electron microscope (FF-TEM). A small amount of sample solution was placed on a 0.1mm thick copper disk covered with a second copper disk. Then the copper sandwich with the sample was plunged into liquid propane cooled by liquid nitrogen. Fracturing and replication were carried out on a Balzers BAF-400D equipment at -150 °C. Pt/C was deposited at an angle of 45°. The replicas were examined on a JEOL JEM-1400 TEM operated at 120 kV. The

images were recorded on a Gatan multiscan CCD and processed with digital micrograph.

Dynamic light scattering (DLS). The droplet size distributions of the micelles and the vesicle phase were determined by dynamic light scattering (DLS, DynaProNanoStar, Wyatt Instrument Co.) with an argon-ion laser operating at 658 nm. All measurements were made at the scattering angle of 90°. The temperature was controlled with a thermostat (F31C, Julabo) with an accuracy of ± 0.1 °C.

Small angle X-ray scattering (SAXS). The SAXS measurements were performed using Anton-paar SAX Sess mc^2 system with Ni-filtered Cu Kα radiation (0.154 nm) operating at 50 kV and 40 mA. The samples were held in a capillary. The temperature was controlled using a computer controlled Peltier heating system (Hecus MBraun Austria).

Turbidity measurements. The turbidity for the DA-AA mixed solutions was measured using a UV-Vis spectrometer (Hitachi U-4100, Japan). The absorbance at 400nm was chosen as the turbidity. A cuvette with 1 cm pathway was used. All the measurements were conducted at 25±0.1°C.

Fourier transform ion cyclotron resonance mass spectrometer (FT-MS). ESI-MS measurements were carried out on an APEX IV FT-MS (Bruker, USA). The operating conditions of the ESI source: positive ion mode; spray voltage 3300 V; capillary voltage3800 V, capillary temperature 200 °C; skimmer1 33.0 V, skimmer2 28.0 V; sheath gas nitrogen pressure 0.3 bar.

2. Results

1) Size distributions of the DA-AA mixed solution.

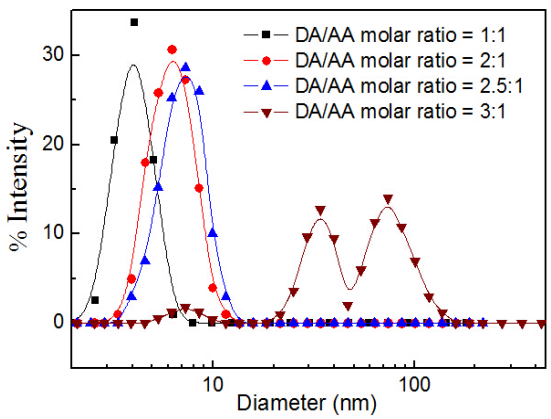


Fig. S1 Size distributions of the DA-AA mixed solutions at different DA/AA molar ratios.

2) Variation in pH and turbidity against DA/AA molar ratios.

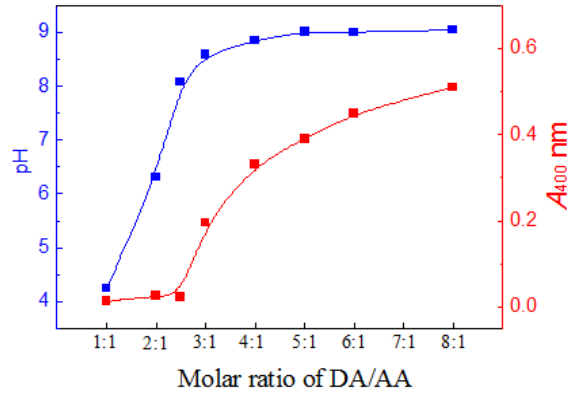


Fig. S2 Variation in pH (blue line) and turbidity (red line) against DA/AA molar ratios. The AA concentration is 50 mM.

3) SAXS patterns of the DA-AA mixed solution.

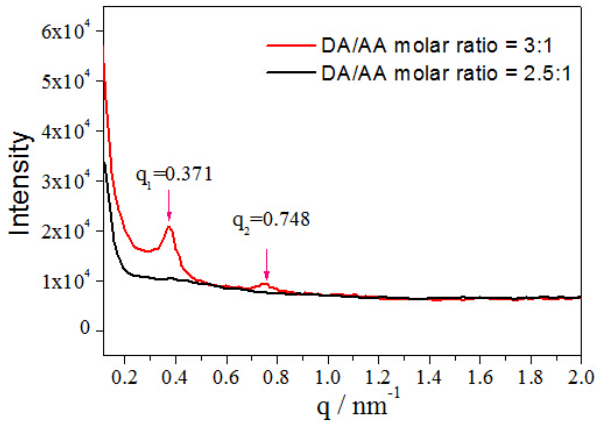


Fig. S3 SAXS patterns of the DA-AA mixed solutions at different DA/AA molar ratios.

4) The species distribution of adipic acid and dodecylamine.

The pK_{a1} and pK_{a2} values of adipic acid are 4.42 and 5.41, respectively. And the pK_b value of dodecylamine is 3.7. The species distribution of adipic acid and dodecylamine at the different pH value is all obtained by the eq as following[1]:

1. C. Zhou, X. Cheng, O. Zhao, S. Liu, C. Liu, J. Wang and J. B. Huang, *Soft Matter,* 2014, **10**, 8023.

$$x_i = \frac{[H^+]^i \prod_{i=0}^{n-i} K_{a_i}}{\sum_{i=0}^{n} [H^+]^i \prod_{i=0}^{n-i} K_{a_i}} (K_{a_0} = 1; i = 0, 1 \ldots, n)$$

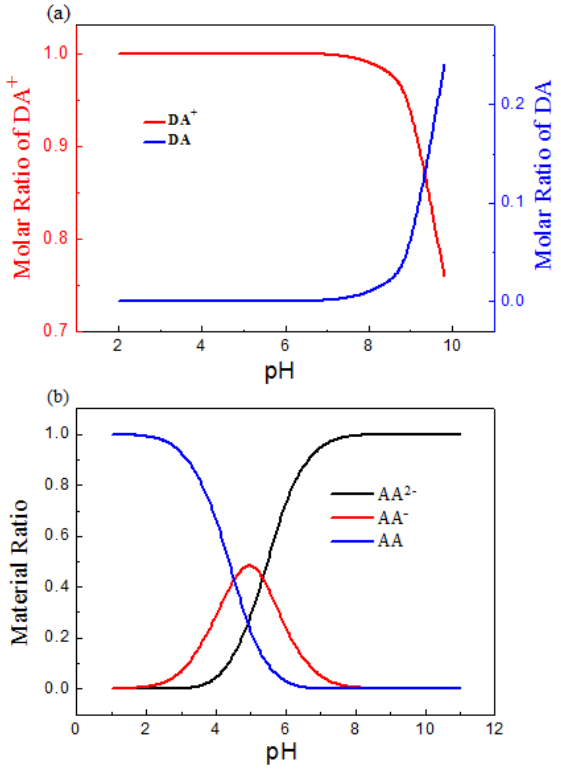
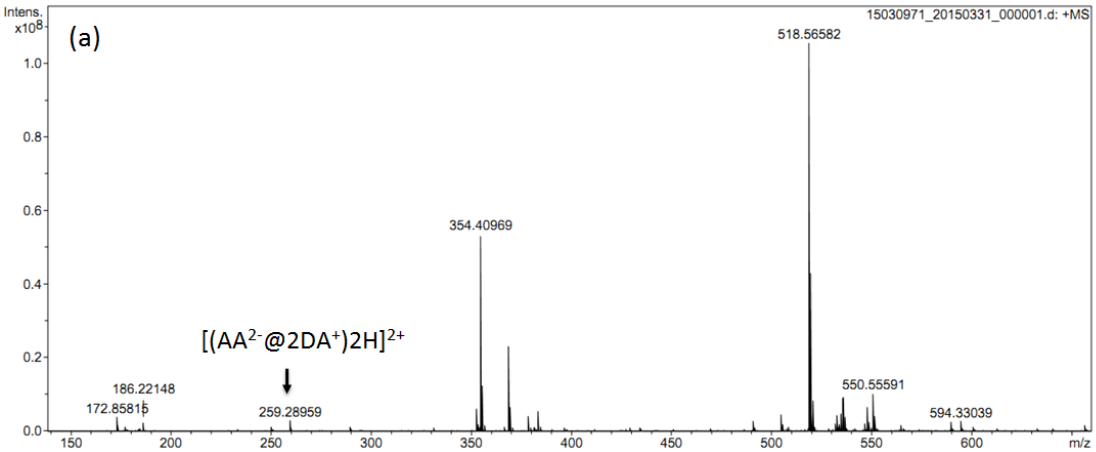


Fig. S4 The species distribution of (a) dodecylamine and (b) adipic acid solutions at 25°C.

5) The MS results.



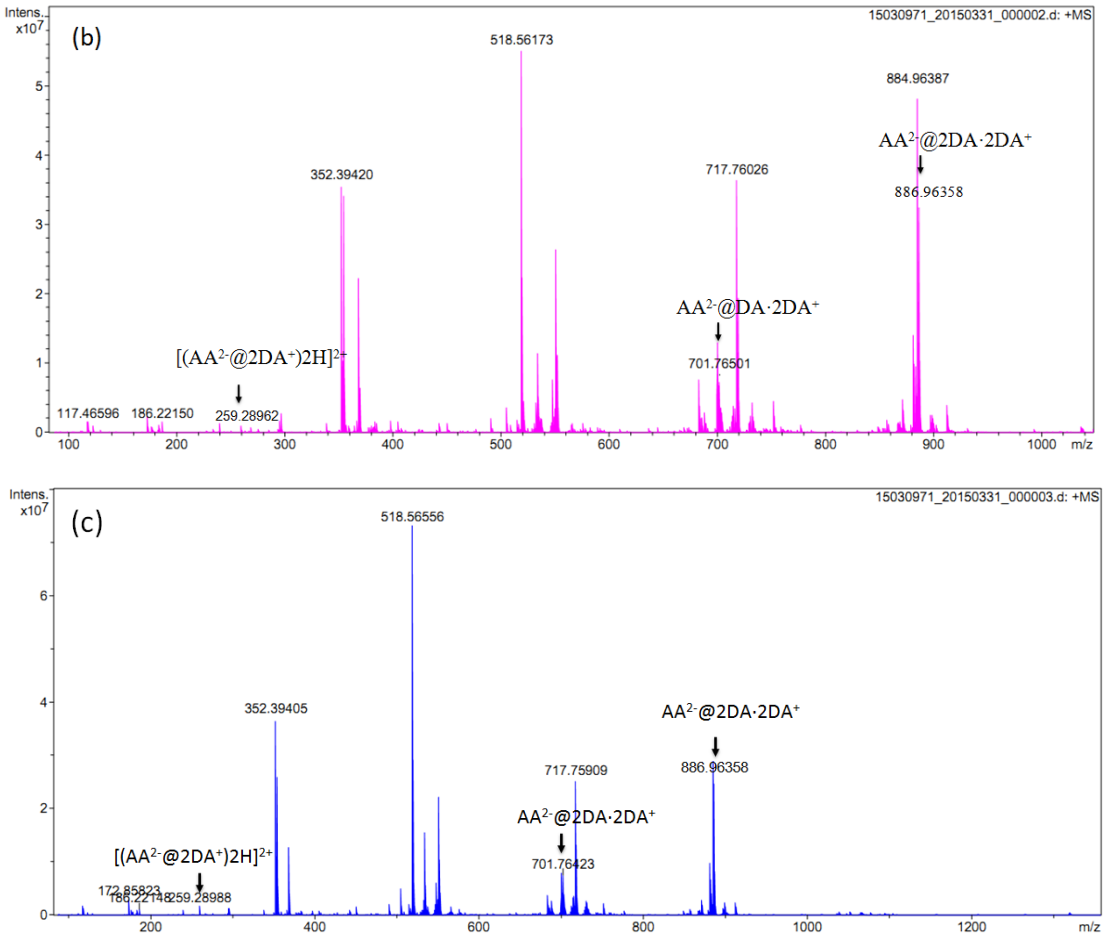


Fig. S5 ESI-MS profiles of the DA-AA mixed solutions at different DA/AA molar ratios: (a) 2:1, (b) 3:1 and (c) 5:1.

6) Variation in turbidity against AA concentration.

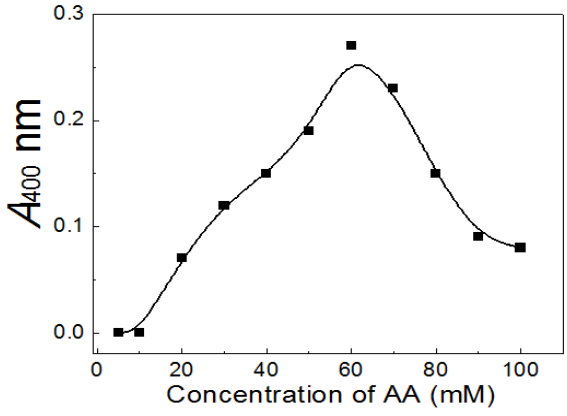


Fig. S6 Variation in turbidity against AA concentrations. The DA/AA molar ratio is 3:1.

7) Variation in pH and turbidity of the DA-AA mixed solution with the treatment of CO_2 and N_2.

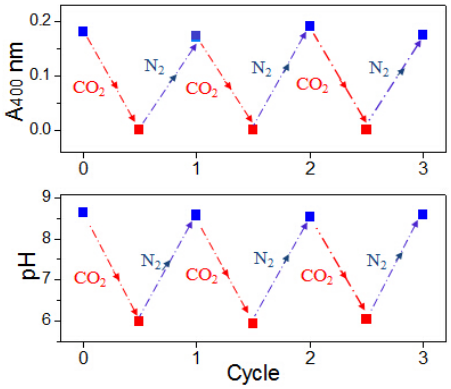


Fig. S7 Variation in pH and turbidity of the DA-AA mixed solution with the treatment of CO_2 and N_2.

8) Variation in size distributions of the DA-AA mixed solution with the treatment of CO_2 and N_2.

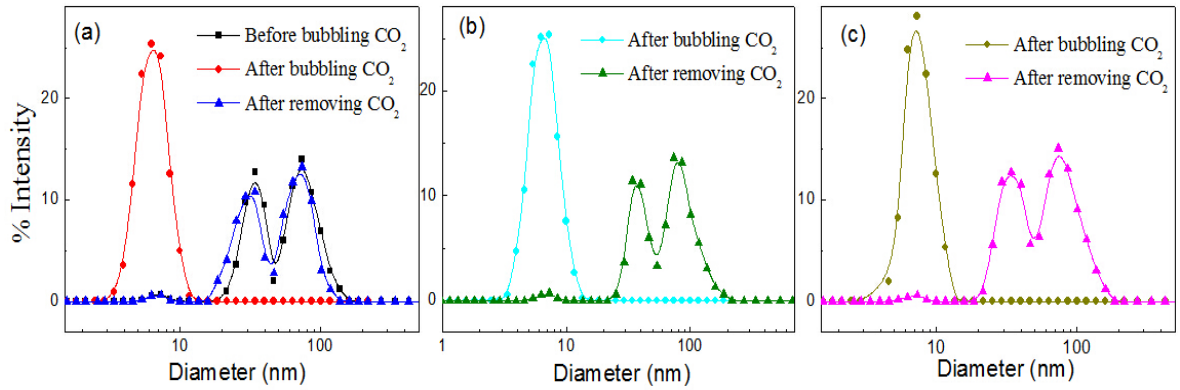


Fig. S8 Size distributions of the DA-AA mixed solution measured over repeated cycles of bubbling and removing CO_2. Cycle times: (a) 1; (b) 2; (c) 3. The AA concentration is 50 mM. The DA/AA molar ratio is 3:1.

9) Aggregate morphology of the DA-AA mixed solution measured over repeated cycles of bubbling and removing CO_2.

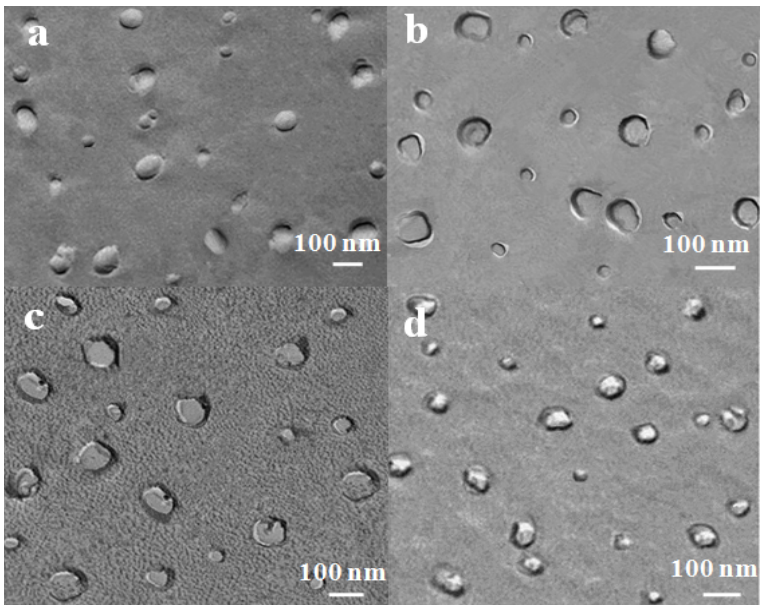


Fig. S9 FF-TEM images of the DA-AA mixed solution measured over repeated cycles of bubbling and removing CO_2. Cycle times: (a) 0; (b) 1; (c) 2; (d) 3. The AA concentration is 50 mM. The DA/AA molar ratio is 3:1.