

## Supporting Information

### **Self-assembly of NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH and SDS into nanodiscs or nanoribbons regulated by pH**

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## **1. Materials**

$\text{NH}_2-(\alpha,\text{L-lysine})_3\text{-COOH}$ ,  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ ,  $\text{NH}_2-(\alpha,\text{L-lysine})_7\text{-COOH}$ , and  $\text{NH}_2-(\alpha,\text{L-lysine})_{15}\text{-COOH}$  were purchased from Scilight Biotechnology, LLC, China. The purity of all of them is higher than 98%. SDS,  $\text{K}_2\text{PtCl}_4$ , Pyrene, and glutaraldehyde (GA, 50 wt.% solution in water) were all obtained from solarbio, Shanghai. All polypeptides used in this study are linear polymers where each amino acid residue participates in two peptide bonds and is linked to its neighbours in a head-to-tail fashion rather than forming branched chains.

## **2. Self-assembly of disc-like structures of $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ , and SDS in aqueous solution**

500  $\mu\text{L}$  of  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  (0.8 mM) was mixed with equal volume of SDS at a  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH/SDS}$  molar ratio of 1 to 10, and resulting mixture was allowed to stand for 3 days. The supernatant was collected, followed by analyses by TEM, AFM, and LSCM.

## **3. Effect of the $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH/SDS}$ ratio on the formation of the disc-like structures**

Different volumes (48–112  $\mu\text{L}$ ) of SDS (50 mM) were mixed with  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  solution in  $\text{ddH}_2\text{O}$  to make a  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH/SDS}$  ratio of 1/6, 1/10 and 1/14 in eppendorf tubules, respectively. The reaction mixture was allowed to stand for 10 h at room temperature  $\sim 25^\circ\text{C}$ . Then, the supernatant was collected for TEM analyses.

## **4. Kinetics of the formation of the disc-like structures**

4.5 mL of  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  (0.8 mM) was mixed with equal volume of SDS at a  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH/SDS}$  molar ratio of 1 to 10, and resulting mixture was divided into nine equal

parts. Then, a cultivation time of 0, 1 h, 2 h, 5 h, 10 h, 24 h, and 3 days at 25 °C was, respectively, conducted to observe different morphologies assembled from NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH and SDS. After different cultivation times, the supernatants of these nine parts were observed by TEM.

## **5. Effect of pH on the morphology of self-assembly of NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH and SDS**

1.5 mL of NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH (0.8 mM) was incubated with equal volume of SDS at a NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH/SDS molar ratio of 1/10, and resulting mixture was divided into three equal parts. The pH of the first part was adjusted to pH 5.0 by adding NaOH solution to the mixture, while adjusting the pH of the second and the third to 7.0 and 11.0 with NaOH solution using the same method, respectively. Resulting mixture was allowed to stand for 3 days. The supernatants of these three mixtures were observed by TEM.

## **6. Transmission Electron Microscopy (TEM) analyses**

Transmission electron microscope (TEM) experiments were carried out as following: Liquid samples were directly placed on carbon-coated copper grids and excess solution removed with filter paper, and then were stained using 2% uranyl acetate for 2 min. Transmission electron micrographs were imaged at 80 kV through a Hitachi H-7650 scanning electron microscope.

## **7. Atomic Force Microscope (AFM) analyses**

An aliquot (5  $\mu$ L) of the sample solution (0.4 mM in ddH<sub>2</sub>O, prepared as described in the text) was pipetted on to freshly cleaved mica and dried at room temperature before imaging. The AFM images were collected in tapping mode using a Nanoman VS equipped with a 20  $\mu$ m  $\times$  20  $\mu$ m scanner. The scanning speed was at a line frequency of 1 Hz. The images were saved at a resolution of 512  $\times$  512 points.

## 8. Laser Scanning Confocal Microscopy

Laser scanning confocal microscopy of the supernatant of a mixture of  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH and SDS in  $\text{H}_2\text{O}$  (prepared as described in the text) was performed on a Leica TCS SP5 Confocal Microscope equipped with a 488/340 nm Ar laser line (30 mW) for the dye excitation. The sample (200  $\mu\text{L}$ ) was mixed with a cationic DAPI and an anionic FITC hydrophilic fluorescent dyes, respectively. The sample was allowed to stand for 2 hours to allow the dye to absorb into the disc-like assemblies prior to imaging. Imaging of an xy plane with an optical slice of 5  $\mu\text{m}$  clearly showed that the assemblies of  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH and SDS were disc-like.

## 9. Circular Dichroism (CD)

Measurements were performed on a Pistar  $\pi$ -180 CD spectropolarimeter using a quartz cell with the 1 mm path length at 25 °C. After poly( $\alpha$ , L-lysine) with polymerization degree of 5 ( $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH) was mixed with SDS at a ratio of 1 to 10 at different pH values (5.0, 7.0, and 11.0), respectively, resulting solutions were allowed to stand for 3 days. Then precipitates were removed by centrifugation, and resulting supernatant was used for CD measurements with  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH in  $\text{H}_2\text{O}$  as control. Each spectrum was an average of ten scans from 190 nm to 260 nm at a bandwidth of 1 nm.

## 10. Isothermal Titration Calorimetry (ITC)

ITC experiments were carried out at 25 °C on the Nano-ITC II Instruments (TA Instrument). Prior to analyses,  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH and acetyl  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH were dissolved in 50 mM Mops buffer at pH 7.03, respectively. The SDS was also dissolved in the same above buffer. Before each titration, all solutions were degassed thoroughly under vacuum with stirring. The solution in the sample cell was stirred at 150 rpm to ensure rapid mixing of the titrant upon injection. Titrations were

performed by an automated sequence of 24 injections, each of 2  $\mu\text{L}$   $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH/acetyl  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH (4.5 mM) titrate into the sample cell containing 190  $\mu\text{L}$  of SDS (3 mM), spaced at 300 s intervals to ensure complete equilibration. A background titration, consisting of the same titrant solution but only the buffer solution in the sample cell, was subtracted from each experimental titration to account for heat of dilution. Three titrations were carried out for each measurement, and the reported experimental values are the average of individual best-fit values, fitting with independent binding model in the Nano Analyze software provided by TA Instruments. Raw data were processed using the Origin 8.0 software.

## **11. X-ray powder diffraction experiments**

X-ray powder diffraction was performed using a D/Max 2500 VB2+/PC. The X-ray generator was set to an acceleration voltage of 40 kV and a filament emission of 50 mA. Samples were scanned between  $1^\circ$  ( $2\theta$ ) and  $10^\circ$  ( $2\theta$ ) using a step size of  $0.002^\circ$  ( $2\theta$ ) and a count time of 0.12 s. The compact powdered samples (the disc-like assemblies formed by  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH plus SDS and SDS alone powders) were placed directly on a flat vitreous sample holder and measured directly within this apparatus.

## **12. Preparation of platinum nanodiscs by using $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH/SDS nanodiscs as templates**

In a typical synthesis, 10  $\mu\text{L}$  of 20 mM  $\text{K}_2\text{PtCl}_4$  (pH 5.0) which was aged for one day was added to 1 mL of a solution containing  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH (0.4 mM) and SDS (4.0 mM) in distilled water. Resultant solution was adjusted to pH 5.0, followed by standing at room temperature ( $25^\circ\text{C}$ ) for 3 days. After precipitate was removed, all supernatant was collected, to which 20  $\mu\text{L}$  of 50% glutaraldehyde (pH 5.0) was added under stirring. Resultant solution was allowed to stand for 12 h. To this solution

was added 50  $\mu\text{L}$  of L-ascorbic acid solution (13.2 mg) in distilled water (pH 5.0) at 25  $^{\circ}\text{C}$ . After 2 h, 0.5 mL of the same  $\text{K}_2\text{PtCl}_4$  aqueous solution (pH 5.0) was mixed with the above resultant solution, followed by standing 2 h. Finally, the pH value of resultant solution was adjusted to 5.0 or 11.0 for TEM analyses.

### **13. Preparation of platinum wires by using $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH/SDS}$ nanodiscs as templates**

Typically, 10  $\mu\text{L}$  of aged  $\text{K}_2\text{PtCl}_4$  (20 mM, pH 11.0) was added to 1 mL of a solution containing  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  (0.4 mM) and SDS (4.0 mM) in distilled water. Resultant solution was adjusted to pH 11.0, followed by standing at room temperature (25  $^{\circ}\text{C}$ ) for 3 days. To this solution was added 50  $\mu\text{L}$  of L-ascorbic acid solution (13.2 mg) in distilled water (pH 11.0) at 25  $^{\circ}\text{C}$ . After 2 h, 0.5 mL of the same  $\text{K}_2\text{PtCl}_4$  aqueous solution (pH 11.0) was added to the above resultant solution. After 2 h, the pH value of resultant solution was adjusted to 11.0 for TEM analyses.

### **14. SDS cmc measurements in the absence and presence of $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ by spectroscopic analysis**

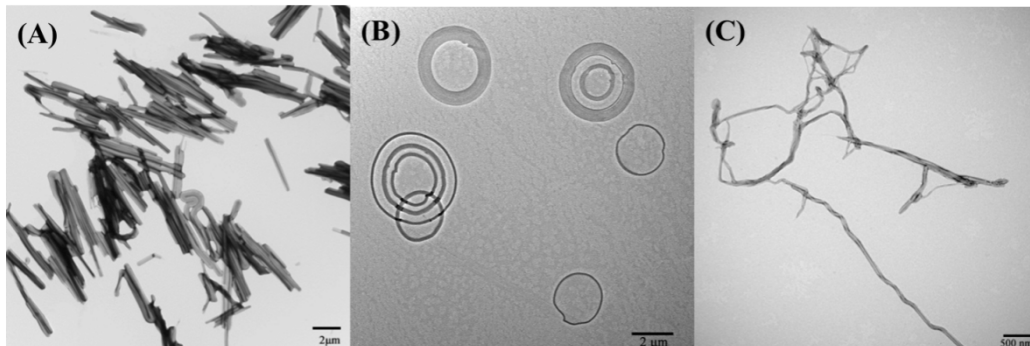
Pyrene-saturated aqueous solutions were prepared as previously described.<sup>16,17</sup> Typically, 2.5 mg of pyrene was added into 500 mL of ddH<sub>2</sub>O. After this solution was stirred for more than 24 h at room temperature in the dark, insoluble pyrene was removed by filtration. Increasing amounts of SDS/pyrene-saturated solution were mixed with 15 mM  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ /pyrene-saturated solutions (53.4  $\mu\text{L}$ ) in eppendorf tubules. Resultant solution was adjusted to pH 5.0 and 11.0, respectively, followed by standing at room temperature in the dark for 10 min before measurements. The pyrene concentration was ca.  $1.0 \times 10^{-6}$  M in all samples for analysis. The fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian Palo Alto, USA). For

experiments with pyrene, slit widths were set at 10 nm (excitation) and 10 nm (emission), and the excitation wavelength was 332 nm. The  $I_7/I_3$  ratio was calculated as the ratio of peak I (374 nm) and peak III (385 nm) in the vibration fine structure of pyrene monomer emission.

## 15. The supposed formation process of disc-like assemblies

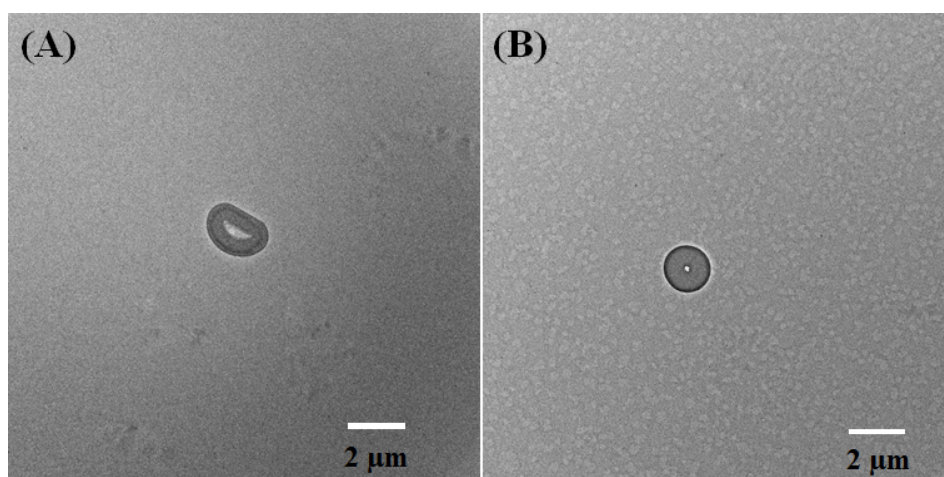
The growth of the nanobelt structures (Fig. 4B), which were formed at the early phases of disc-like assemblies, along each dimension is obviously regulated by different forces. One dimensionality is clearly linked to fast growth along the direction of the hydrophobic interactions with respect to a much slower lateral adhesion among them. A single nucleation event followed by uniform growth in the fast and slow directions, in analogy to living polymerization, is a possible explanation. Lateral growth of the nanobelt should depend mainly on electrostatic interactions between different molecules because one  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH-SDS}_5$  complex has two hydrophilic heads,  $\alpha\text{-COO}^-$  and  $\alpha\text{-NH}_3^+$ . Agreeing with this view, ITC results show that, similar to  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ , acetyl  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  (where  $\alpha\text{-NH}_3^+$  of  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  was acetylated) also can bind up to five of SDS molecules with a comparable binding constant as  $(2.76 \pm 0.12) \times 10^4 \text{ M}^{-1}$  (Fig. S4C and D), but no disc-like nanostructure was observed by TEM under the same conditions. Therefore, such acetylation could eliminate the electrostatic interactions between different  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH-SDS}_5$  complexes, thereby preventing lateral growth of the nanobelt. Further support for this idea comes from ITC results showing that the value of  $\Delta H^\circ$  ( $-12.95 \pm 0.08 \text{ KJ/mol}$ ) from the reaction of acetyl  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  and SDS is only one fourth of that from  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$  and SDS ( $-46.38 \pm 1.22 \text{ KJ/mol}$ ) (Table S1, and Fig. S4), suggesting that there is no polymerization reaction occurring in the solution except for the electrostatic interaction between SDS and the side chains of acetyl  $\text{NH}_2-(\alpha,\text{L-lysine})_5\text{-COOH}$ .

### Supplementary Figures (Figs. S1-8) and Table S1

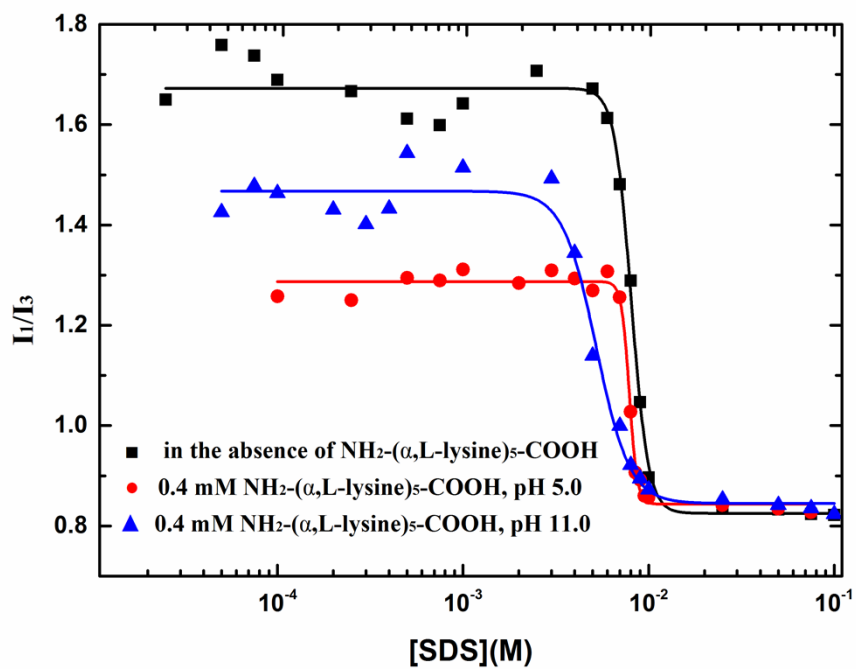


**Fig. S1** Effect of the ratio of SDS to  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH}$  on the shape of assemblies of  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH}$  and SDS as revealed by TEM. (A) The  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH/SDS}$  ratio of 1/6. (B) The  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH/SDS}$  ratio of 1/10. (C) The  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH/SDS}$  ratio of 1/14. Upon incubation of  $\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH}$  with SDS at different ratios for 10 h, respectively, all the samples were negatively stained with 2% (w/v) uranyl acetate aqueous solution, followed by TEM analyses. Conditions:  $[\text{NH}_2\text{-(}\alpha\text{,L-lysine)}_5\text{-COOH}] = 0.4 \text{ mM}$ , in  $\text{H}_2\text{O}$ ,  $25 \text{ }^\circ\text{C}$ .

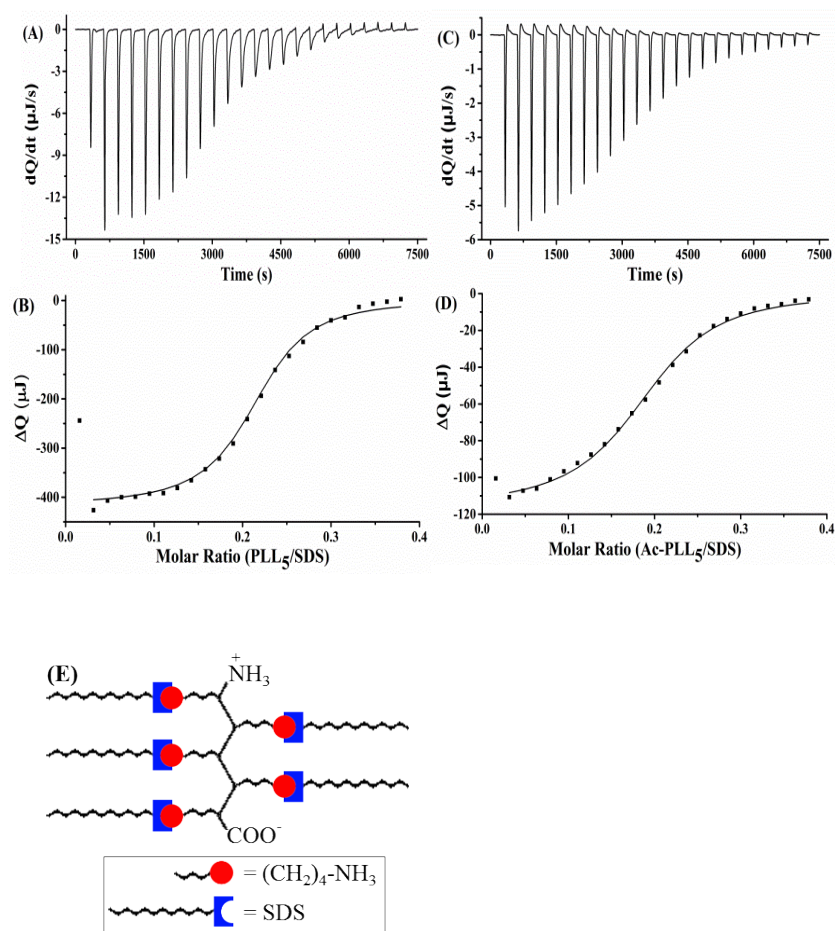




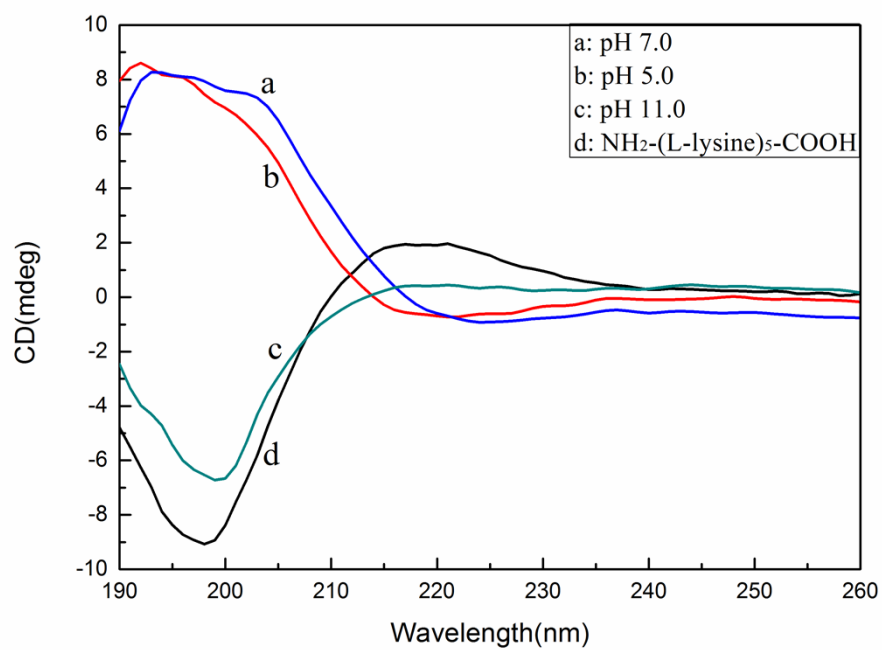
**Fig. S2** TEM images of disc-like structures formed upon mixing  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH with SDS at a ratio of 1 to 10 in different absolute concentrations. (A) The concentration of  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH and SDS were 0.1 and 1.0 mM, respectively. (B) The concentration of  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH and SDS were 0.2 and 2.0 mM, respectively.



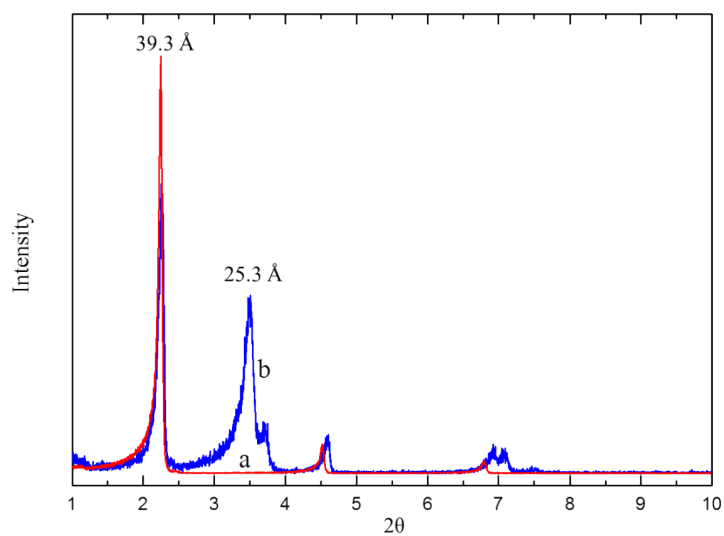
**Fig. S3** Plots of  $I_1/I_3$  of pyrene (ca.  $1 \mu\text{M}$ ) solubilized in water (■), and  $0.4 \text{ mM NH}_2$ - $(\alpha,\text{L-lysine})_5\text{-COOH}$  (● pH 5.0, ▲ pH 11.0) solutions as a function of SDS concentration at  $25 \text{ }^\circ\text{C}$ .



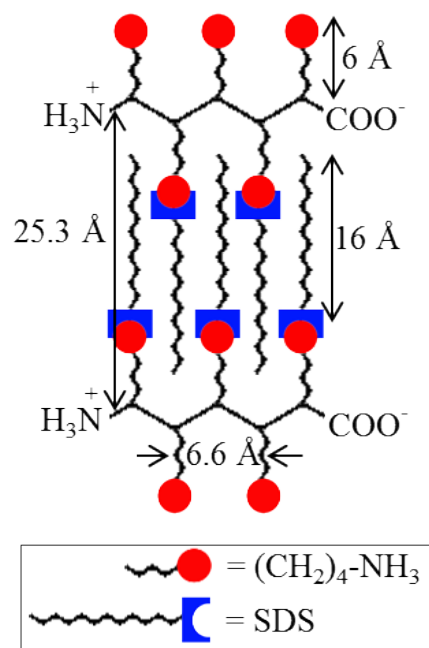
**Fig. S4** Calorimetric titration of SDS with  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH or acetyl  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH. (A) Raw data of SDS and  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH. (B) A titration plot of the integrated heat versus the  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH /SDS molar ratio. (C) Raw data of SDS and acetyl  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH. (D) A titration plot of the integrated heat versus the acetyl  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH /SDS molar ratio. (E) Schematic representation of the structure of  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5$ -COOH-SDS<sub>5</sub> complex.



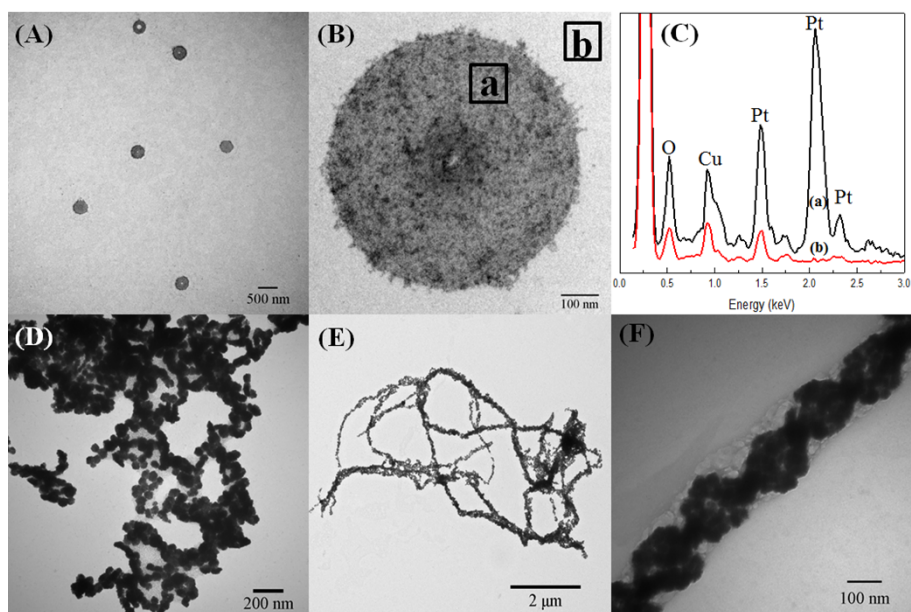
**Fig. S5** Characterization of the secondary structure of self-assemblies of  $\text{NH}_2-(\alpha, \text{L-lysine})_5\text{-COOH}$  and SDS at different pH values.



**Fig. S6** Small-angle X-ray diffractometer traces of both the disc-like assemblies formed by  $\text{NH}_2$ -( $\alpha$ ,L-lysine) $_5$ -COOH plus SDS (curve b) and SDS alone (curve a) powders. The powder of the disc-like assemblies were prepared by mixing  $\text{NH}_2$ -( $\alpha$ ,L-lysine) $_5$ -COOH with SDS at a ratio of 1 to 10 in  $\text{H}_2\text{O}$  for 3 days, and resulting supernatant was collected, followed by lyophilization.



**Fig. S7** Schematic representation of the structure of nanobelts assembled from  $\text{NH}_2$ - $(\alpha,\text{L-lysine})_5\text{-COOH}$  and SDS as shown in Figure 4B. Nanobelts are intermediates for the formation of the disc-like assemblies.



**Fig. S8** TEM images of the platinum discs (A, B) and nanowires (E, F). (C) Energy dispersive X-ray detection of the platinum disc as marked in (a) and (b) of Fig. 6B. (D) No platinum disc was found with either aged  $\text{K}_2\text{PtCl}_4$  + ascorbic acid or the  $\text{NH}_2$ -( $\alpha$ ,L-lysine) $_5$ -COOH/SDS solution + aged  $\text{K}_2\text{PtCl}_4$  + ascorbic acid in the absence of glutaraldehyde at final pH 5.0 or 11.0. The platinum discs and nanowires were observed by TEM without uranyl.

**Table S1.** Best fit parameters for ITC measurements of SDS binding to NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH or acetyl NH<sub>2</sub>-( $\alpha$ ,L-lysine)<sub>5</sub>-COOH in 50 mM Mops buffer, pH 7.0, 25 °C.<sup>a</sup>

sample	$K$ (M <sup>-1</sup> )	$\Delta H^\circ$ (kJ/mol)	$n$	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol · K)
NH <sub>2</sub> -( $\alpha$ ,L-lysine) <sub>5</sub> -COOH	$(7.09 \pm 0.15) \times 10^4$	-46.38 ± 1.22	0.22 ± 0.01	-27.69 ± 0.05	-62.69 ± 4.26
Acetyl NH <sub>2</sub> -( $\alpha$ ,L-lysine) <sub>5</sub> -COOH	$(2.76 \pm 0.12) \times 10^4$	-12.95 ± 0.78	0.21 ± 0.01	-25.35 ± 0.10	41.58 ± 2.95

<sup>a</sup>The reported thermodynamic quantities are apparent values. Standards errors from replicate determinations are indicated.