

## Supporting Information

### Manipulating Assembly of Cationic Dipeptide by Sulfonic Azobenzenes

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#### Experimental Section

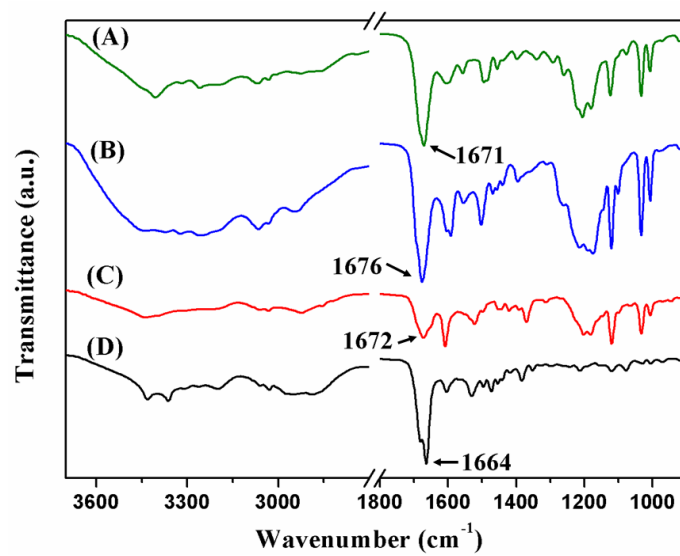
*Materials:* The cationic dipeptide (CDP, H-Phe-Phe-NH<sub>2</sub>·HCl) was purchased from Bachem (Budendorf, Switzerland). 1,1,3,3,6,6-hexafluoro-2-propanol (HFIP) was obtained from Sigma-Aldrich. Methyl orange (MO) was purchased from Alfa Aesar and used as received. Azobenzenes were synthesized according to the literature.<sup>1</sup>

Azobenzene molecule 4-[(4-Hydroxy)phenylazo]benzenesulfonic acid (HPABS) was synthesized as following. Firstly, p-aminobenzene sulfonic acid (3.5 g, 20 mmol) was dissolved in 3 mL of concentrated HCl and a small amount of water. Then the mixture was cooled to 0 °C using ice bath and another 3 mL of concentrated HCl was added with strong stirring. After that, NaNO<sub>2</sub> solution (1.5 g NaNO<sub>2</sub> dissolved in 10 mL water) was slowly added to the mixture drop by drop at 0 °C. With strong stirring, a phenol solution (1.9 g (20 mmol) phenol dissolved in 50 mL of K<sub>2</sub>CO<sub>3</sub> aqueous solution) was slowly added to the above mixture drop by drop at 0 °C. After reacting for 2 h, the pH value of the reaction liquid was adjusted to 2.0 using 0.1 M HCl solution. The yellow precipitate was filtrated out and dried under vacuum. The crude product was purified by recrystallization from water/ethanol (yield: 76%). <sup>1</sup>H NMR (400MHz, [D<sub>6</sub>]-DMSO, 25 °C, 7.85 (d, 2H; Ar-H), 7.8 (s, 4H; Ar-H), 6.95 (d, 2H; Ar-H)).

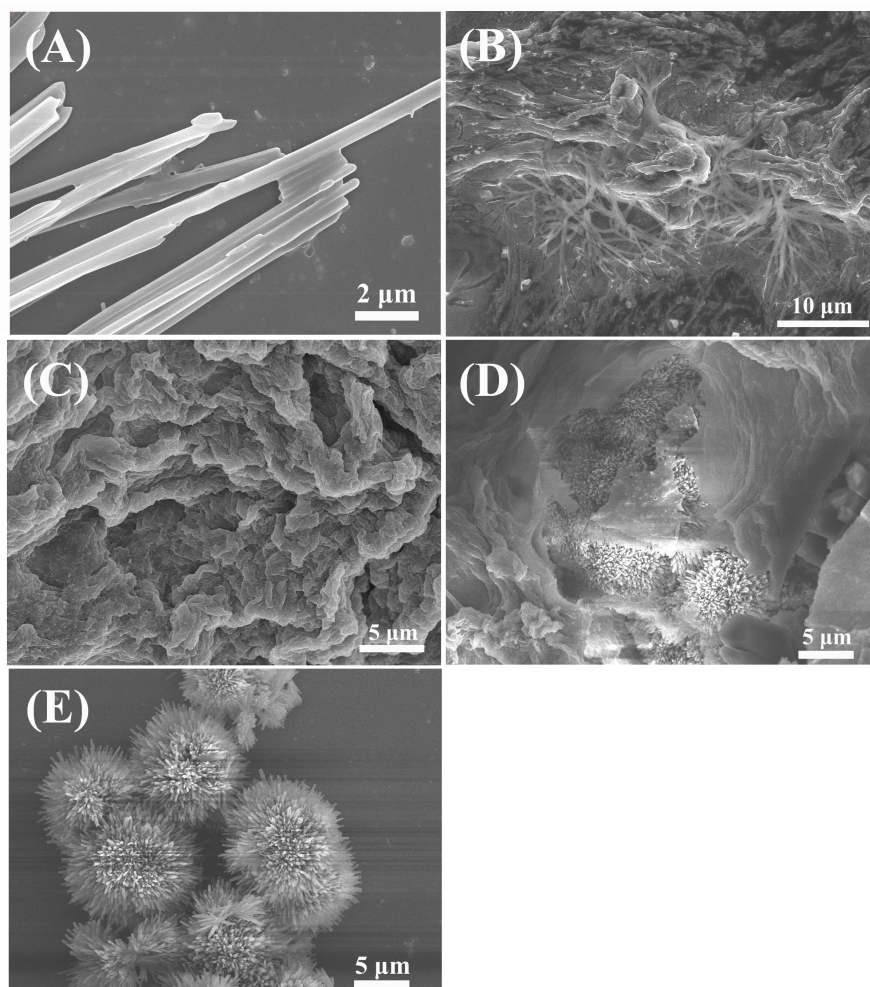
The synthesis of HPABS followed the same procedure only change phenol into salicylic acida (2.8 g, 20 mmol) (yield: 70%). <sup>1</sup>H NMR (400MHz, [D<sub>6</sub>]-DMSO, 25 °C, 8.34 (s, 1H; Ar-H), 8.10 (q, 1H; Ar-H), 7.76-7.84 (m, 4H; Ar-H), 7.15 (d, 1H, Ar-H)).

Preparation and characterization of co-assembled structures of CDP and azobenzenes: An aqueous solution of 6 mM azobenzen (500  $\mu$ L) was added to a 15  $\mu$ L of 200 mM CDP/HFIP solution at room temperature. This immediately resulted in the formation of yellow precipitate. After aging for several hours, the yellow precipitate was collected for further characterization.

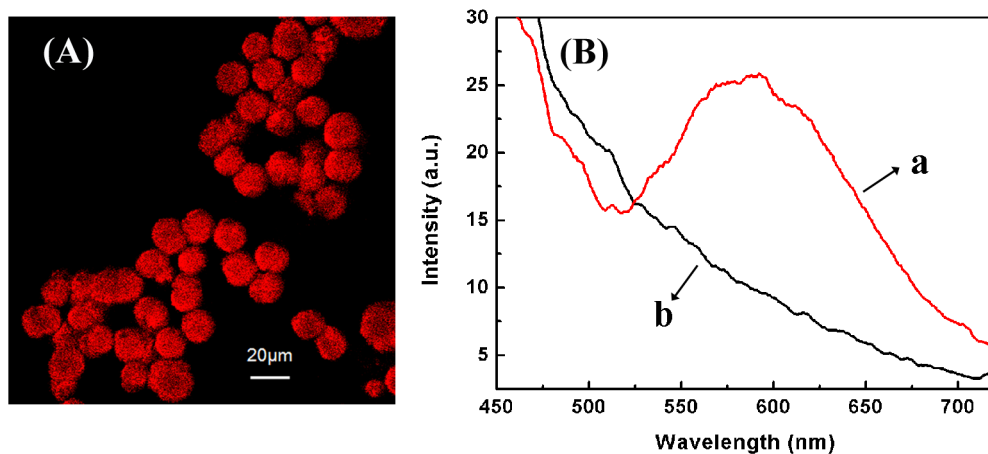
*Characterization:* The SEM images of the samples were taken by S-4800 (HITACHI, Japan) scanning electron microscopy. The obtained precipitate was carefully picked up and transferred to silicon substrate for the SEM measurement. Then the sample was dried under vacuum and coated by a thin layer of platinum.  $^1\text{H}$  NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. The FTIR spectroscopy was recorded by Bruker TENSOR-27 spectrophotometer. The precipitate was dried under vacuum and then pressed into KBr pellet For FTIR spectroscopy measurement. X-Ray diffraction patterns were measured at 25  $^\circ\text{C}$  using Rigaku. Datas were collected on Rigaku D/max 2500 instrument equipped with a Cu filter under the following conditions: scan speed,  $2^\circ/\text{min}$ ; Cu  $\text{K}\alpha$  radiation,  $\lambda = 1.5405 \text{ \AA}$ . The confocal-microscopy images (CLSM) were obtained using an Olympus FV1000 CLSM. For CLSM measurement, a drop of the sample suspension was put on a glass side and dried under vacuum. Photoluminescence spectra were performed on a F-280 Fluorescence Spectrophotometer.



**Fig. S1** FTIR spectra of (A) urchin-like structures; (B) flower-like structures (C) plate-like structures and (D) CDP powder.



**Fig. S2** Morphology changes of the nanostructures via adding different amount of azobenzene (A: 0 mg/mL, B: 0.6 mg/mL, C: 1.0 mg/mL, C: 2.0 mg/mL, D: 4.0 mg/mL) to 500 μL CDP nanotube dispersion solution.



**Fig. S3** (A) CLSM image of microspheres; (B) FL spectra of urchin-like microspheres (a) and azobenzene (b).

- 1 C. Gong, K.-L. Wong and M. H. W. Lam, *Chem. Mater.*, 2008, **20**, 1353.