Supporting Information

Construction of giant branched nanotubes from cyclodextrin-based supramolecular amphiphiles

1. Materials

Dichloromethane was rigorously dried with calcium hydride and distilled under reduced pressure . β-CD was purchased from Tianjinfuchen, recrystallized three times from deionized water, and dried for 3 days at 80 ºC in a vacuum oven. Thiourea , 4-toluenesulfonyl chloride, trichloroethylene, sodium hydroxide, hydrochloric acid, hydrogen peroxide, methyl 3,4,5-trihydroxybenzoate(methyl gallate), 1-bromododecane,1-adamantanamine hydrochloride, thionyl chloride, triethylamine and other solvents were commercially available and used directly as received.

2. Instruments and methods

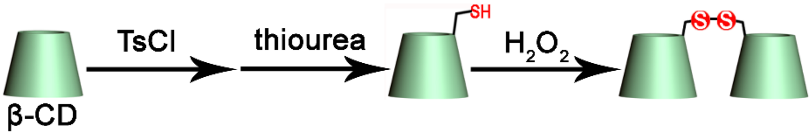
Optical microscope: A drop of the sample solution was placed on a colorless piece of glass and air-dried before measurement. The images were recorded on OLYMPUS BX61 apparatus.

SEM: SEM images were captured using a JEOL JSM 6700F apparatus. A drop of the aqueous solution was dripped directly onto a silicon wafer and air-dried.

TEM*:* The sample was prepared by placing a drop of the stock solution on a 300-mesh, carbon-coated copper grid and air-dried before measurement. The observation was performed with a JEOL1011 transmission electron microscope operating at an acceleration voltage of 200 kV.

XRD analysis**:** A big drop of the sample solution (10^{-4}mol/L) was dripped on a silicon wafer and the water was evaporated. The dripping-evaporation process was repeated several times in order that the sample is thick enough to operate the XRD measurements. The thickness of the bilayer could be obtained through calculating according to the Bragg equation.

3. Synthesis of the host molecules

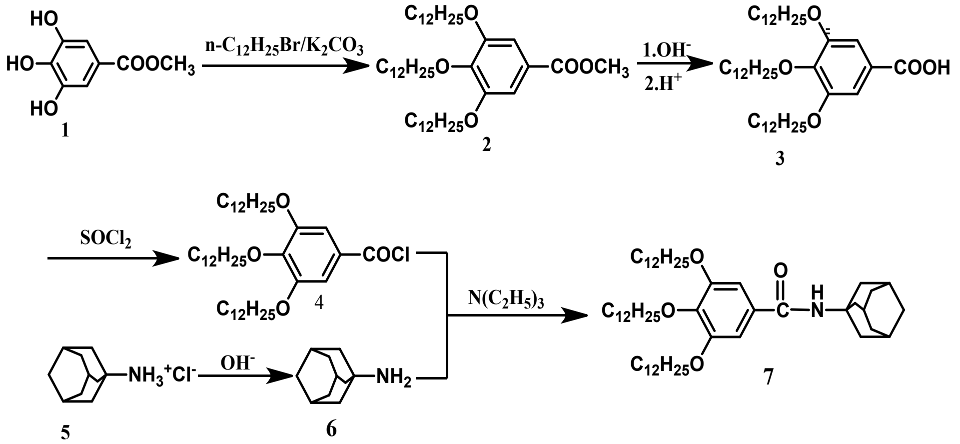


Scheme S1. The synthetic route of the host molecules：6-thio-β-cyclodextrin and disulfide linked β-CD dimmer.

Synthesis of 6-thio-β-cyclodextrin**:** 6-TsO- cyclodextrin was synthesized similar to the previous procedure[1].6-TsO-cyclodextrin (4.5g, 3.5mmol), thiourea (5.0g, 65.8mmol) , dissolved in 240mL of methanol-water mixture(methanol: water=4:1),was refluxed for 50 hours. After removing the solvent by the rotary evaporator, 65mL of methanol was added to the residue. White solid was filtered after stirring for 1.5 hours. The sample obtained was dissolved in 140mL of aqueous NaOH (10%) and stirred for 5 hours at 50℃. Added hydrochloric acid(10%) to make the pH of the solution to be 2. 10mL of trichloroethylene was added and the resulting white precipitate was collected after stirring for 1d. The product collected was recrystallize from water and dried in a vacuum oven at 60℃. The final product was obtained as white solid (1.3g , 1.1mmol, 31%). MS (MALDI -MS) = 1173.178[M + Na]$^+$. ^{1}H-NMR (500 MHz, DMSO-d6) = 5.60- 5.80 (m, 14H), 4.81-4.89 (m, 7H), 4.40-4.65 (m, 6H), 3.25-3.81 (m, 40H), 2.72-3.02 (m, 2H), 2.05 (t, 1H).

***Synthesis of disulfide cyclodextrin*:** Excess H_2O_2 was added to the aqueous solution of CD-SH (1g, 0.869mmol,). After stirring over night, the reaction was completely accomplished (detected by thin layer chromatography (TLC)). The resulting solution was freeze-dried and the product was obtained as a white solid (0.95g, 0.411mmol,95%). MS (ESI-MS) = 1150.4[M + 2H]$^+$. ^{1}H-NMR (500 MHz, DMSO-d6) = 5.60- 5.90 (m, 28H), 4.81-4.91 (m, 14H), 4.38-4.61 (m, 12H), 3.22-3.42 (m, 80H), 2.68-3.04 (m, 4H).

4. Synthesis of the guest molecule adamantanol-1-3,4,5-trihydroxybenzoicamide



Scheme S2. The synthetic route of the guest molecule.

The guest molecule was synthesized according to the previous work of our group^2. Methyl 3,4,5-trihydroxybenzoate (**1**, 1g, 5.43 mmol) and K_2CO_3 (10 g) that is roasted was added to a deoxygenated mixture of DMF (15 mL) and 1 -bromododecane (6 mL, 25.03 mmol)) under nitrogen for 1 h. The mixture was heated at 75 °C for 12 h. Then plenty of water was added to the reation mixture when the temperature equals to room temperature. **2** (3.10 g, 4.5 mmol, 83%) was gotten as a white solid after filtrating and recrystallizing the crude product in acetone for 3 times. ^{1}H NMR ($CDCl_3$, 500 MHz) = 7.21 (s, 2H), 4.05-3.90 (m, 6H), 1.88 (m, 4H), 1.79 (m, 2H), 1.49 (m, 6H), 1.29 (m, 48H), 0.89 (t, 9H).

Excess potassium hydroxide (5.6 g, 0.1 mol) and the solution of **2** (1.0 g, 1.45 mmol) in ethanol (100 mL, 95%) was refluxed for 2 h. Added hydrochloric acid(15%) to make the solution pH to be weak acid. A lot of water was added and the precipitate was collected. Then recrystallized the precipitate from acetone for 3 times to get 3,4,5- trihydroxybenzoic acid (**3**) as a white solid (0.64 g, 0.9 mmol, 62%). ^{1}H NMR ($CDCl_3$, 500 MHz) =7.11 (s, 2H), 4.09 (m, 6H), 1.90 (m, 4H), 1.82 (m, 2H), 1.51 (m, 6H), 1.28 (m, 48H), 0.89 (t, 9H).

Adding dropwise the aqueous solution of sodium hydroxide to the solution of adamantadine hydrochloride (310 mg, 1.65 mmol) in deionized water (25 ml) under the condition of stirring. Extracted the solution by dichloromethane for three times and removed the solvent by the rotary evaporator. Then dried the collected under vacuum to get the white solid (**6**) for further use.

3,4,5- trihydroxybenzoic acid **3** (1.0g, 1.48mmol) was dissolved in little thionyl chloride (about 1 ml) and stirred for 4h in room temperature to get **4**. Removed thionyl chloride and redissolved the residue in anhydrous dichloromethane together with triethylamine (3ml). Added dropwise the solution of **6** in anhydrous dichloromethane(25ml) into it and stirred overnight under the condition of ice bath. Removed the solvent and the product was purified by column chromatography (silica gel, dichloromethane as eluent). The final product was obtained as an orange solid **7**(0.78 g, 0.98mmol, 66%). ^{1}H NMR (CDCl3, 500 MHz)=6.88 (s, 2H), 5.58 (s, 1H), 4.10(m, 6H), 2.00 ppm(m, 9H), 1.76 (m, 12H), 1.38 (m, 6H), 1.24 (m, 48H), 0.84 (t, 9H). MS (MALDI -MS) = 809[M + H]$^+$.

5. Preparation of the branched nanotubes

Typically, host molecule β-CD (**2**, 22.7mg), CD-S-S-CD (**2b**, 46mg), and guest molecule adamantane-1-3,4,5-trihydroxybenzoicamide(**1**,16.16mg) was respectively dissolved in 2 mL DMF. Then, 16μL **2**, 4μL **2b** and 24μL **1** were mixed together by ultrasonic at 30℃ till a clear solution was obtained. After complexation for 20 minutes, we carried the secondarily self-assemble of the supramolecular amphiphile in water. The amphiphile (**2**, **2b** with **1**) (20 μL) was slowly dropwised into a flasket with 4 mL deionized water in it under ultrasonication at 35℃. The opalescence appeared immediately, which indicated the formation of aggregates. 40 minutes later, a drop of the sample solution was placed on a slide and air-dried before measurement.

6. Optical microscopy characterization of the branched nanotubes

The ‘branched nanotubes’ with different number of branches was extracted out, and the structure is represented.

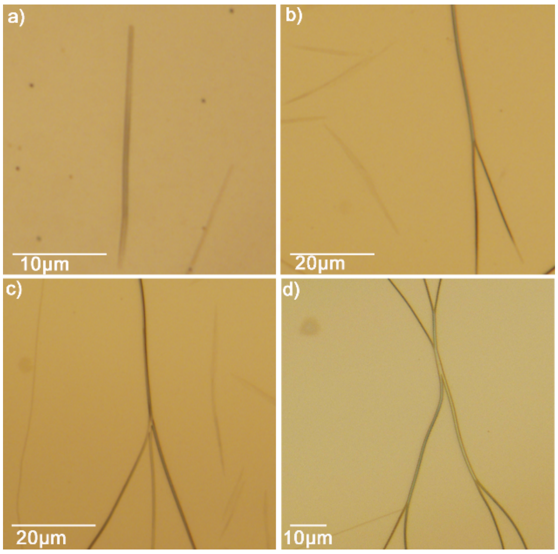
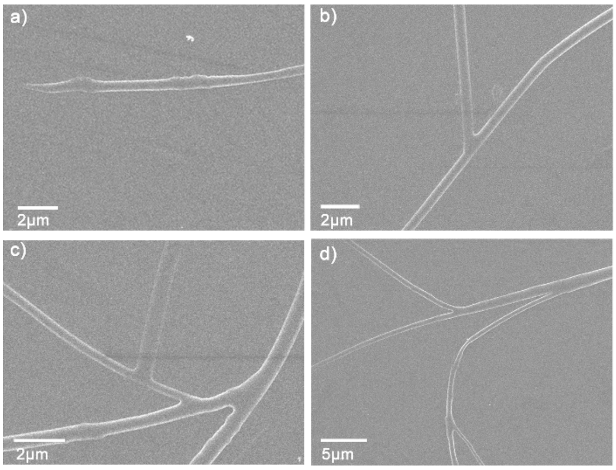


Figure S1. The optical microscopy images of the branched nanotubes formed by β-CD/CD-S-S-CD at a ratio of 4:1. (a-d) The branched nanotubes with different number of branches. The concentration of β-cyclodextrin unite is 5×10^{-5} mol/L.

7. SEM characterization of the branched nanotubes

SEM was used to further exploit the morphology of the branched nanotubes. The giant branched nanotubes with different number of branches are presented. It should be pointed that the junction is very smooth, indicating that we undoubtedly get the branched nanotubes.

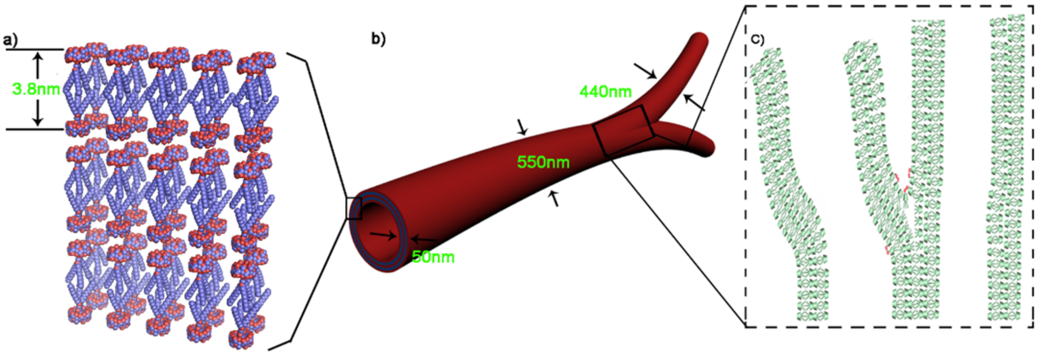
The diameter of the 'backbone' is large up to 1μm, but the diameter of the 'branch' is thinner, about 400-800nm.



Figue S2. The SEM images of the branched nanotubes formed by β -CD/CD-S-S-CD at a ratio of 4:1. (a-d) the branched nanotubes with different number of branches. The concentration of β-cyclodextrin unite is 5×10^{-5} mol/L.

8. Analysis of the size of the mutilayer and the branched nanotube

The Bragg peak is extracted from the XRD data (Fig. 2b) and the bilayer thickness was calculated to be 3.8 nm according to the Bragg equation. The thickness of the wall is about 50nm according to Fig. 1f. we deduce that the wall of the branched nanotube is made up of about 13 bilayers of the amphiphiles.



Scheme S3 Schematic structures of (a) the mutilayer structure formed by supramolecular amphiphiles. (b) the self-assembled branched nanotube. And(c) the proposed self-assembled branched multilayers.

[1] Z. Dong, J. Liu, S. Mao, X. Huang, B. Yang, X. Ren, G. Luo and J. Shen, *J. Am. Chem. Soc.* 2004, **126**, 16395-16404.

[2] Y. Tang, L. Zhou, J. Li, Q. Luo, X. Huang, P. Wu, Y. Wang, J. Xu, J. Shen and J. Liu, *Angew. Chem., Int. Ed.* 2010, **49**, 3920-3924