

Supporting Information for

Creating Chirality in the Inner Walls of Silica Nanotubes through a Hydrogel Template: Chiral Transcription and Chiroptical Switch

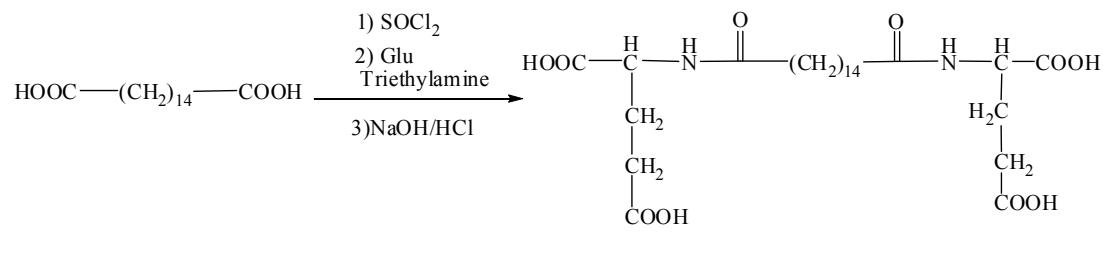
Jian Jiang, Tianyu Wang, Minghua Liu*

Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, 100190, China

E-mail:liumh@iccas.ac.cn

Experimental details

1. Synthesis of the gelator molecules



Synthesis of N, N-hexadecanedioyl-di-L-glutamic acid. 858 mg of hexadecanedioic acid was added to 30 mL of petroleum ether, then the solution was heated to reflux and 3 mL of SOCl_2 was added dropwise. The solution was kept under refluxing for 8 h. When the petroleum ether was removed, 953 mg of the colorless oil was obtained.

480 mg of diethyl ester L-glutamic acid, 3 mL of triethylamine, and 10 mL of dichloromethane was mixed and stirred for 30 min. To this mixture, 646 mg of the above colorless oil was added under ice bath. The mixture was again kept stirring for another 3h at room

temperature. The resulted mixture was then washed with 10 mL×3 water, 10 mL 2 N HCl aqueous solution, 10 mL saturated NaHCO₃ aqueous and 10 mL distilled water, respectively. The organic solution was dried with MgSO₄. When the solvent was removed , the white solid was obtained. The solid was then added to 10 mL of 3N NaOH aqueous solution, and stirred at 40°C for 3 h. The mixture was treated with 6 N HCl to get pH=1 solution, and white solid was obtained, which was recrystallized in water to get the product with a yield of 84.0 %. ¹H-NMR (400 MHz, DMSO) δ 1.23 (Strong s, 20H), 1.47(s, 4H), 1.74 - 1.76 (m, 2H), 1.94-1.97 (m, 2H), 2.09 (t, *J*=7.10 Hz, 4H), 2.25 (t, *J*=7.40 Hz, 4H), 4.18 - 4.20 (m, 2H), 8.00 (s, 1H), 8,02(s, 1H); MAIDI-TOF MS [M+Na⁺] 567.2.

Synthesis of N, N-hexadecanedioyl-di-D-glutamic acid. D-HDGA was prepared by the same method above with a yield of 86.1%. ¹H-NMR (400 MHz, DMSO) δ 1.23 (Strong s, 20H), 1.47 (s, 4H), 1.74 - 1.76 (m, 2H), 1.94 -1.96 (m, 2H), 2.09 (t, *J*=7.24 Hz, 4H), 2.25 (t, *J*=7.56 Hz, 4H), 4.19 - 4.20 (m, 2H), 8.00 (s, 1H), 8,02(s, 1H); MAIDI-TOF MS [M+Na⁺] 567.2.

2. Preparation of the hydrogels.

HDGA was dissolved in water under heating up to boiling to transparent. Then the solution was cooled down in room temperature and a transparent hydrogel was obtained. The gel was confirmed by the invert test tube methods. After the test tube was inverted, if there is no fluid in the upside tube, then the gel was formed. The hydrogel was further cast on a mica surface and their AFM was measured.

3. Preparation of silica nanotubes through hydrogel as a template.

550 mg of L-HDGA or D-HDGA was added to 100 mL water and heated to be dissolved. After cooling down to room temperature a hydrogel was formed. The gel was then dispersed into 800 mL of water and the solution was stirred for 20 min. To which 250 μL of APES, 2500 μL of TEOS was added and further stirred for 3 h. The mixture was left at room temperature for 5-10

days. And then the mixtures were filtered and washed with hot ethanol to obtain white solid as silica nanotubes. Such silica nanotubes are capped. In order to open the cap and remove the remained bolaamphiphiles inside in the wall, following method was used.

200 mg of silica nanotubes were dispersed into 30 mL of ethanol solution under sonication for 15 min, and then 3 mL ethanolamine was added. The mixture was heated to reflux for 12 h under stirring. The nanotubes were obtained by filtration wasn't washed with ethanol three times. In this way, the inner side of the silica nanotubes contains the free amino groups were obtained.

4. Loading TPPS into the inner side of the SiNTs.

10 mg of the open SiNTs was dispersed into 10 mL 10^{-2} M TPPS aqueous solution, which was adjusted to pH=3 with 0.1 M HCl aq. The mixture was stirred for 4 h at room temperature, and then the solution was subjected to centrifugation and filtered, washed with water three times to give the TPPS-loaded SiNTs.

5. Preparation of 4-carboxyazobenzene modified SiNTs.

40 mg of 4-carboxyazobenzene was added to 10 mL petroleum ether, then 1 mL of sulfonyl dichloride was added and the solution was heated to reflux for 6 h. After removing the solvent, the yellow oil was obtained. It was then dissolved into 10 mL of hexane, and then 20 mg of SiNTs and 20 uL of triethylamine were added, the mixture was stirred for 40 h at room temperature. After filtering, the nanotubes were washed with hexane, ethanol and water repeatedly for removing the absorbed substituted, the 4-carboxyazobenzene modified SiNTs was obtained.

6. Photo irradiation of the nanotubes

5 mg of the 4-carboxyazobenzene modified silica nanotubes was dispersed into 10 mL ethanol and water mixture solution (volume ratio=5:1) and then irradiated with alternative light irradiation. The modified nanotubes were firstly irradiated with UV-365 nm for 20 min and then visible light

for 10 minutes. During the irradiation switch, the UV-Vis and CD spectra of the dispersion was measured.

7. Characterization

SEM (scanning electron microscope) was performed using a Hitachi S-4300 system with an accelerating voltage of 15 kV. Samples for SEM were prepared by spinning the nanotubes on silicon slices. TEM (transmission electron microscope) images were obtained on a JEM-100CX II electron microscope operating at an accelerating voltage of 100kV. The TEM samples were prepared by placing a small amount of nanotubes on carbon-coated copper grids (300mesh).

UV-vis and CD spectra were obtained using JASCO UV-550 and JASCO J-810 spectrophotometers, respectively.

8. Several supporting data.

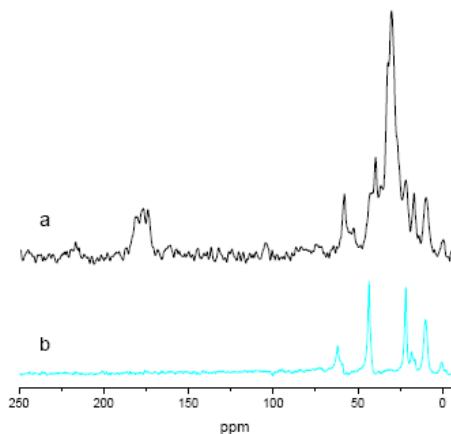


Figure S1. Solid state ^{13}C NMR of the SiNTs before (a) and after (b) removing the hydrogel.

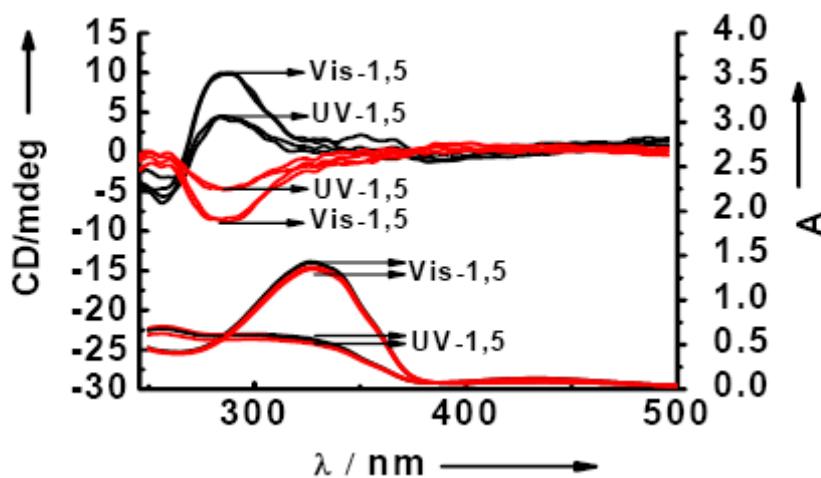


Figure S2. The CD (up) and UV (down) reversible of azobenzene modified M-SiNTs (red) and P-SiNTs (black), “vis-1,5” means the spectra for the samples irradiated with visible light for one and five cycles, respectively. “UV-1,5” means the spectra for the samples irradiated with 365 nm light for one and five cycles, respectively.

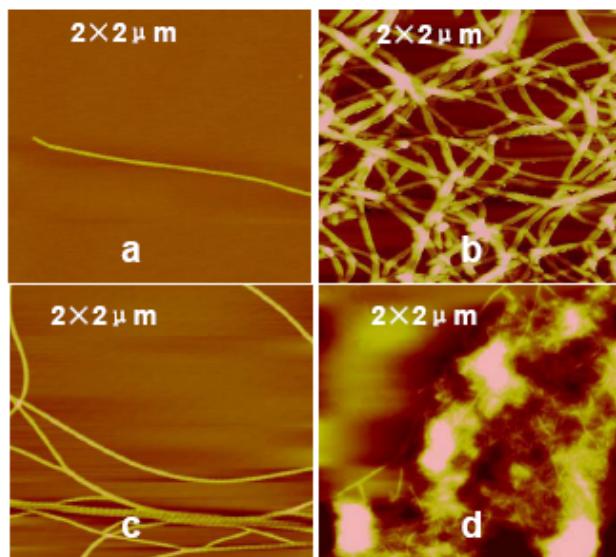


Figure S3. AFM images of growth process of silica nanotubes. (a) hydrogel. (b) hydrogel with **APES** and **TEOS** for 5 days. (c) hydrogel with only **APES** for 5 days. (d) hydrogel with only **TEOS** for 5 days. These figures suggest that in order to get **SiNTs**, a template hydrogel is necessary.

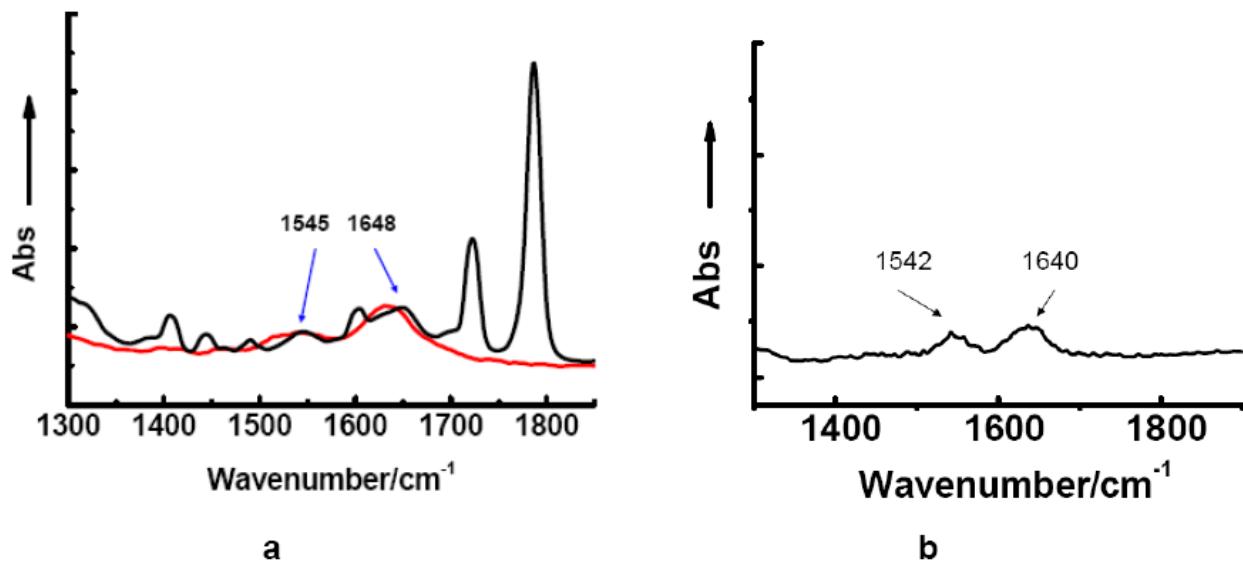


Figure S4. (a) FT-IR spectra of SiNTs before (red line) and after (black line) covalently linking 4-carboxyazobenzene. The peaks on 1545 and 1648 cm^{-1} indicate the formation of amide bond, which confirmed 4-carboxyazobenzene covalently linked to SiNTs successfully. The additional peaks at 1720 and 1790 cm^{-1} were due to azobenzene acid anhydride. (b) FT-IR spectra of Azo-modified SiNTs after washing with CH_2Cl_2 , the absorption bands 1720 and 1790 cm^{-1}

disappeared, which verified azobenzene acid anhydride was removed, while two bands at 1542 and 1640 cm⁻¹ remained, confirmed that Azo was covalently linked to SiNTs actually.

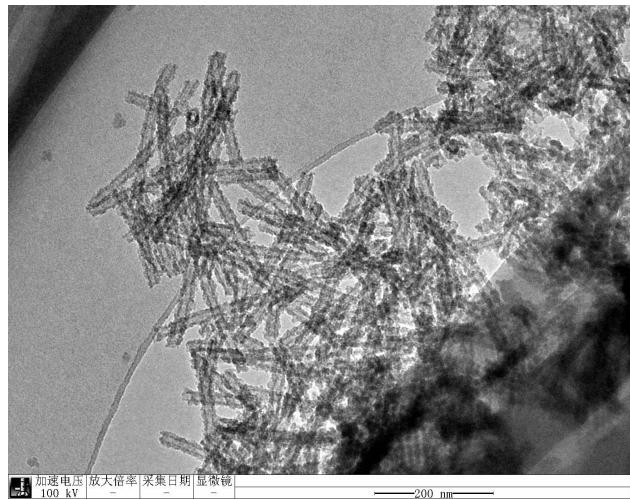


Figure S5. TEM image of **Azobenzen** modified silica nanotubes. The TEM images show that the modification did not change the morphologies of the nanotubes.