A New Synthesis Strategy for Chiral CdS Nanotube Based on A Homochiral MOF Template

Xuan Kuang, Yu Ma*, Caiyun Zhang, Hao Su, Jine Zhang and Bo Tang*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, P. R. China.

E-mail: tangb@sdnu.edu.cn
Fax: (+86) 531-8618-0017

Materials: Cadmium nitrate tetrahydrate, L-leucine, D-leucine, sodium carbonate, sodium borohydride and 4-pyridinecarboxaldehyde were obtained from Aladdin (Aladdin Chemistry Co. Ltd., Shanghai, China). Ultrapure water (18.2MU cm) was obtained from a Water Pro Water Purification System (Labconco Corporation, Kansas City, USA). Unless otherwise stated, all chemicals and reagents used were at least of analytical grade and as received without further purification.

Apparatus: The FT-IR (KBr pellet) spectrum was recorded (400—4000 cm$^{-1}$ region) on a Nicolet Magna 750 FT-IR spectrometer. The chemical shifts were reported in δ relative to TMS. The solid state CD spectra were recorded on a J-815 spectropolarimeter (Jasco, Japan). The SEM images were recorded on a FEI QUANTA FEG250 scanning electron microscope at 15.0 kV.

Experimental Section

Synthesis of homochiral MOF1: The ligand [N-(4-Pyridylmethyl)-L-leucine·HBr] (L-HL) was synthesized according to the literature. Homochiral porous MOF was synthesized by rapidly mixing the ligands (0.023 g, 0.1 mmol) in 1 mL water and cadmium nitrate tetrahydrate (0.03 g, 0.1 mmol) in 1 mL ethanol at room temperature (25 °C). The mixture turned turbid immediately. After 5 min ultrasound-guided treatment, colorless rod-shaped crystals were obtained.

Synthesis of CdS nanotubes by Method I: TAA (75 mg, 20 mmol) as a source solution of S$^2_-$ were added into 2 mL suspended methanol solution of MOF1 (430 mg, 1 mmol) with stirring. After transferring into a serum bottle, the mixture reacted at 70 °C for 50 min in a conditioning oven.

Synthesis of homochiral CdS by method II: In a typical procedure for the preparation of ordered CdS nanotube arrays, TAA (150 mg, 40 mmol) as a source of S$^2_-$ and cadmium nitrate tetrahydrate (70 mg, 0.2 mmol) as a source of Cd$^{2+}$ were added into the solution of the ligands (45 mg, 0.2
mmol) in 6 mL ethanol and 100 μL water with 5 min ultrasound-guided treatment at atmospheric pressure. Then the mixture was allowed to stand at 25 °C for 24 h. The mixture was centrifuged (2 000 rpm) for 15 s, washed with ethanol three times, and let the faint yellow powder products steep in water under ultrasound-guided treatment at room temperature for 5 min to remove unnecessary MOF crystals.

The antithesis of CdS was synthesized exactly as above, except d-HL was used instead of l-HL.

**General procedures for fluorescence titration of CdS nanotubes with d- and l-Asp**

Titration experiments were carried out by adding 2 ml water of d- or l-Asp with 0.01 mmol to CdS nanotubes which were made from 0.2 mmol of MOF1. After stirring 10 min, the mixture were isolated by centrifugation (10 000 rpm) and dried at 70 °C. The solid-state fluorescence spectra were recorded at room temperature. The excitation wavelength is 480 nm and the slit width is set as 2nm/2nm.

Fig. S1. PXRD patterns of (a) simulated [{ZnLBr}·H₂O]ₙ and (b) as-synthesized [{CdLBr}·H₂O]ₙ.
**Fig. S2** SEM images of the products formed at different reaction times by method I. (a) Low-magnification and (b) high-magnification SEM images of MOF obtained by ultrasound-guided treatment, (c) SEM images of products obtained after a reaction time of 1 min by method I, (d) products obtained after a reaction time of 2 min by method I, (e) low-magnification and (f) high-magnification SEM images of CdS nanotubes obtained after a reaction time of 50 min by method I.
Fig. S3. SEM image of chiral CdS nanotubes templated by MOF2

Fig. S4. (a) UV-vis absorption spectrum of MOF. (b) CD spectra of enantiomeric MOF.

Fig. S5. FT-IR spectra of (a) the ligands, (b) MOFs and (c) helical CdS nanotubes.
**Fig. S6.** EDX spectrum of CdS nanotubes obtained after a reaction time of 60 min.

**Fig. S7.** SEM images of the products formed in (a) H$_2$O, (b) acetonitrile, (c) dimethyl formamide, (d) dimethyl sulfoxide and (e) ethylenediamine.

**Fig. S8** Room temperature emission spectra of CdS nanotubes made from MOF2 interaction with 1 nmol of Asp: black, emission spectrum of helical CdS nanotubes without Asp; red, helical CdS nanotubes with 1 nmol l-Asp; blue, CdS nanotubes with 1 nmol d-Asp. All measurements were performed on solid samples at an excitation wavelength of 480 nm.