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Single-handed helical carbonaceous bundles prepared using a chiral polybissilsesquioxane

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ABSTRACT

Left-handed helical polybissilsesquioxane bundles were prepared through a self-templating approach. After carbonization and removal of silica, left-handed helical carbonaceous bundles constructed by fine nanofibers were obtained. They were characterized using transmission electron microscopy, field-emission scanning electron microscopy, powder X-ray diffraction, Raman spectroscopy, N₂ sorptions and diffuse reflectance circular dichroism (DRCD). The Raman spectra and X-ray diffraction pattern indicated that the carbon was amorphous. Mesoporous were identified, which can be originated from the voids among the ultra-fine nanofibers. The DRCD spectrum indicated that they exhibited optical chirality. This material may have potential as catalyst supports, chirality sensors and adsorbents.

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1. Introduction

One dimensional (1-D) nanomaterials are of great interest because of their important role in mesoscopic physics and nanoscale device fabrication [1–3]. Especially, chiral and helical 1-D carbon nanostructures possess high conductivity, elasticity, optical chirality and electromagnetic wave absorption properties, which have potential as micromagnetic sensors, mechanical microsprings, chirality sensors and electromagnetic wave absorbers [4–6]. Up to now, spring-like carbon micro/nano-wires, twisted carbon nanoribbons and helical carbon nanotubes have been reported. They are generally prepared by chemical vapor deposition using catalysts, following vapor–liquid–solid and catalytic anisotropy mechanisms [7,8]. However, the handedness of these 1-D carbon nanostructures is difficult to control. The polysilsesquioxanes can be used as precursors for carbonaceous nanomaterials, and the products can positively retain the mesostructures of the polysilsesquioxanes [9–12]. We have reported single-handed helical carbonaceous nanotubes from 4,4'-biphenylene bridged polybissilsesquioxane nanotubes which were prepared through an external templating approach [13]. In this work, single-handed helical polybissilsesquioxane bundles were prepared through a self-templating approach. After being carbonized in Ar, single-handed helical carbon/silica bundles were obtained. The removal of silica induced the formation of single-handed helical carbon bundles with optical chirality. To our knowledge, this is the

first report of single-handed helical carbonaceous bundles which possess optical chirality.

2. Experimental section

General methods: FT-IR spectra were recorded using KBr pellets for solids on a Nicolet 6700 FT-IR spectrometer. ¹H NMR spectra were recorded using a Varian NMR 400 spectrometer in DMSO-*d*₆ solutions using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed using a Perkin Elmer series II CHNS/O analyzer 2400. Transmission electron microscopy (TEM) images were obtained using an FEI TecnaiG220 at 200 kV. Field-emission scanning electron microscopy (FESEM) was performed using a Hitachi 4800 instrument at 3.0 kV. Wide angle X-ray diffraction (WAXRD) pattern was obtained using an X'Pert-Pro MPD X-ray diffractometer using Cu K α radiation with a Ni filter (1.542 Å). Specific surface area and pore-size distribution were determined by the Brumauer–Emmett–Teller (BET) and Barrett–Joyner–Halton (BJH) methods using N₂ adsorption isotherm measured by a Micromeritics Tristar II 3020 instrument. The circular dichroism (CD) spectra were obtained using an AVIV 410 spectrophotometer. Diffused reflection CD (DRCD) spectra were obtained using a JASCO 815 spectrophotometer. Raman spectra were obtained using a Jobin Yvon Horiba HR 800 Labram confocal microprobe Raman system. The Ar laser excitation wavelength was 514.5 nm.

Materials: (S,S)-**11e12** was synthesized according to literature (Fig. 1) [14,15]. Sodium hydroxide, dioxane, methanol, acetone and

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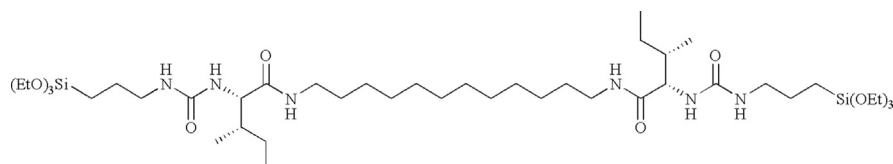


Fig. 1. Molecular structure of the bis-silsesquioxane (*S,S*)-Ile12.

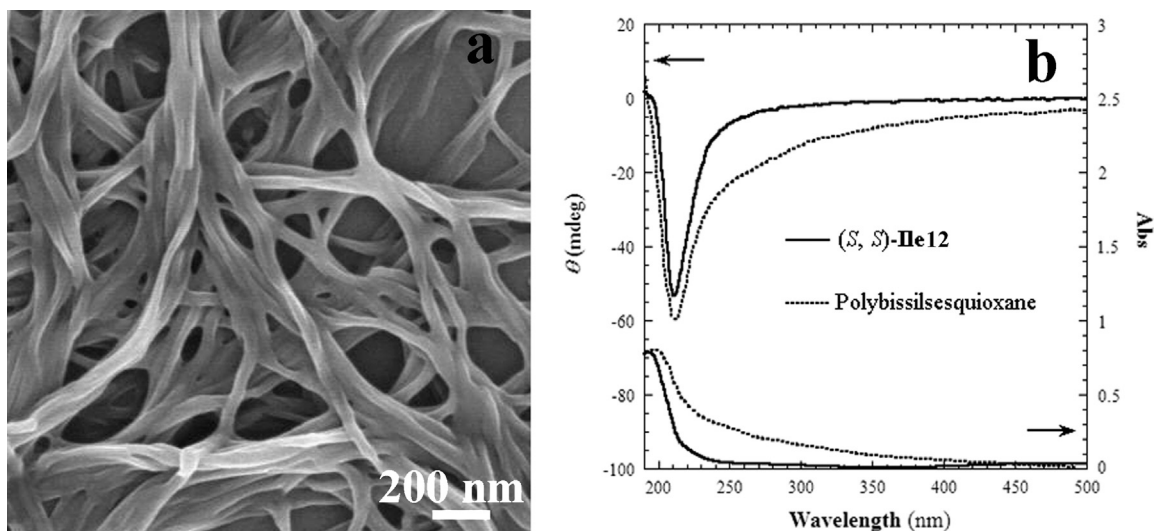


Fig. 2. (a) FESEM image of the xerogel of (*S,S*)-Ile12 prepared at a concentration of 5 mg mL⁻¹ in 1,4-dioxane; (b) CD and UV spectra of compound (*S,S*)-Ile12 and polybis-silsesquioxane.

HF aqueous solution (≥ 40 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Characterization of compound (*S,S*)-Ile12: IR(KBr, cm⁻¹): FT-IR (KBr, cm⁻¹): 3284 ($\nu_{\text{N-H}}$, amide I), 1629 ($\nu_{\text{C=O}}$, amide I), 1560 ($\delta_{\text{N-H}}$, amide II). ¹H NMR (400 MHz, DMSO-*d*₆, TMS, 25 °C) δ =0.52 (t, J =8.5 Hz, 4H; CH₂-Si), 0.81 (m, 12H; CH₃(Ile)), 0.97–1.02 (m, 4H; CH₂(Ile)), 1.13 (t, J =6.9 Hz, 18H; CH₃-CH₂OSi), 1.23 (s, 16H; alkylene chain), 1.35–1.41 (m, 8H; CH₂-CH₂NHCO), 1.56 (m, 2H; CH(Ile)), 2.93–3.14 (m, 8H; CH₂-NHCO), 3.73 (q, J =7.0 Hz, 12H; CH₂-OSi), 3.97 (dd, $J_1=J_2=7.0$ Hz, 2H; CH-Ile), 5.89 (d, J =9.4 Hz, 2H; CONHCH(Ile)), 6.07 (t, J =5.4 Hz, 2H; CONHCH₂-Ile), 7.90 (t, J =5.5 Hz, 2H; NH-CONH). Elemental analysis: C₄₄H₉₂N₆O₁₀Si₂ (M_w : 921.41), calcd (%): C, 57.35; H, 10.06; N, 9.12. Found: C, 56.69; H, 9.62; N, 9.34.

Synthetic procedure for the left-handed helical polybis-silsesquioxane bundles: Bis-silsesquioxane (*S,S*)-Ile12 (40 mg, 0.043 mmol) was dissolved in 1.0 mL of dioxane under heating. When it formed gel at room temperature, 1.0 mL of 0.2 M NaOH aq. was dropped on the surface of gel. The reactants were kept under static condition at 25 °C for 10 days. The product was subsequently washed with water, methanol, and acetone and finally dried in air.

Synthetic procedure for the left-handed helical carbonaceous bundles: The above obtained single-handed helical polybis-silsesquioxane nanofibers were carbonized at 650 °C for 4.0 h with a heating rate of 2.0 °C min⁻¹ in Ar. Left-handed helical carbon/silica bundles were obtained by cooling to room temperature naturally. After that, the carbon/silica bundles were immersed in 10 wt% HF aqueous solution for 4.0 h to remove the silica and then washed with deionized water, followed by being dried in vacuum at 40 °C overnight. Helical carbonaceous bundles were obtained finally.

3. Results and discussion

(*S,S*)-Ile12 forms an opaque gel in 1,4-dioxane at a concentration of 5.0 mg mL⁻¹ (Fig. 2a) [5,6]. The diameters of the gel fibers

range from 50 to 100 nm. Few of them are left-handedly twisted. The CD and UV spectra of (*S,S*)-Ile12 were taken at a concentration of 11 mg mL⁻¹ in 1,4-dioxane. One negative CD signal is identified at 211 nm, which is originated from the left-handed stacking of the carbonyl groups (Fig. 2b). The CD spectrum of the polybis-silsesquioxane shows a stronger and broader negative CD signal at 211 nm, indicating that the chirality transferred from the small molecule to the polymer. As reported, the chiral bridged organic groups in the silsesquioxanes self-assembled through weak interactions. The morphologies of the self-assemblies were transcribed to the polybis-silsesquioxane solids by polycondensation [16,17].

The FESEM image of the left-handed helical polybis-silsesquioxane bundles was shown in Fig. 3a. The polybis-silsesquioxane bundles are constructed coiled nanofibers, whose diameters range from hundreds of nanometers to several micrometers. The helical pitches are about one to several micrometers. The FESEM and TEM images of the left-handed helical carbon/silica bundles were shown in Fig. 3b and d, respectively. Mesopores within the bundles were identified from the TEM image. Left-handed helical carbonaceous bundles were obtained after removal of silica using HF aqueous solution (Fig. 3c and e). Both the morphology and handedness did not change much.

For the left-handed helical carbonaceous bundles, the D and G band was observed at 1349 and 1605 cm⁻¹ in the Raman spectrum, respectively (Fig. 4a). The I_G/I_D ratio is 0.77, indicating the carbon was amorphous [18]. Two broad peaks at 2θ of 25.1 and 43.1° were observed in the WAXRD pattern, which were the characteristic of the (0 0 2) and (1 0 0) planes in graphite, respectively (Fig. 4b). The presence of these peaks might be ascribed to the graphitization of the polybis-silsesquioxane nanofibers. However, the peaks are broad and weak, indicating no large crystalline domains within the sample. The N₂ adsorption–desorption isotherms of carbonaceous bundles were shown in Fig. 4c. The sample showed type-IV isotherms with a capillary-condensation step appeared at relative pressure (P/P_0) between 0.8 and 1.0,

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