

Nanotubes Fabricated from Sandwich-Type Mixed (Porphyrinato)(phthalocyaninato)europium Complex by Template Technique

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Nanotubes of sandwich-type mixed (porphyrinato)(phthalocyaninato)europium(III) double-decker, $H\{Eu(TCIPP)[Pc(\alpha-OC_4H_9)_8]\}$ [TCIPP = 5,10,15,20-tetrakis(4-chlorophenyl)porphyrinate; $Pc(\alpha-OC_4H_9)_8 = 1,4,8,11,15,18,22,25$ -octakis(1-butyloxy)phthalocyaninate] were fabricated by using nanoporous anodized aluminum oxide (AAO) membrane as the template. The tubular structure was investigated by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and UV–visible spectroscopy. It was found that the outer diameter of the nanotubes was matched with the pore diameter of AAO membrane very well. HRTEM micrographs reveal that the walls of the nanotubes have orderly layered structure and the distance between the adjacent layers is 0.58 nm, which agrees well with the size (thickness) of one double-decker molecule, indicating that the nanotubes are supramolecular structures formed from the double-decker molecules due to $\pi-\pi$ interaction between the macrocycles. UV–vis spectroscopic results of the nanotubes also confirmed the formation of J-aggregates of the complex molecules, consistent with HRTEM investigation results.

Introduction

Various kinds of nanotubes have been prepared since the discovery of carbon nanotubes by Iijima in 1991 owing to their excellent mechanical, electrical, and thermal properties.¹ Recently, much more research interest has been induced into nanotubes formed from a variety of materials including C_{60} , metals, inorganic compounds, and polymers.^{2–4} Different preparation methods such as hydrothermal synthesis, self-assembly, surfactant-assisted synthesis, and template synthesis were used to prepare these nanotubes.⁵ It is worth noting that, among these methods, the template synthesis pathway has attracted much attention due to its versatility. Furthermore, in the template synthesis method, alumina membranes are usually employed as templates to produce various kinds of nanotubes due to their tunable pore dimensions over a wide range of diameters (7–300 nm), narrow pore size distribution, and good thermal and mechanical stability.⁶

Porphyrin/phthalocyanine complexes, in particular their sandwich-type rare earth compounds, have been extensively and intensively investigated as advanced molecular materials.⁷ This class of complexes, with either a double- or a triple-decker molecular structure, usually exhibits strong $\pi-\pi$ intramolecular interaction, resulting in intriguing electronic and optical properties and potential applications as gas sensors and organic field-effect transistors (OFETs).⁸ Among all the related investigations toward applications, one of the focuses is the fabrication and preparation of designable assemblies and nanomaterials.^{9–12} Recently, a composite porphyrin nanotube was produced by electrostatic force between two oppositely charged monomeric

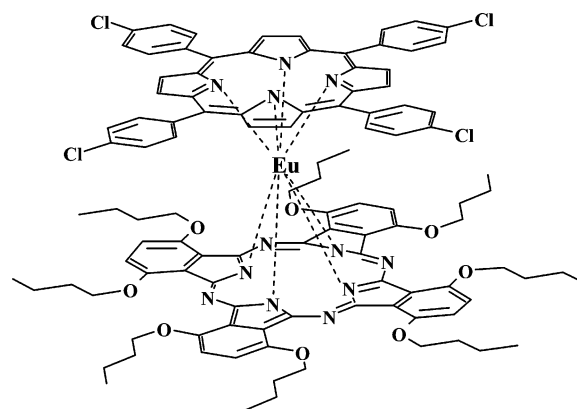


Figure 1. Schematic molecular structure of the double-decker complex $H\{Eu(TCIPP)[Pc(\alpha-OC_4H_9)_8]\}$.

porphyrin compounds, for which the photocatalytic activity to reduce the aqueous metal cations was also demonstrated.¹⁰ According to Müllen and co-workers, nanotubes of monomeric naphthalocyaninato nickel complex were also successfully fabricated by a template method.^{12a} These results seem to represent the most important achievement toward utilization of porphyrin/phthalocyanine nanotubes.^{10b,11,13} However, to the best of our knowledge, nanotubes composed of sandwich-type porphyrinato/phthalocyaninato rare earth complexes have not yet been reported. It is therefore of interest to fabricate sandwich porphyrinato/phthalocyaninato rare earth complexes into nanotubes with special structures and functionalities.

In the present paper, we describe the preparation and characterization of nanotubes of a sandwich-type mixed (porphyrinato)(phthalocyaninato)europium(III) double-decker, $H\{Eu-$

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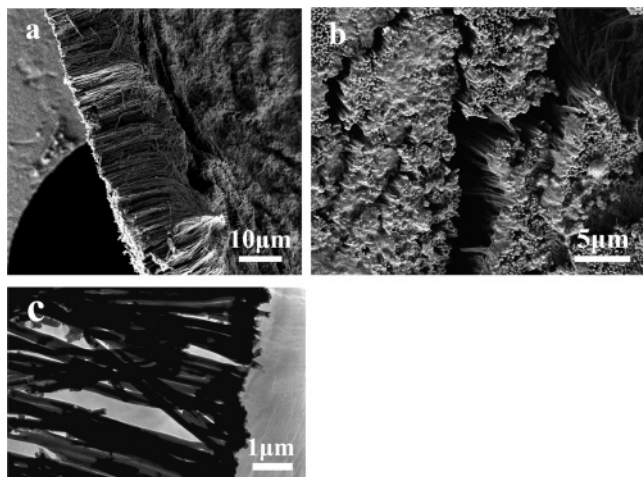


Figure 2. Aligned nanotubes of the double-decker complex generated within alumina membrane after immersion for 4 days. SEM images: typical side view (a) and top view (b). TEM image (c).

(TCIPP)[Pc(α -OC₄H₉)₈], fabricated using nanoporous anodized aluminum oxide (AAO) as template.

Experimental Section

Materials. The mixed (porphyrinato)(phthalocyaninato)-europium double-decker compound H{Eu(TCIPP)[Pc(α -OC₄H₉)₈]} (Figure 1), was prepared according to published procedure.¹⁴ Porous anodized alumina oxide (AAO) membranes were purchased from Whatman Co. (60 μ m thickness); the average pore size of the membrane was 200 nm (evaluated by scanning electron microscopy, SEM). Tetrahydrofuran (THF) was purchased from Tianjin Chemical Co.

Preparation of Nanotubes. The AAO membrane was cleaned for 10 min in an ultrasonic bath using solvents of different polarities including water, ethanol, acetone, and chloroform. After being dried in a vacuum, the clean membrane was immersed into the THF solution of double-decker complex of 5.0 mg/mL concentration for several hours and dried again in a vacuum; it was then immersed in aqueous solution of NaOH (3 mol·L⁻¹) to remove the AAO membrane. The template-free sample was washed with double-distilled water, dried in a vacuum, and submitted to various kinds of microscopic and spectroscopic measurements.

Characterization. The template-free sample was dispersed in water. A drop of the sample solution was put on a carbon-coated copper grid and dried in a vacuum at room temperature overnight for transmission electron microscopic (JEOL, JEM-100CX II, 100 kV), high-resolution transmission electron microscopic (JEOL-2010, 200 kV) equipped with energy-dispersive X-ray spectroscopy (EDS), and field emission scanning electron microscopic (JEOL, JSM-6700F) investigations. UV-vis spectra were recorded on a Hitachi U4100 UV-vis spectrophotometer (Japan) and Fourier transform infrared spectra were recorded in KBr pellets with 2 cm⁻¹ resolution using a Bio-Rad FTS-165 spectrometer.

Results and Discussion

TEM and SEM Images. Figure 2 shows the SEM images of the aligned nanotubes of the double-decker complex formed in the nanochannels of the AAO template, which were selectively etched with an aqueous solution of NaOH. After complete removal of the template, nanotubes with lengths of several to tens of micrometers were obtained, which aligned into parallel

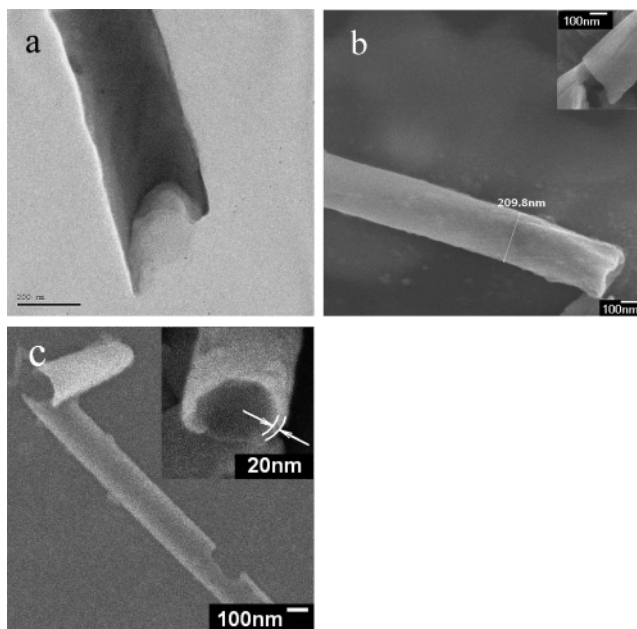


Figure 3. TEM (a) and SEM (b) images of individual nanotube generated within alumina membrane after immersion for 4 days; (c) SEM image of the same nanotube generated within alumina membrane after immersion for 12 h.

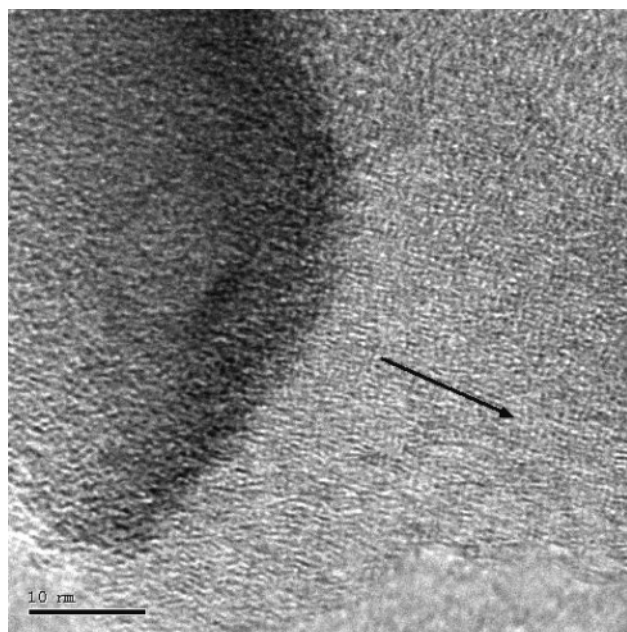


Figure 4. HRTEM image of nanotubes generated within alumina membranes. The arrow is the nanotube axis.

arrays of nanotubes as shown in Figure 2c. However, the ordered arrays were easily broken into individuals by ultrasonication, as shown in Figure 3.

As expected, the shape and size of the nanotubes obtained are in accordance with the dimensions of the template channels. Most of the nanotubes are cylindrically shaped with open tips. The average outer diameter is about 200 nm, which well matches the template channels. It is worth mentioning that nanotubes with one closed bottom were occasionally observed (Figure 3c), and were formed naturally on the inner surface of the pores when the template preparation pathway was employed accordingly.¹⁵

The nanotubes were further investigated by HRTEM, Figure 4. As shown in the high-resolution image, well-defined walls

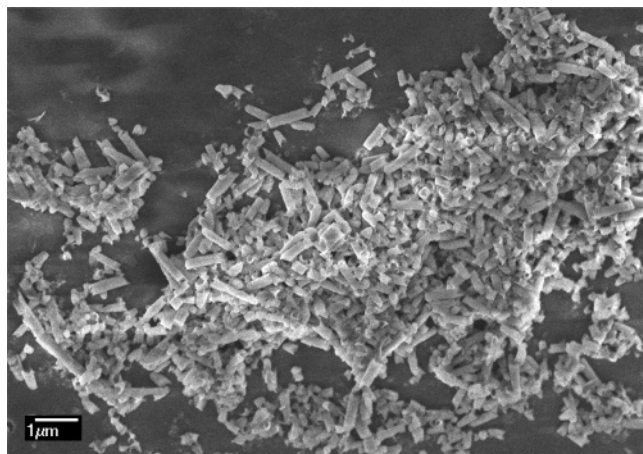


Figure 5. SEM images of damaged nanotubes generated within alumina membrane after annealing at 250 °C for 20 h.

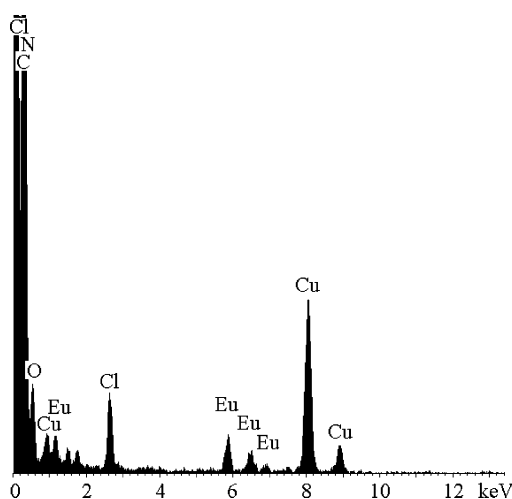


Figure 6. Energy-dispersive analysis of a single nanotube of the double-decker complex.

were formed and ordered layers with a layer-to-layer distance of about 0.58 nm were aligned. This value is in good agreement with the farthest distance between the phthalocyanine (Pc) ring plane and the porphyrin (Por) ring plane in the double-decker molecule, i.e., the thickness of a double-decker molecule obtained by CPK model. Nevertheless, the layers were found to be parallel to the tube axis, indicating the possible column fabrication of the π -stacked Pc and Por disks in short-range intermolecular interactions. The tube walls were thus constructed from well-ordered, layered Pc and/or Por disks, with the stacking of the disk normal perpendicular to the tube axis. This result is in line with those reported previously that the disk-like molecules with substituents containing oxygen atom(s) usually form columnar supramolecular structures on the alumina surface by face-on π - π stacking,^{12,16} indicating that the ordered self-assembly of the double-decker molecules at the inner surface of AAO template plays an important role in the formation of wall structures of nanotubes. When the AAO membranes were immersed in the THF solution of the double-decker complex, a

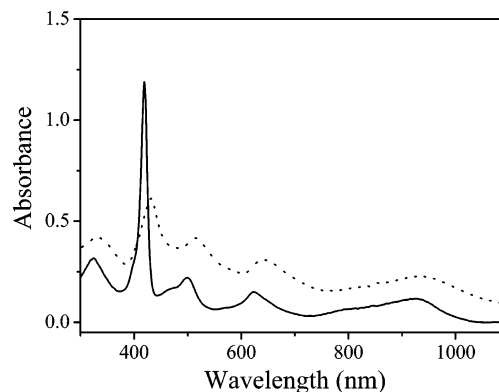


Figure 7. Electronic absorption spectra of the double-decker in CHCl_3 (solid line) and nanotubes dispersed in distilled water (dotted line).

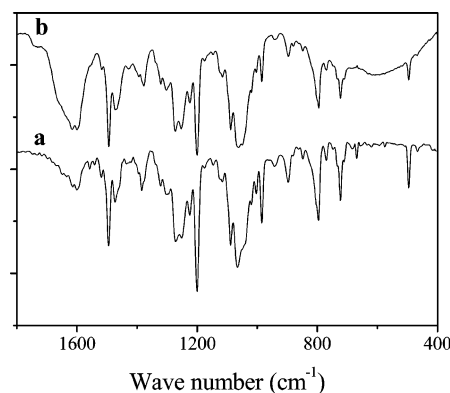


Figure 8. IR spectra of double-decker (a) and nanotubes after removal of the template (b) in the region of 400–1800 cm^{-1} with 2 cm^{-1} resolution.

thin film formed in the inner surface of pores covered the pore walls in the initial stage of wetting since the cohesive driving force for complete filling is much weaker than the adhesive force. As a consequence, complete filling is prevented by solvent evaporation, thus preserving a nanotubular structure.⁴ A self-assembly process of double-decker molecules occurs simultaneously, at the inner surface of the template, during the evaporation course of the solvent, inducing the formation of orderly layered stacking. Moreover, the capillary effect is favorable for growth of the nanotubes in pores of membrane owing to the high aspect ratio of the pores of alumina membranes.¹⁵

In contrast with the system reported by Müllen and co-workers, in which thermal treatment was found important for reorganizing the naphthalocyanine disks into more ordered architectures,^{12a} the opposite effect was observed in the present case. Compared with the spontaneously formed double-decker nanotubes, thermal treatment was not found to improve the order of the Por/Pc stacking in the nanotubes formed. TEM images for the samples obtained by being annealed at 250 °C for 25 h show only short nanotube fractions, Figure 5, indicating limited mechanical strength of corresponding nanotubes. Moreover, electron diffraction is not detected, which gives further evidence for the noncrystallinity of the nanotubes obtained.

TABLE 1: Electronic Absorption Data of Double-Decker Compound $\text{H}\{\text{Eu}(\text{TCIPP})[\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8]\}$ in CHCl_3 and Corresponding Nanotubes Dispersed in Distilled Water

	wavelength/nm				
$\text{H}\{\text{Eu}(\text{TCIPP})[\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8]\}$	324	419	499	623	928
nanotubes	331	432	515	641	934

It has also been found that the wall thickness of nanotubes formed is dependent on the immersion time. As indicated in Figure 3, the nanotubes with wall thicknesses of less than 20 nm were formed by immersing the AAO template into the THF solution of double-decker compound for 12 h, while those of more than 20 nm thickness were immersed for 4 days, clearly revealing that the wall of nanotubes becomes thicker along with the immersion time. This suggests that fully developed, mechanically stable, good-quality multilayered nanotubes of double-decker compound could be formed only when the AAO template was immersed in corresponding solution for a relatively long time.

EDS Analysis. The successful preparation of double-decker nanotubes was further confirmed by the elemental signatures of C, Eu, Cl, N, and O in the energy-dispersive X-ray analysis as shown in Figure 6. The result indicates unambiguously that these nanotubes are composed of the double-decker molecules.

UV-Vis Spectra. The UV-vis spectra of the compound in solution and in nanotubes dispersed in distilled water are compared in Figure 7 and the data are summarized in Table 1. As can be seen in Figure 7, the great similarity in the electronic absorption spectra between the nanotubes obtained and the double-decker compound in solution gives unambiguous evidence for the composition of nanotubes from the double-decker molecules. The broadening and significant red shift for all the absorption bands including those contributed mainly by porphyrin and phthalocyanine Soret and Q bands of nanotubes, compared with those of the double-decker compound in solution, reveal intensive intermolecular interaction in the nanotubes and suggest the formation of double-decker J-aggregates in the nanotubes.¹⁷ This result is consistent with the HRTEM investigation described above, giving further support to the proposed formation mechanism of the nanotubes; i.e., the ordered self-assembly of the double-decker molecules due to the π - π supramolecular interaction at the inner surface of AAO template plays an important role in the formation of nanotubes.

IR Spectra. The IR spectra of the synthesized double-decker compound and nanotubes after removal of the template are compared in Figure 8. In line with the results obtained from UV-vis and other microscopic techniques, good correspondence in the IR spectra between the synthesized double-decker compound and nanotubes obtained further confirms the composition of nanotubes from the double-decker molecules.

Conclusion

In summary, sandwich-type mixed (porphyrinato)(phthalocyaninato)europium double-decker compound was used for the first time as a building block to fabricate nanotubes in a nanochannel template. Well-defined nanotubes with an average diameter of ca. 200 nm were obtained due to the π - π supramolecular interaction through a self-assembly process during the solvent evaporation course. Owing to the rich optical and electrochemical properties as well as the special electronic structure of sandwich-type porphyrinato and/or phthalocyaninato rare earth complexes, the nanotubes obtained are expected to have applications in nanoelectronics.

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