Nanometer-Level Sol−Gel Transcription of Cholesterol Assemblies into Monodisperse Inner Helical Hollows of the Silica

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Dimeric azobenzene-appended cholesterol organogel **1** was synthesized and its gelation ability was evaluated in organic solvents. It can gelate 1-hexanol, 1-octanol, toluene, *m*-xylene, and *p*-xylene, under 5.0 wt %, indicating that **1** acts as a versatile gelator of various organic solvents. To obtain visual insights into the aggregation mode, we observed the xerogel structure of 1-octanol and *m*-xylene gels **1** by TEM and SEM. They revealed a typical helical fiber structure with 50−100 nm of outer diameters, suggesting that the organogel **1** grows into the bundled fiber structure in the absence of any additive. Also, we observed the CD spectrum of 1-octanol gel **1** to characterize the aggregation mode in the gel phase. In the CD spectrum, the $\lambda_{\theta=0}$ value appeared at 365 nm, which is consistent with the absorption maximum at $\lambda_{\max} = 365$ nm. It is known that azobenzene-appended cholesterol gelators with natural (S) C-3 configuration tend to give a negative sign for the first Cotton effect, indicating that the dipole moments of azobenzene chromophores tend to orient in the anticlockwise direction. Sol−gel polymerization of tetraethoxysilane (TEOS) was carried out using the organogel **1** as a template. We observed the SEM pictures of the silica obtained from 1-octanol gel **1**. The silica nanotube showed the fibrous structure with ca. 30-nm outer diameter and a few micrometers length. Very surprisingly, the TEM picture revealed the inner helical structure of a silica nanotube with ca. 7.5-nm inner diameter and long helical pitch, which is comparable with the width of one-dimensional molecular stacking **1** on the basis of the interdigitated van der Waals interaction between cholesterol moieties. These results indicate that the organogel **1** was successfully transcribed into the silica nanotube by the intermolecular hydrogen-bonding interaction between the amino group of the gelator and anionic silica particles.

Introduction

Inorganic materials, although diverse in composition, lack structural variety, which is one of the characteristics of supramolecular and other organic structures. Since inorganic materials with well-defined three-dimensional (3-D) structures have many potential applications (catalysis, chromatography, adsorbents, controlled release materials, etc.), scientists working in materials as well as in other fields of chemistry have devoted a great deal of their research effort toward the development of efficient and innovative fabrication methods to obtain these challenging materials.[1−10] In particular, nanometer-sized inorganic materials are generally accepted as the generation materials in research fields such as catalysts[11] and electrodevices.[12−15]

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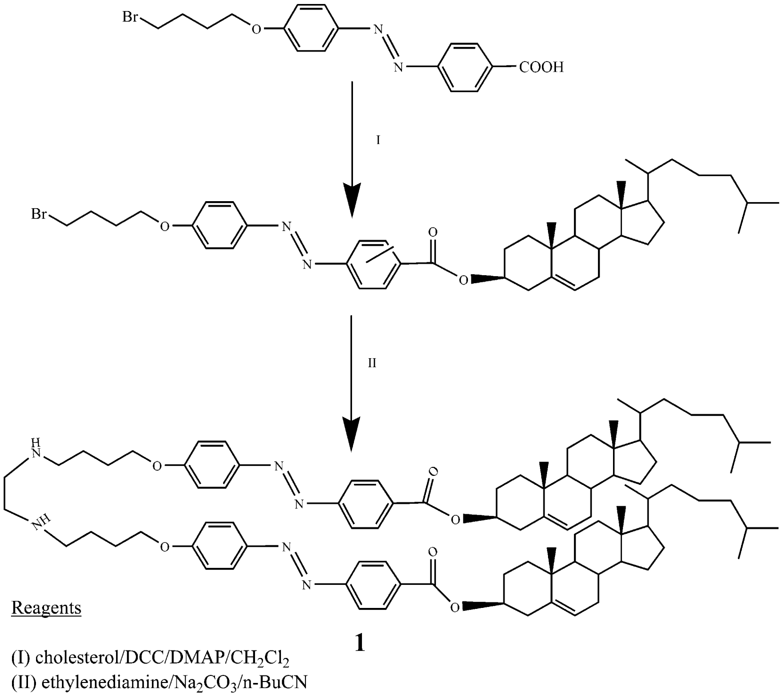
Scheme 1



Reagents

(I) cholesterol/DCC/DMAP/CH_2Cl_2
(II) ethylenediamine/Na_2CO_3/n-BuCN

Recently, we[16−17] and Hanabusa et al.[18] reported the preparation of a helically structured silica and tantalum oxides by sol−gel transcription in chiral organogel systems, respectively. Their studies suggested that a unique superstructure of the organogel fiber can be transcribed into the inorganic structure. However, their helical inorganic materials have been characterized by the broad size distribution as well as micrometer-sized inner diameter because bundled fibers of organic assemblies acted as a template. Furthermore, most of the organic chiral assembling superstructures were not replicated into helical inorganic materials by the sol−gel transcription process, but just gave the linear hollow fiber.[9,10]

To create nanometer-sized inorganic materials that can accurately reflect helical characterization of a template, we have designed compound **1** as a template in the sol−gel reaction which has two cholesterol skeletons as a chiral aggregate-forming site and two amino groups as an acidic proton or cationic binding sites. We have found that **1** gelates various organic solvents under 1.0−5.0 wt %. Interestingly, we noticed that the speed of bundle growth of this gelator is relatively slow and would provide us with a greater chance to transcribe nanosized incipient fibers into silica morphology. Here, we report that the sol−gel transcription of this gel system with tetraethoxysilane (TEOS) results in "helical inner hollow silica" with ca. 7.5-nm inner diameter, which is comparable to the width of one-dimensional molecular stacking **1**. This is a rare example of the chiral hollow stack immobilized in an inorganic material.

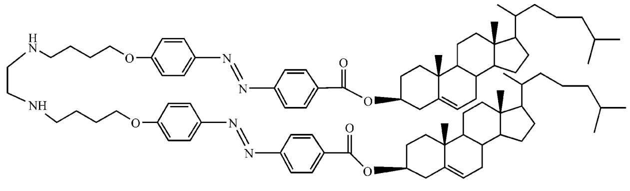
Table 1. Gelation Ability of 1 in Organic Solvents[a]

solvent	**1**	solvent	**1**	solvent	**1**
methanol	S	benzylamine	PG	propionic acid	PG
ethanol	S	ethylenediamine	PG	benzene	S
1-butanol	PG	DMSO	S	toluene	G
1-hexanol	G	acetonitrile	I	*p*-xylene	G
1-octanol	G	acetic acid	I	*m*-xylene	G
benzyl alcohol	PG				

[a] Gelator = 5.0 wt %; G, stable gel formed at room temperature; S, soluble; I, insoluble; PG, partially gelatinized.

Results and Discussion

Self-assembling Structure of Organogel. Compound **1** was synthesized by treating ethylenediamine with a monobromobutyloxyazobenzene derivative of cholesterol in refluxing *n*-butyronitrile for 48 h (Scheme 1).[6] Compound **1** was obtained in 70% yield, after workup with chromatography and identified by IR, ^1H NMR, ^{13}C NMR, and MS spectral evidence and elemental analyses.



1

The gelation ability of compound **1** was estimated in various organic solvents. As summarized in Table 1, **1** can gelate 10 out of 16 solvents such as 1-hexanol, 1-octanol, toluene, *m*-xylene, and *p*-xylene, under 1.0−5.0 wt %, indicating that **1** acts as a versatile gelator of various organic solvents.

To obtain visual insights into the aggregation mode, we observed the xerogel structure of 1-octanol and

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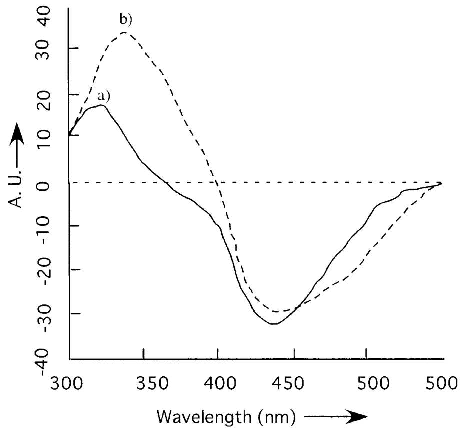

Figure 1. CD spectra of (a) 1-octanol gel **1** and (b) 1-octanol gel **1** after sol−gel transcription.

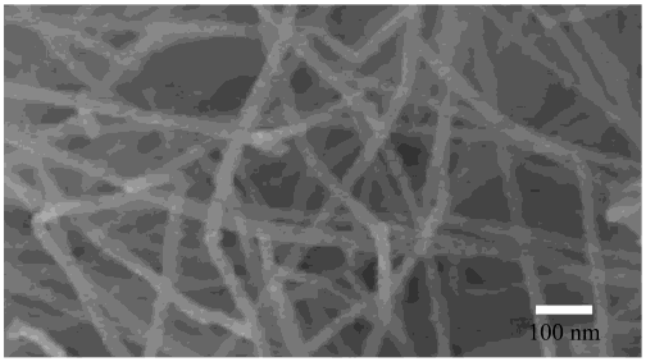

Figure 2. SEM picture of the silica nanotube obtained from 1-octanol gel **1** after calcination.

m-xylene gels **1** by TEM and SEM. They revealed a typical helical fiber structure with 50−100 nm of outer diameters, suggesting that the organogel **1** grows into the bundled fiber structure in the absence of any additive. Also, we observed the CD spectrum of 1-octanol gel **1** to characterize the aggregation mode in the gel phase as shown in Figure 1. In the CD spectrum, the $\lambda_{\theta=0}$ value appears at 365 nm (Figure 1a), which is consistent with the absorption maximum at $\lambda_{\max} = 365$ nm. It is known that azobenzene-appended cholesterol gelators with natural (S) C-3 configuration tend to give a negative sign for the first Cotton effect, indicating that the dipole moments of azobenzene chromophores tend to orient into the anticlockwise direction.[11,16] In addition, it is expected that **1** in the organogel adopts a folded conformation to enjoy efficient intramolecular and intermolecular cholesterol−cholesterol and azobenzene−azobenzene interactions.[16] The CD spectrum of the silica obtained after sol−gel transcription is similar to that of the organogel state, which will be explained later in more detail.

Sol−Gel Transcription. Sol−gel polymerization of TEOS was carried out to transcribe the novel superstructure formed in the organogel into the silica structure, using **1** according to the method similar to that described previously.[5−7] The details of the sol−gel experiments are described in the Experimental Section.

We observed the SEM pictures of the silica obtained from 1-octanol gel **1** after calcination (Figure 2). The silica nanotube shows the fibrous structure with ca. 30-nm outer diameter and a few micrometers length. The yield for the silica nanotube was almost 100%. This result indicates that the organogel **1** was successfully transcribed into the silica nanotube by the intermolecular hydrogen-bonding interaction between the amino group of the gelator and anionic silica particles. Furthermore, the well-defined silica before calcination showed a fibrous structure with the same size of that obtained after calcination. The silica obtained from 1-hexanol gel **1** also gave the same morphology as that obtained from 1-octanol gel **1**.

To further corroborate that the organogel gel superstructure really acts as a template for the growth of the silica nanotube, we took the TEM picture after removal of **1** by calcination. Figure 3 shows low and high magnifications of TEM pictures of the silica obtained from 1-octanol gel **1**. It is clear that the centeral part of the material is light and both edges are dark, implying the well-defined hollow nanotube structure. The silica nanotube possesses ca. 7.5-nm inner diameter with long helical pitch, which is comparable with the width of one-dimensional molecular stacking **1** (7.5 nm by the CPK model on the basis of interdigitated van der Waals interaction between cholesterol moieties: Figure 3d). Both end parts of the tube indicate that the channel is open. In addition, according to a BET method (Figure 4), average inner diameter and surface area of the silica nanotube were evaluated to be 7.0−7.5 nm with narrow distribution and 374.5 m^2/g, respectively.

Once again, we measured the CD spectrum of the silica nanotube after sol−gel polymerization to confirm the template effect (Figure 1b). The CD spectrum obtained after sol−gel polymerization is very similar to that of the organogel **1** before polymerization of TEOS, but the $\lambda_{\theta=0}$ value shifts to a longer wavelength (398 nm). This result implies that the well-ordered chiral packing structure of organogel **1** is still retained in the inside of the silica tube. Also, the results obtained so far consistently support the view that **1** aggregates into a one-dimensional chiral stack, along which sol−gel polymerization of TEOS proceeds in the gel phase. The size of the inner hollow suggests that the incipient organogel fibers are encapsulated in these silica tubes.

More interestingly, careful examination of the high-magnification TEM pictures reveals that these silica nanotubes have the helical inner hollow (see arrows in Figure 3b,c), strongly suggesting that the helical packing structure of cholesterol gelator **1** was directly reflected into the silica structure. This result is a rare example for the silica tubes because most of the chiral assembling structures of organogelators could not be reflected in the silica structure.

We propose the mechanism for the formation of a novel helical silica structure from the organogel **1** (Figure 5). The gelator **1** forms the incipient helical fiber structure in the presence of TEOS (Figure 5c; lower) whereas the incipient helical fiber of the gelator **1** grows into the bundled fibrils in the absence of TEOS (Figure 5c; upper). Oligomeric silica species are adsorbed onto the surface of the helical fiber structure of **1** (Figure 5c) as the growth of incipient helical fiber is relatively slow in comparison to the polymerization rate of TEOS, and the polymerization further proceeds along these single

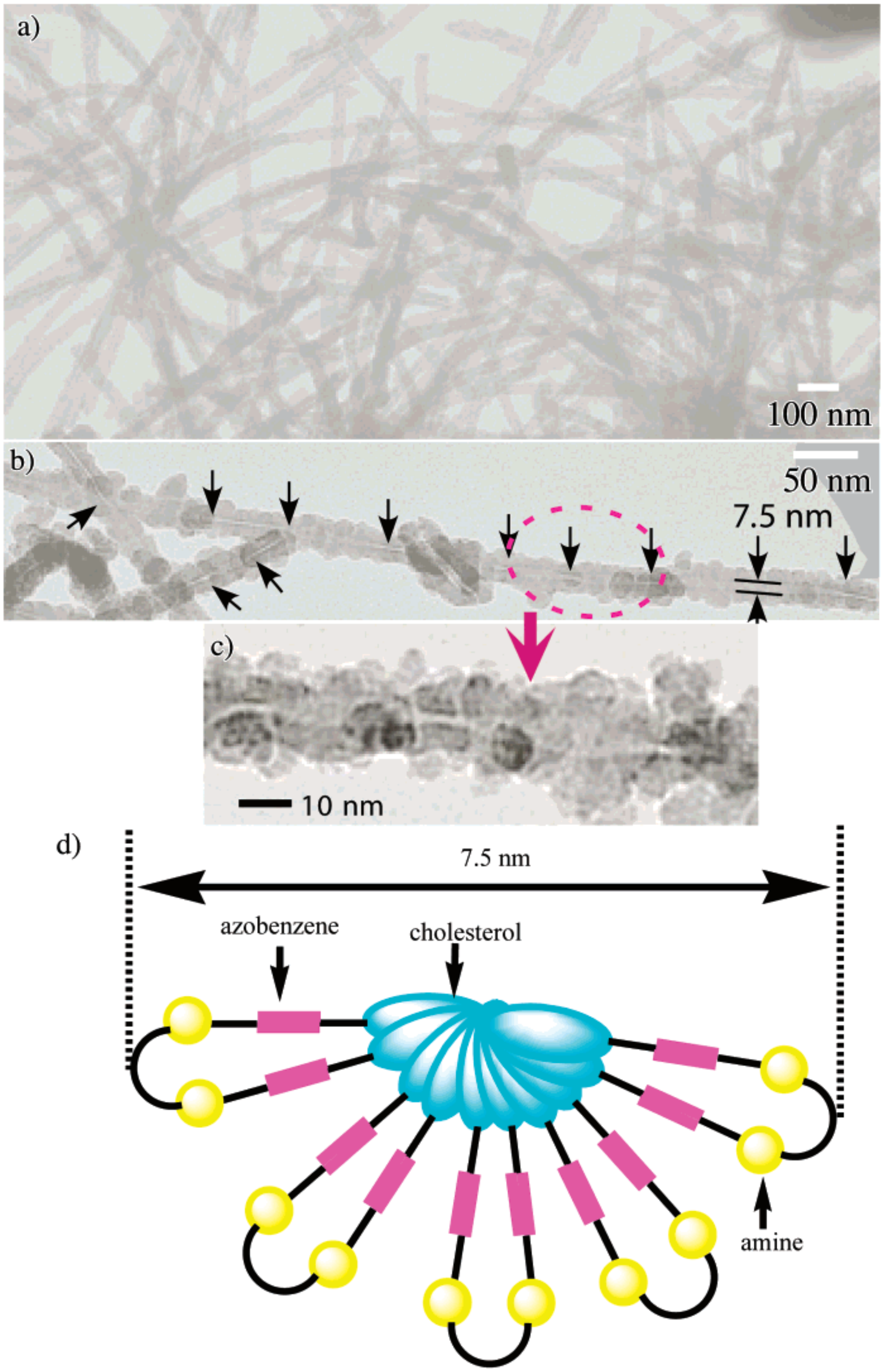

Figure 3. (a) Low-magnificiation and (b and c) high-magnification TEM pictures of the silica nanotube obtained from 1-octanol gel **1** after calcination and (d) schematic representation of one-dimensional molecular stacking of **1**. Arrows indicate the helical structure.

fibers. This propagation mode eventually yields the novel inner helical silica according to combustion of gelators by calcination (Figure 5d).

Conclusions

The present paper has demonstrated that nanometer-level sol–gel transcription of organic assemblies is possible when the incipient organic assembly can exist stably in the gel phase. Until now, the silica superstructures obtained by template transcription of organic assemblies have been characterized by the broad size distribution. This polydispersed nature has made their chemical applications difficult. We believe that the creation of the new silica nanotube with nearly monodispersed hollow size is essential and applicable to other related transcription systems. Particularly, the helical hollow of the silica will be useful as a catalyst in asymmetric synthesis.

Experimental Section

Apparatus for Spectroscopy Measurements. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 apparatus. IR spectra were obtained in KBr pellets using a Shimadzu FT-IR 8100 spectrometer, and MS spectra were obtained by a Hitachi M-250 mass spectrometer. Circular dichroism (CD) spectra were measured on a JASCO J-820KS spectrophotometer (cell diameter 0.1 mm).

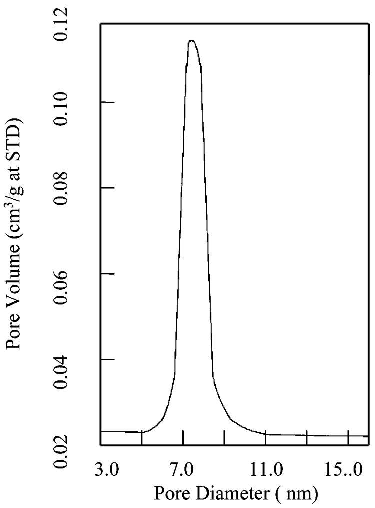

Figure 4. Pore size distribution of the silica nanotube by a BET method.

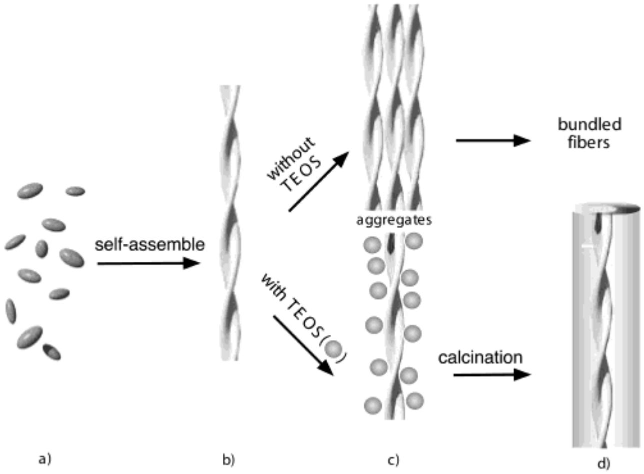

Figure 5. Schematic representation for the creation of the helical structure of the silica from the organogel state **1**: (a) gelator, (b) incipient organogel fiber, (c) silica adsorption (lower) and aggregation of organogel fiber (upper), and (d) the inner helical structure of the silica formed after calcination.

SEM and TEM Measurements. For energy-filtering transmission electron microscopy (EF-TEM) a piece of the gel was placed on a carbon-coating copper grid (400 mesh) and removed after 1 min, leaving some small patches of the gel on the grid. Then, this was dried for 1 h at low pressure. The specimen was examined with Carl Zeiss EM902, using accelerating voltage of 80 kV and a 16-mm working distance. Field emission scanning electron microscopy (FE-SEM) was taken on a Hitachi S-4500. To observe the morphology of the silica nanotube, the samples were prepared by adhering a large number of the silica particles before and after calcination onto a carbon film on a Cu grid.

Gelation Test of Organic Fluids. The gelator and the solvent were put in a septum-capped test tube and heated in an oil bath until the solid was dissolved. The solution was cooled at room temperature. If the stable gel was observed at this stage, it was classified as G in Table 1.

Sol−Gel Polymerization of TEOS. Compound **1** (2−5 mg) was dissolved in 1-octanol or 1-hexanol (200 mg) by heating. The gel sample was cooled to room temperature. TEOS (20−50 mg), benzylamine (10−25 mg) as a catalyst, and water (10−25 mg) were added to the gel sample. Then, the sample was heated until clear solution was obtained and then left at ambient temperature for 2−14 days. Subsequently, the sample was heated at 200 °C for 2 h, 500 °C for 2 h under a nitrogen atmosphere, and then kept at 500 °C under aerobic conditions for 4 h.

4-*n*-Monobromobutoxyl-4′-[(cholesteryloxy)carbonyl]-azobenzene (3). 4-[(Bromobutoxyphenyl)azo]benzoic acid **2** (0.7 g, 1.86 mmol) and cholesterol (0.718 g, 2.23 mmol) were dissolved in 20 mL of dichloromethane under a nitrogen atmosphere. The solution was maintained at 0 °C using an ice bath. The dicyclohexylcarbodiimide (DCC) (0.383 g, 1.86 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (0.022 g, 0.186 mmol) were then added, the reaction mixture being stirred for 4 h at 0 °C. The reaction mixture was filtered and the filtrate was washed with acidic and basic aqueous solutions (50 mL each). The organic layer was evaporated to dryness. The residue was purified by a silica gel column eluting with THF/*n*-hexane (1:6 v/v) to give compound **6** in 26% yield as a yellow solid (mp 141.5 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.17 (2H, d, $J = 9.0$), 7.72 (2H, d, $J = 9.0$), 7.90 (2H, d, $J = 9.0$), 7.10 (2H, d, $J = 9.0$), 5.45 (1H, d, $J = 6.3$), 5.02−4.88 (1H, m), 41 (2H, t, $J = 6.3$), 3.52 (2H, t, $J = 6.2$), 2.49 (2H, d, $J = 6.2$), 2.28−0.94 (35H, m), 0.88 (3H, s); δ_c (75 MHz, $CDCl_3$): 165.1, 161.88, 155.20, 146.98, 139.9, 130.2, 125.18, 122.84, 122.28, 114.72, 67.22, 66.67, 56.67, 56.11, 50.01, 42.30, 39.71, 39.50, 38.20, 37.01, 36.64, 36.17, 35.79, 33.32, 31.92, 31.86, 29.3, 28.32, 28.01, 27.88, 27.78, 24.28, 23.82, 22.83, 22.56, 21.04, 19.38, 19.38, 18.71, 11.86. MS(m/z) = 745 $[M + H]^+$. IR (KBr, ν_{max}/cm^{-1}): 3005 (Ar), 2935 (−CH), 1722 (−C═O), 1603, 1579, 1500, 1468 (Ar), 1284, 1116, 1047 (−C−O).

4-(2-Ethyldiamino)butoxy-4′-bis[(cholesteyloxy)carbonylazobenzene]. A mixture of compound **3** (0.1 g, 0.14 mmol), 1,2-diaminoethane (0.04 g, 0.67 mmol), and sodium carbonate (0.3 g, 6.7 mmol) in dry butyronitrile (10 mL) was refluxed for 24 h. The solution was filtered after cooling, the filtrate being concentrated to dryness by a vacuum evaporator. The residue was purified by an aluminum oxide column with ethanol/dichloromethane to give the desired product in 43.3% yield as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.17 (4H, d, $J = 9.1$), 7.93 (4H, d, $J = 9.1$), 7.85 (4H, d, $J = 9.0$), 7.02 (4H, d, $J = 9.0$), 5.42 (2H, d, $J = 6.5$), 4.0−3.5 (6H, m), 3.0−0.9 (104H, m). MS (m/z) = 1392 $[M + 2H]^+$. IR (KBr, ν_{max}/cm^{-1}): 3005 (Ar), 2943 (−CH), 2868, 1715 (−C═O), 1595, 1582, 1500, 1468, 1419 (Ar), 1404, 1275, 1140, 1109 (−C−O). Anal. Calcd for $C_{90}H_{128}N_6O_6$: C, 77.77; H, 9.28; N, 6.05. Found: C, 75.52; H, 9.45; N, 7.95.

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