Creation of Double Silica Nanotubes by Using Crown-Appended Cholesterol Nanotubes

Jong Hwa Jung,*[a, b] Seok-Hoon Lee,[a] Jong Shin Yoo,[a] Kaname Yoshida,[b] Toshimi Shimizu,[b] and Seiji Shinkai*[c]

Abstract: New crown-appended cholesterol-based organogelators **1**–**3**, which have one or two cholesterol skeletons as a chiral aggregate-forming site, two amino groups as an acidic proton binding site, and one crown moiety as a cation binding site, were synthesized, and the gelation ability was evaluated in organic solvents. These gelators could gelatinize several organic solvents under 1.0 wt%, indicating that **1**–**3** act as a versatile gelator of various organic solvents. We observed CD spectra of the acetic acid or propionic acid gels of **1**–**3** to characterize the aggregation mode in the organogel system. In the CD spectrum of the acetic acid gel **1**, the positive sign for the first Cotton effect indicates that the dipole moments of azobenzene chromophores tend to orient into the clockwise direction. On the other hand, propionic acid gels **2** and **3**, bearing only one cholesterol, moiety exhibit a negative sign for the first Cotton effect, strongly suggesting that the dipole moments of the azobenzene chromophores orient into the anticlockwise direction. The TEM images of the **1**+acetic acid gel resulted in the helical ribbon and tubular structures. Sol-gel polycondensation of tetraethoxysilane (TEOS) was carried out with **1**–**3** as templates in the gel phase. The silica obtained from the **1**+acetic acid gel showed the helical ribbon with 200–1700 nm width and the tubular structure of the silica with constant about 560 nm outer diameter. As far as can be recognized, all the helicity possesses a right-handed helical motif. Since the exciton coupling band of the organogel also shows *P* (right-handed) helicity, we consider that a microscopic helicity is reflected by a macroscopic helicity. On the other hand, the tubular structure of the silica obtained from the organogels **2** and **3** is somewhat different from that prepared from the organogel **1**. The careful examination of SEM and TEM pictures revealed that the tube wall of the silica features a roll-paper-like multilayer structure. Thus, this paper demonstrates successful and rare examples for precise transcription of gel superstructures into inorganic silica materials.

Keywords: crown compounds · double-layered tubes · gels · helical structures · silicates · sol-gel processes

Introduction

Both in natural and artificial systems, the self-assembly of *organic* building blocks give rise to supramolecular structures of various sizes, shapes, chemical compositions, and functions. In order to develop novel *inorganic* materials that closely correspond to these organic assemblies, one potential approach is to transcribe them to produce inorganic replicas, thus mimicking biomineralization processes. Amphiphilic molecules, for example, exhibit one of the richest polymorphism of structures and mesophases.[1] Among these, vesicles,[2] ultra-thin membranes,[3] and others[4] have been utilized as templates to create nano-sized inorganic materials.[5] In order to "design" the sizes and shapes of such materials (as organic compounds and assemblies can be "designed"), it is essential to explore and elucidate the transcription mechanisms of various organic precursors.

Recently, numerous thermoreversible physical gels formed with low-molecular-weight organic molecules have been reported.[6–10] The interest shown lies in the numerous potential applications envisaged for these materials, such as hardeners of solvents, drug delivery systems, membranes, and sensors. Very recently, organogels were applied as novel media to produce various structures of the silica such as linear,[11a,b] lamellar,[11c–e] and helical fibers,[11f] and spheri-

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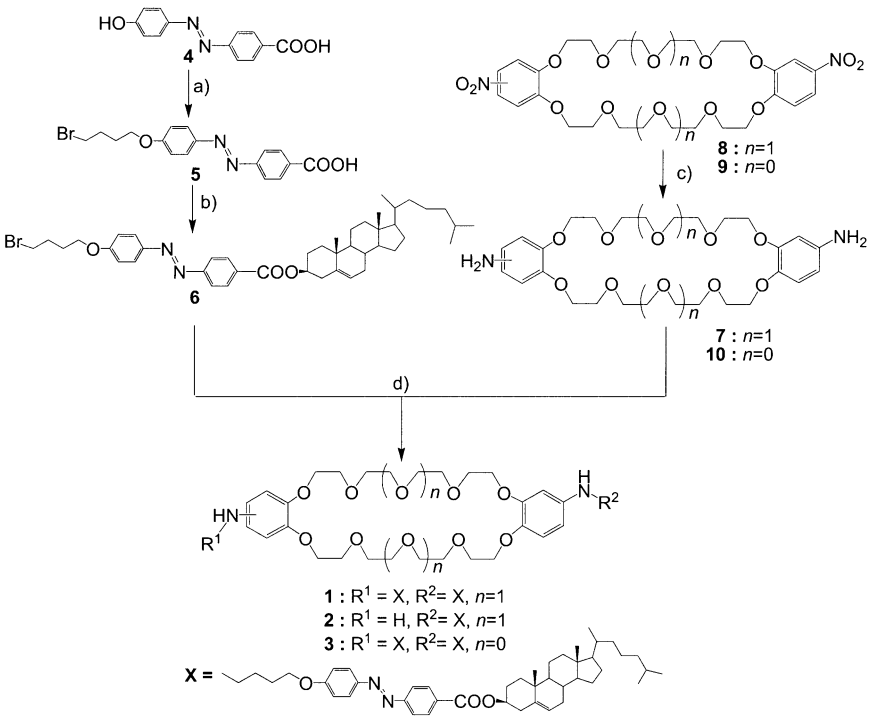
cal[11g] structures by sol-gel polycondensation. These results indicate that the superstructures formed in organogels are useful as templates to create various silica structures. One particularly interesting class of gelators, crown-appended cholesterol-based gelators, frequently resulted in various novel structures such as the fibrous, lamellar,[11d] vesicular,[11g] and multilayered tubular[11c] structures.

The groups of Kunitake and Schnur found that certain amphiphiles can form the tubular structure through the helical ribbon structure in aqueous solution.[1, 12] They possess a polar head group and suitable chiral hydrophobic groups to form stable aggregates. On the other hand, certain gemini-type gelators which consist of two components, gave helical ribbon structures in aqueous and organic solvents;[13] however, the formation mechanism of the tubular structure was not confirmed in these gel systems. It thus occurred to us that judging from the versatility of crown-appended cholesterol-based gelators,[11d,e,g] one might be able to find both structures, growing from the twisted ribbon to the tubule (as suggested by Kunitake et al.[12] for the aqueous solution system). In addition, superstructures created from these gelators might be useful as templates for the transcription into the silica structures.

With these objects in mind, we have designed compounds **1**–**3**, which have one or two cholesterol skeletons as a chiral aggregate-forming site, two amino groups as an acidic proton binding site, and one crown moiety as a cationic binding site. We have studied the influence of the crown size induced into the amphiphiles by circular dichroism (CD), SEM, and TEM, and evaluated their sol-gel transcription into the silica structures. We have found that **1**–**3** not only gelate various organic solvents under 1.0 wt%, but enable us to observe both the helical ribbon and tubule structures. In addition, **1** acts as a template for sol-gel polycondensation of TEOS to produce the novel "helical ribbon" silica and the "double-layered tubular" silica, whereas **2** and **3** induce only the "roll-paper-like multilayered tubular" structure of silica. Also, we could synthesize various morphologies of silica, such as double-layer, helical, and vesicular structures, by changing the sol-gel reaction temperature using the organogel **1**. To the best of our knowledge the influence of of changes in the sol–gel reaction temperature on the silica morphologies and the growth mechanism from the helical ribbon of an organogel into the tube has not yet been reported. To the best of our knowledge, these are the first examples not only for the morphology control of the silica in the self-assembled superstructure system, but also for the growth mechanism from the helical ribbon of an organic self-assembly into the tubular structure through sol-gel transcription.

Results and Discussion

Characterization of organogel superstructures by circular dichroism (CD), SEM, and TEM: Compounds **1**–**3** were synthesized according to the method reported previously (Scheme 1).[11c] The gelation ability of compounds **1**–**3** was estimated in various organic solvents. As summarized in Table 1, they can gelate acetic acid, propionic acid, acetonitrile, 1-hexanol, DMSO, and/or DMF under 1.0 wt%, indicating that they act as a versatile gelator of various organic solvents.



Scheme 1. Reagents and conditions of crown-appended cholesterol gelators **1**–**3**. a) Dibromobutane, KOH, ethanol; b) cholesterol, DCC, DMAP, dichloromethane; c) PdC, H_2, dimethylacetamide anhyrate; d) Na_2CO_3, *n*-butyronitrile.

To characterize the aggregation mode in the organogel phase, we observed CD spectra of acetic acid and propionic acid gels of **1**–**3**. In the CD spectrum of acetic acid gel **1**, the

Table 1. The gelation ability of **1**–**3** in organic solvents.[a]

	1	**2**	**3**
methanol	I	I	I
ethanol	I	I	I
1-butanol	G	P	P
1-hexanol	G	G	G
DMSO	G	G	G
DMF	G	G	G
acetic acid	G	P	P
propionic acidG	G	G	
acetone	G	I	I
acetonitrile	G	I	I
chloroform	S	S	S
tetrahydrofuran	S	S	S

[a] Gelator = 1.0 wt%; G = stable gel formed at room temperature; S = solution; I = insoluble, P = precipitation.

$\lambda_{\theta=0}$ value appears at 353 nm, which is consistent with the absorption maximum at $\lambda_{max} = 353$ nm. One can thus assign the CD spectrum to the exciton coupling band, although it is somewhat asymmetric (Figure 1). It is known that azobenzene-appended cholesterol gelators with natural (*S*)

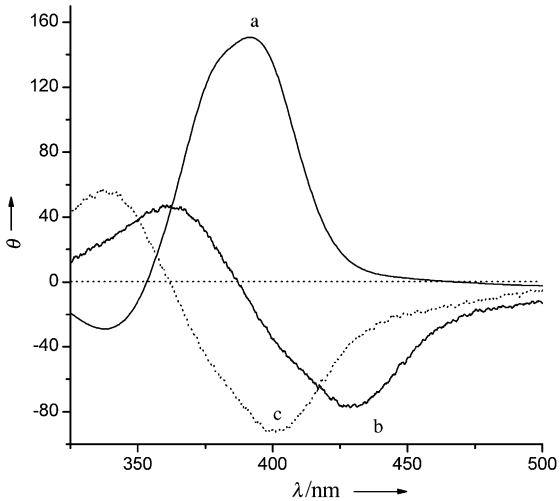


Figure 1. CD spectra of the organogels a) **1**, b) **2**, and c) **3**.

C-3 configuration tend to give a positive sign for the first Cotton effect (Figure 1a), indicating that the dipole moments of azobenzene chromophores tend to orient into the clockwise direction.[11e,f] In contrast, gels **2** and **3** bearing only one or two cholesterol moiety exhibit a negative sign for the first Cotton effect (Figure 1b and c), indicating that the dipole moments of the azobenzene chromophores orient into the anticlockwise direction. In all cases, it was confirmed that the contribution of linear dichroism (LD) to the true CD spectra is negligible. These CD data support the view that the aggregation mode of **1** is somewhat different from those of **2** and **3**. It is undoubted that the organogels of **2** and **3** are formed by both intermolecular cholesterol–cholesterol and azobenzene–azobenzene interactions; the former interaction in the central columnar aggregate and the latter in the side chain aggregate around the central column. On the other hand, in the organogel compound **1** may adopt a folded conformation to enjoy efficient intramolecular cholesterol–cholesterol and azobenzene–azobenzene interactions; this may be the origin of the positive sign for the first Cotton effect.

To obtain visual insights into the aggregation mode, we observed the xerogel structures of organogels **1**–**3** by TEM and SEM. Figure 2 shows a TEM and SEM pictures of the xerogels **1**–**3** obtained from acetic acid or propionic acid. Very interestingly, the xerogel **1** mainly consists of the tubular structures with about 520 nm outer diameter, but also contains the helical ribbon with 1700 nm pitch (Figure 2a and b). In addition, the SEM picture of the xerogel **1** also reveals the characteristic right-handed helical ribbon structure. These results indicate that the structure of the organogel process involves several metastable intermediate structures, namely, the linear ribbon, the helical ribbon, and the tubule. However, observation of the growing step for helical ribbon

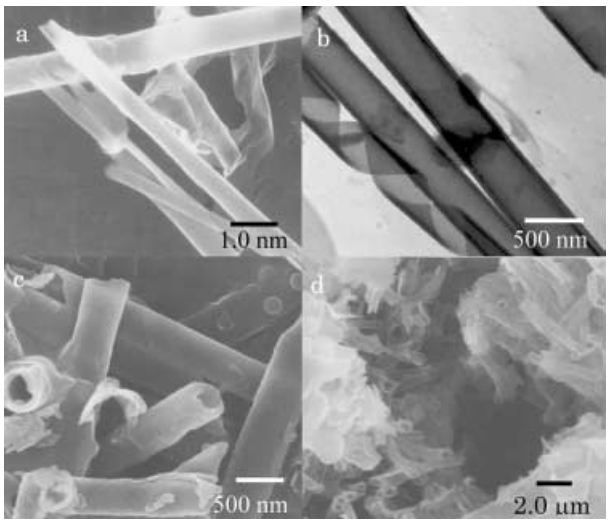


Figure 2. SEM (a) and TEM (b) pictures of the xerogel **1** prepared from acetic acid, and SEM pictures of the xerogels **2** (c) and **3** (d) prepared from propionic acid.

structure into at tube is very difficult due to an extremely fast growing rate.

To the best of our knowledge, it is very a rare example for the direct observation of the growing process of these superstructures by self-assembly. Most of organic tubes reported so far are produced in aqueous solution, and not in gel systems. In particular, the structure of **1** is quite different from those of sugar amphiphiles, previously reported by our group, which have long aliphatic groups.[14] These amphiphiles were transformed from the helical ribbon structure (its presence is assumed) into the tubular structure with 10–100 nm of diameters in aqueous solution by heating, whereas **1** can form both the helical ribbon structure and the tubular structure with approximately 520 nm out diameter.

The organogels **2** and **3** featured the tubular-like structures with 45–75 nm wall thickness and 170–390 nm inside tube diameter as shown in Figure 2c and d. Very careful examination of these pictures reveals that the wall consists of a multilayer-like structure. These results indicate that the balance between the hydrophilicity and the hydrophobicity in amphiphiles is of importance to develop the tubular structure through the helical ribbon structure.

Influences on sol–gel transcription temperature: To transcribe the superstructure formed in the organogel into the silica structure, we carried out sol–gel polycondensation of TEOS using **1**–**3** in the acetic acid or propionic acid gel phase according to the method described previously.[11] We observed SEM and TEM pictures of the silica obtained from **1**–**3** after calcination. Figure 3 shows the TEM pictures: the silica obtained from acetic acid gel **1** possesses the helical ribbon structure with various width (450–1500 nm) of ribbon and the tubular structure of the silica with a constant outer diameter of about 560 nm. As far as can be recognized, all the helicity possesses a right-handed (*P*) helical motif. Since the exciton-coupling band of the organogel also shows *P* helicity, we consider that a microscopic helicity is reflected by a macroscopic helicity. These results indicate that the novel helical

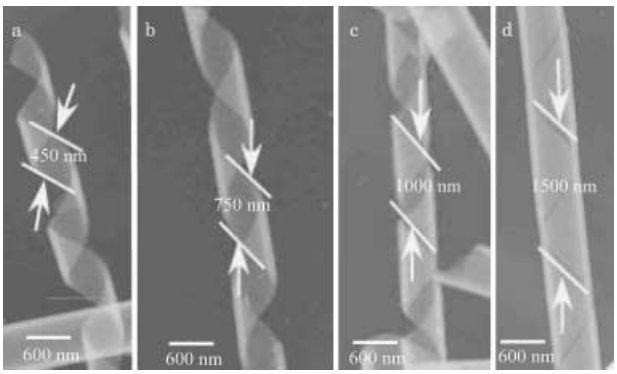


Figure 3. TEM pictures (a, b, c, and d) of the silica obtained from the **1**+acetic acid gel after calcinations.

ribbon structure and the tubular structure of the organogel **1** have successfully been transcribed into the silica structures. Also, these findings strongly suggest that the organic tube formed by self-assembly was produced with the growth of width of the helical ribbon and constant pitch angle as shown in Figure 4b, rather than by the mechanism in Figure 4a; also

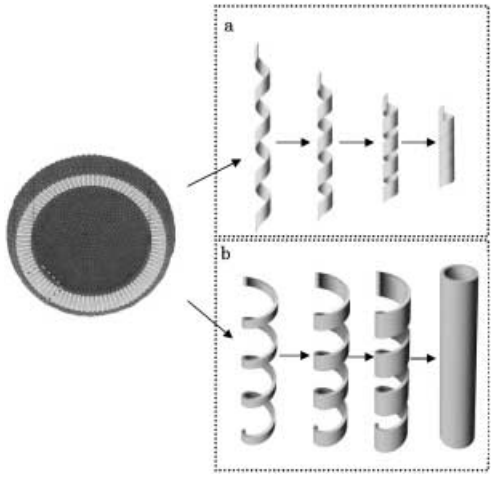


Figure 4. Representation for tubular formation mechanisms of the **1**+ acetic acid gel; a) tube formed by changing of pitch angle, b) tube formed with the growth in width of the helical ribbon.

the growth of organic tube was fixed by absorption of rigid silica particles (Figure 4b). This mechanism is quite different from observed for natural cholesterol tube by Chung et al.,[16] which had two different pitch angles. In addition, it was confirmed by high-magnification TEM that the silica consists of double layers with an interlayer distance of 8–9 nm (Figure 5a). The size of the space between layers of the silica obtained by Method A (see Experimental Section) suggests that helical ribbon and tubular structures of the incipient organogel **1** are encapsulated in the silica particles. In addition, these results indicate that TEOS (or oligomeric silica particles) was adsorbed onto both surfaces of the tubules with 8–9 nm thickness. Therefore, the tubular silica possesses two hollow cavities. The smaller hollow with 8–9 nm layers was created by organogel template, whereas the larger hollow, with inner diameters of approximately 480 nm, was created by the growth of the helical ribbon.

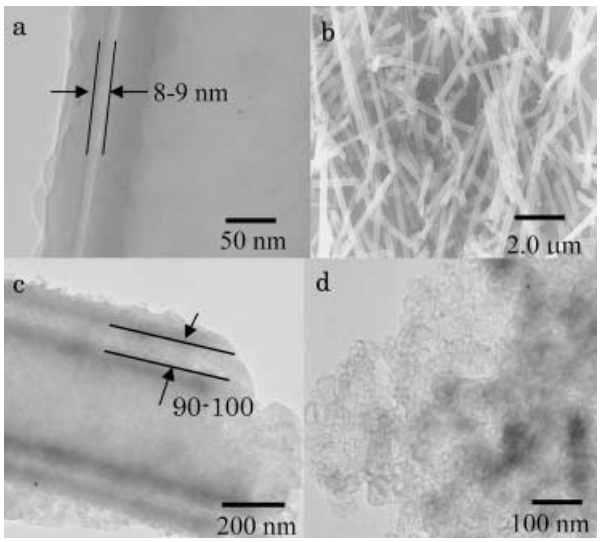


Figure 5. SEM or TEM pictures a) of the silica obtained from the **1**+acetic acid gel by method A, b) and c) by method B, and d) by method C after calcination.

In the absence of heating after TEOS and water addition (Method B), the silica resulted in the tubular structure with 600 nm outer diameter, 340 nm inner diameter, and 90–100 nm spaces (Figure 5b and c); however, no helical ribbon structure was observed. This result consistently supports the view that the organic tube is made up of the multi-layered packing structure. Also, this strongly confirms the aforementioned assumption that the silica particles are adsorbed onto both the surface and the inner of tubular structure of the organogel **1** obtained through several metastable intermediate structures.

In method C, the silica gave the vesicular structure with 30–50 nm diameters by sol–gel polycondensation at a temperature above the sol–gel phase-transition temperature of organogel **1** (Figure 5d). This result suggests that the self-assembled superstructure of organogel **1** exists as the vesicle at temperatures above the sol–gel phase-transition temperature. In addition, these findings indicate that a variety of superstructural silica materials, such as vesicular and tubular structures, can be created at different temperatures of sol–gel polycondensation by using the organic tube as a template.

Figure 6 displays SEM pictures of the silica obtained from propionic acid gels **2** and **3** after calcination. The tubular structure of the silica obtained from the organogels **2** and **3** is somewhat different from that prepared from the organogel **1**. Very interestingly, the tube wall of the silica features a roll-paper-like multilayer structure, as shown by careful examination of SEM and TEM measurements. Also, the helical ribbon structure of the silica was not obtained by this method.

We now propose the mechanism for the formation of both spherical structures and the co-existence of helical ribbons and double tubes with 8–9 nm and 90–100 nm spaces as shown in Figure 7. In case of Method A, oligomeric silica particles are adsorbed onto the surface of the helical ribbon, to give a tubular structure with 8–9 nm thickness, before complete growth into the tube (Figure 7a); this leads to a mixture of the helical ribbon and double layered tubes with

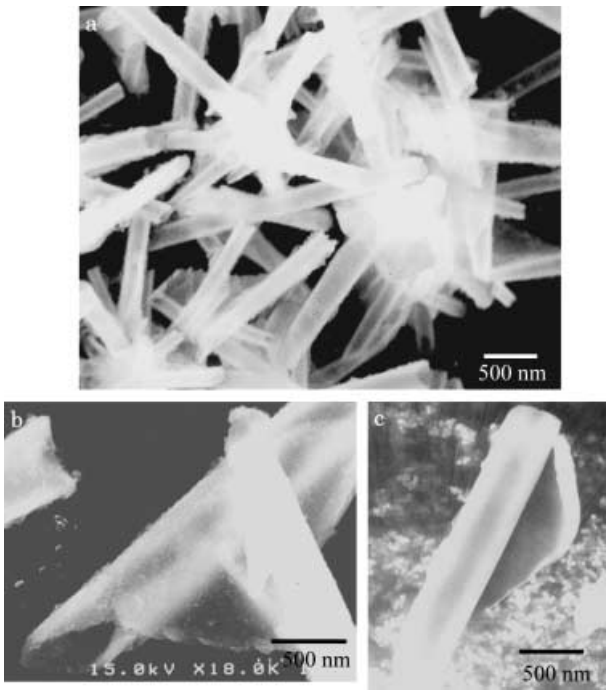


Figure 6. SEM pictures of the silica obtained from the **2**+propionic acid gel (a and b) and the **3**+propionic acid gel (c).

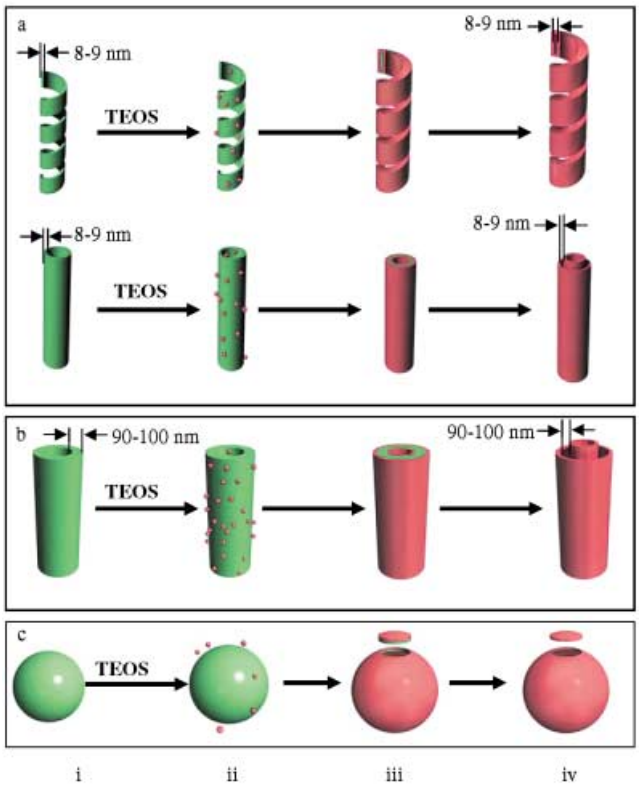


Figure 7. Schematic representation of sol–gel transcription of the organogel **1**: i) template, ii) sol–gel polycondensation, iii) before calcination, and iv) after calcination (SEM and TEM images in Figures 2, 3, and 5).

8–9 nm spaces between layers. In contrast, in case of Method B, silica particles are adsorbed onto the surface of the tubular structure with 90–100 nm wall thickness of acetic acid gel **1** (Figure 7b); this gave only the double-layered silica tube. Also, this silica morphology is clearly different between **1** and **3**: compound **1** gave the tubular and the helical ribbon structures, whereas **3** gave the roll-paper-like structure.[11c] This implies that growth mechanism for tubular structure of the self-assembled **1** is quite different from that of **3**. The self-assembled **1** spontaneously grows up from vesicle to the helical ribbon to the tubular structure, whereas the compound **3** self-assembles into the roll-paper-like structure. In addition, these two different morphologies of the self-assembly are accurately reflected into the silica structures by the sol–gel method.

Conclusion

The present paper has demonstrated that the organogelators **1**–**3**, bearing different crown-ring size, such as dibenzo[30]-crown-10 and dibenzo[24]crown-8, create the novel helical and/or tubular structures in organic solvents. The organogel morphology is clearly different between **1**, and **2** and **3**; compound **1** gave the tubular structure from the helical ribbon, whereas organogelators **2** and **3** formed the paper-like tubular structures. Also, the tubular structure of organogel **1** is formed from the growth in the ribbon width and with constant diameter. Sol–gel polycondensation of TEOS in the presence of the helical structure of **1** leads to the formation of the helical ribbon and double-layered tubular structures of silica in the gel phase. This is a very rare example of chiral inorganic materials. The helical ribbon structures of silica are created with aid of hydrogen-bonding as well as electrostatic interactions. On the other hand, the organogel **1** also produced the vesicular structure of the silica at temperatures above the sol–gel phase-transition temperature. The organogels **2** and **3** induced the tubular structures of silica. The results clearly indicate the versatility of the template method by using organogels for the creation of various silica structures.

In general, organic materials are capable of constructing a variety of supramolecular structures that reflect their own molecular shape, whereas "shape design" is very difficult from inorganic materials. The present findings suggest, as also suggested by a few other research groups, that various novel assembly structures created by weak intermolecular forces can be imprinted as permanent structures in inorganic materials. The present study clearly demonstrates that the organogel system is one of the most suitable molecular assemblies for this transcription. We believe that the silica structures presented here, with the unique higher-order morphology, are still very useful as unique catalysts for asymmetric syntheses without chiral organic ligands.[17]

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.

TEM and SEM observations: For transmission electron microscopy (TEM), a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after 1 min, leaving some small patches of the gel

on the grid. After specimens had been dried at low pressure, its was stained with 10 ~ 15 μL drops of uranyl acetate (2.0 wt % aqueous solution). Then, this was dried for 1 h at low pressure. The specimen was examined with an Hitachi H-7100 microscope, with an accelerating voltage of 75 – 100 kV and a 16 nm working distance. Scanning electron microscopy (SEM) was performed on a Hitachi S-4500 microscope. The silica was coated with palladium – platinum and observed by 5-–15 kV of the accelerating voltage and the emission current of 10μA.

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 to room temperature. If the stable gel was observed at this stage, it was classified as G in Table 1.

Sol-gel polycondensation of TEOS

Method A: Compounds **1** – **3** (6.63×10^{-3} mol) were dissolved in acetic acid or propionic acid (200 mg) by heating. The gel sample was cooled to room temperature. TEOS (20 mg) and water (6.0 mg) were then added to gel sample. The reaction mixture was then reheated until it became homogeneous, and then it was placed at room temperature for 2 – 14 days.

Method B: Compound **1** (6.63×10^{-3} mol) was dissolved in acetic acid (200 mg) by heating. The gel sample was cooled to room temperature. TEOS (20 mg) and water (6.0 mg) were the added to gel sample. Without the heating process, this reaction mixture was placed at room temperature for 2 – 14 days.

Method C: Compound **1** (6.63×10^{-3} mol) was dissolved in acetic acid (200 mg) by heating. The gel sample was cooled to room temperature. TEOS (20 mg) and water (6.0 mg) were then added to gel sample. The reaction mixture was then reheated until it became homogeneous, and then it was maintained at 80 °C for 2 days. The products obtained by three methods were calcinated 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 to remove the gelators. The silica thus obtained was colorless.

4-(Hydroxyphenyl)azobenzoic acid (4) and 4-(*n*-bromobutoxylphenyl)-azobenzoic acid (5): These compounds were prepared as described previously.[11c],[11g]

4-*n*-bromobutoxyl-4′-[(cholesteryloxy)carbonyl]azobenzene (6): Compound **5** (0.7 g, 1.86 mmol) and cholesterol (0.718 g, 2.23 mmol) were dissolved in dichloromethane (20 mL) under a nitrogen atmosphere. The solution was maintained at 0 °C by an ice bath. Dicyclohexylcarbodiimide (DCC, 0.383 g, 1.86 mmol) and dimethylaminopyridine (DMAP) (0.022 g, 0.186 mmol) were then added, and the reaction mixture was 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 chromatography eluting with THF/*n*-hexane (1:6 v/v) to give compound **6** in 26 % yield as yellow solid. M.p. 141.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.17$ (d, $J = 9.0$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 9.0$ Hz, 2H), 7.10 (d, $J = 9.0$ Hz, 2H), 5.45 (d, $J = 6.3$ Hz, 1H), 5.02 – 4.88 (m, 1H), 41 (t, $J = 6.3$ Hz, 2H), 3.52 (t, $J = 6.2$ Hz, 2H), 2.49 (d, $J = 6.2$ Hz, 2H), 2.28 – 0.94 (m, 35H), 0.88 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 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 ppm; IR (KBr): $\tilde{\nu} = 3005$, 1722, 1603, 1579, 1500, 1468, 1284, 1116, 1047 cm^{-1}; MS(SIMS): m/z: 745 $[M+H]^+$.

Dinitrodibenzo[30]crown-10 (8): HNO_3 (60 %, 1 mL) was added dropwise to a stirred solution of dibenzo[30]crown-10 (0.15 g, 0.28 mmol) in acetic acid (5 mL) and water (1 mL) at 5.0 °C. The reaction mixture was warmed to room temperature over a period of 30 min and stirred for an additional 2 h at room temperature. Then, $NaOH_{aq}$ (1.0 M) was added to the reaction mixture until the solution became neutral. The precipitate was filtered off, to give compound **8** in yield 85.0 % as yellow powder. M.p. 133 – 135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.69$ (brs, 8H), 3.77 (brs, 8H), 3.93 (brs, 8H), 4.22 (brs, 8H), 6.87 (d, $J = 8.4$ Hz, 2H), 7.73 (s, 2H), 7.84 ppm (d, $J =$ 8.4 Hz, 2H); IR (KBr): $\tilde{\nu} = 3005$, 2987, 1508, 1210 cm^{-1}; MS(SIMS): m/z: 644.5 $[M+2H]^+$; elemental analysis calcd (%) for $C_{29}H_{42}N_2O_{14}$: C 54.20, H 6.59, N 4.36; found: C 54.50, H 6.55, N 4.30.

Diaminodibenzo[30]crown-10 (7): Compound **8** (0.134 g, 0.21 mmol) was added to dimethylacetamide anhydrate (20 mL), and the solution was stirred until the solid was dissolved. Then, PdC (10 %, 0.10 g) was added, and hydrogen gas was introduced into the solution for 3 h at room temperature. The reaction mixture was filtered to remove PdC, and the filtrate was evaporated in vacuo to dryness. The residue was purified by a silica gel column chromatography eluting with methanol/chloroform (1:9 v/v) to give **7** as brown solid (0.10 g, 84 % yield). M.p. 68 – 71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.48$ (brs, 4H), 3.68 (brs, 8H), 3.74 (brs, 8H), 3.84 (brd, $J = 12.4$ Hz, 8H), 4.08 (brs, 8H), 6.21 (dd, $J = 8.4$, 2.5 Hz, 2H), 6.29 (brs, 2H), 6.88 ppm (d, $J = 8.4$ Hz, 2H); IR (KBr): $\tilde{\nu}$3350, 3007, 2985, 1521, 1504, 1340, 1205 cm^{-1}; MS(SIMS): m/z: 557.2 $[M+2H]^+$; elemental analysis calcd (%) for $C_{29}H_{42}N_2O_{10}$: C 59.78, H 7.96, N 4.81; found: C 60.02, H 7.90, N 4.53.

Dinitrodibenzo[24]crown-8 (9): This compound was prepared as described above for **8**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.60$ (brs, 8H), 3.73 (brs, 8H), 4.15 (brs, 8H), 6.80 (d, $J = 8.2$ Hz, 2H), 7.73 (s, 2H), 7.79 ppm (d, $J =$ 8.2 Hz, 2H); IR (KBr): $\tilde{\nu} = 3005$, 2987, 1508, 1210 cm^{-1}; MS(SIMS): m/z: 538.5 $[M+2H]^+$; elemental analysis calcd (%) for $C_{24}H_{30}N_2O_{12}$: C 53.53, H 5.62, N 5.20; found: C 54.02, H 5.65, N 5.25.

Diaminodibenzo[24]crown-8 (10): This compound was prepared as described above for **7**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.53$ (brs, 8H), 3.63 (brs, 8H), 4.15 (brs, 8H), 6.21 (dd, $J = 8.4$, 2.5 Hz, 2H), 6.29 (brs, 2H), 6.88 ppm (d, $J = 8.4$ Hz, 2H); IR (KBr): $\tilde{\nu} = 3350$, 3007, 2985, 1521, 1504, 1340, 1205 cm^{-1}; MS(SIMS): m/z: 478.5 $[M+2H]^+$; elemental analysis calcd (%) for $C_{24}H_{34}N_2O_8$: C 60.24, H 7.16, N 5.85; found: C 60.05, H 7.15, N 5.80.

4-[Bis(diaminodibenzo[30]crown-10-butoxy]-4′-[(cholesteyloxy)carbonyl]azobenzene) (1): A mixture of compound **4** (0.24 g, 0.32 mmol), compound **7** (0.085 g, 0.15 mmol), and sodium carbonate (0.317 g, 3.00 mmol) in dry *n*-butyronitrile (30 mL) was refluxed for 72 h. The solution was filtered after cooling and the filtrate was evaporated in vacuo to dryness. The residue was purified by aluminum oxide column chromatography eluting with ethanol/chloroform (1:30 v/v) to give the desired product as yellow solid (20 % yield). M.p. 168.2 – 168.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.70$ (s, 6H), 0.87 (d, $J = 6.6$ Hz, 12H), 0.92 – 2.06 (m, 70H), 2.48 (d, $J = 6.4$ Hz, 4H), 3.16 (t, $J = 6.4$ Hz, 4H), 3.43 (brs, 2H), 3.51 – 3.79 (m, 16H), 3.83 – 3.92 (m, 8H), 4.08 (brs, 8H), 4.78 – 4.93 (m, 2H), 5.44 (d, $J = 3.9$ Hz, 2H), 6.17 (dd, $J = 2.4$ Hz, 4H), 6.22 (brs, 2H), 6.27 (d, $J = 2.4$ Hz, 2H), 6.75 (dd, $J = 9.1$ Hz, 4H), 7.01 (d, $J = 8.4$ Hz, 4H), 7.90 (d, $J = 8.4$ Hz, 4H), 7.94 (d, $J = 8.7$ Hz, 4H), 8.17 ppm (d, $J = 8.4$ Hz, 4H); IR (KBr): $\tilde{\nu} = 3350$, 3007, 2987, 1600, 1585, 1500, 1220 cm^{-1}; MS(SIMS): m/z: 1898.6 $[M+2H]^+$; elemental analysis calcd (%) for $C_{116}H_{162}N_6O_{16}$: C 73.46, H 8.61, N 4.43; found: C 72.71, H 8.73, N 4.45.

4-(Diaminodibenzo[30]crown-10-butoxy)-4′-[(cholesteyloxy)carbonyl]-azobenzene (2): This compound was prepared as described above for **1**. Yellow solid (25 % yield; M.p. 159.5 – 160.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.70$ (s, 6H), 0.87 (d, $J = 6.6$ Hz, 12H), 0.92 – 2.06 (m, 70H), 2.48 (d, $J = 6.4$ Hz, 4H), 3.16 (t, $J = 6.4$ Hz, 4H), 3.43 (brs, 2H), 3.51 – 3.79 (m, 16H), 3.83 – 3.92 (m, 8H), 4.08 (brs, 8H), 4.78 – 4.93 (m, 2H), 5.44 (d, $J = 4.0$ Hz, 2H), 6.17 (dd, $J = 2.6$ Hz, 4H), 6.22 (brs, 2H), 6.27 (d, $J =$ 2.6 Hz, 2H), 6.75 (dd, $J = 9.1$ Hz, 4H), 7.01 (d, $J = 8.4$ Hz, 4H), 7.90 (d, $J = 8.4$ Hz, 4H), 7.94 (d, $J = 8.7$ Hz, 4H), 8.17 ppm (d, $J = 8.4$ Hz, 4H); IR (KBr): $\tilde{\nu} = 3355$, 3007, 2983, 1600, 1585, 1500, 1220 cm^{-1}; MS(SIMS): m/z: 1231.78 $[M+2H]^+$; elemental analysis calcd (%) for $C_{72}H_{102}N_4O_{13}$: C 70.22, H 8.35, N 4.55; found: C 70.52, H 8.21, N 4.50.

4-[Bis(diaminodibenzo[24]crown-8-butoxy)-4′-[(cholesteyloxy)carbonyl]-azobenzene) (3): This compound was prepared as described above for **1**. Yellow solid (32 % yield); m.p. 153.2 – 155.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.70$ (s, 6H), 0.87 (d, $J = 6.6$ Hz, 12H), 0.92 – 2.06 (m, 70H), 2.48 (d, $J = 6.4$ Hz, 4H), 3.16 (t, $J = 6.4$ Hz, 4H), 3.43 (brs, 2H), 3.51 – 3.79 (m, 16H), 3.83 – 3.92 (m, 8H), 4.08 (brs, 8H), 4.78 – 4.93 (m, 2H), 5.44 (d, $J = 4.0$ Hz, 2H), 6.17 (dd, $J = 2.5$ Hz, 4H), 6.22 (brs, 2H), 6.27 (d, $J =$ 2.5 Hz, 2H), 6.75 (dd, $J = 9.2$ Hz, 4H), 7.01 (d, $J = 8.4$ Hz, 4H), 7.90 (d, $J = 8.4$ Hz, 4H), 7.94 (d, $J = 8.7$ Hz, 4H), 8.17 (d, $J = 8.4$ Hz, 4H); IR (KBr): $\tilde{\nu} = 3352$, 3005, 2982, 1600, 1585, 1500, 1220 cm^{-1}; MS(SIMS): m/z: 1820.31 $[M+2H]^+$; elemental analysis calcd (%) for $C_{112}H_{154}N_6O_{14}$: C 74.38, H 8.58, N 4.65; found: C 73.81, H 8.73, N 4.70.

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