Sol-Gel Polycondensation in a Cyclohexane-Based Organogel System in Helical Silica: Creation of both Right- and Left-Handed Silica Structures by Helical Organogel Fibers

Jong Hwa Jung, Yoshiyuki Ono, and Seiji Shinkai*[a]

Abstract: Chiral amide- and urea-type organic gelators (**1**–**6**), based on cyclohexanediamine, have been prepared, and the superstructures of the organogels were evaluated by circular dichroism (CD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The CD spectrum of the amide-based organogel system **1**+**2** exhibited a negative sign for the first Cotton effect, indicating that the dipole moments in the gelator aggregate orient into an anticlockwise direction. In contrast, the system **3**+**4** has a positive sign for the first Cotton effect, indicating that they orient into a clockwise direction. In the mixture of urea- and amide-based organogels, CD spectra of **5**+**2** and **6**+**4** revealed negative and positive signs, respectively. The helical structure of the amide-based organogels **1**+**2** and **3**+**4** clearly showed left- and right-handed structures, respectively, by SEM. To transcribe the chiral, helical structures of the organogels into silica gel, the sol-gel polycondensation of tetraethoxysilane (TEOS) was carried out in acetonitrile or ethanol. Very surprisingly, the left- and right-handed structures of the silica can be created by transcription of left- and right-handed structures of the organogels **1**+**2** (*R* enantiomer) and **3**+**4** (*S* enantiomer), respectively. In addition, in the mixture systems of urea- and amide-based organogels, the right- and left-handed structures of the organogels **5**+**2** (*R* enantiomer) and **6**+**4** (*S* enantiomer) were precisely transcribed into the silica structure. The findings suggest that the sol-gel polycondensation proceeds along the surface of the helical structure of the organogels. We therefore believe that the sol-gel polycondensation by means of molecular assembly templates abundantly built in the organogel phase is a new strategy to create superstructured silica materials.

Keywords: helical structures · organogel · self-assembly · silicates · sol-gel processes

Introduction

A diversity of supramolecular structures can be created, not only in nature but also in artificial systems, by self-assembly of designed "organic" building blocks.[1] In contrast, creation of such diverse supramolecular structures from "inorganic" materials seems to be very difficult or nearly impossible. Is there any innovative method by which inorganic materials can be self-assembled into ordered supramolecular structures? The sole method, if any, would be to create such tailor-made inorganic materials with the aid of a template effect of organic surfactant molecules.[2]

Recently, exploitation of new organic gelators that can gelate various organic solvents has become an active research area of endeavor.[3–11] The gelators can be classified into two categories according to the driving force for molecular aggregation: hydrogen-bond-based gelators and nonhydrogen-bond-based gelators. Typical examples of the former are aliphatic amide- or urea-based cyclohexanediamine derivatives, which have unique helical structures in their fibrous aggregates formed in certain solvents.[3, 4] Typical examples of the latter are cholesterol derivatives. These organogels are of particular importance and interest because of the essential difference from well-known polymer gels in the gelation mechanism and the potential application of gelation phenomena. Fibrous crystal-like aggregates of low-molecular-weight compounds formed by noncovalent interactions are responsible for such gelation phenomena. Hence, the xerogels can exhibit various superstructures, reflecting the unit structure of each gelator molecule. This is a new method for the creation superstructures by molecular assemblies and a reason why the study of organogels is considered to be a new field of supramolecular chemistry.[10, 11] More recently, it was found that certain cholesterol derivatives can gelate even tetraethoxysilane (TEOS); this results in silica formed by sol-gel polycondensation.[12, 13] Very interestingly, it was shown that the sol-gel polycondensation of gelated TEOS solutions affords silica with a novel hollow fiber structure, because the organogel fibers act as a template for the creation of the silica fibers in the TEOS sol-gel polycondensation and, after

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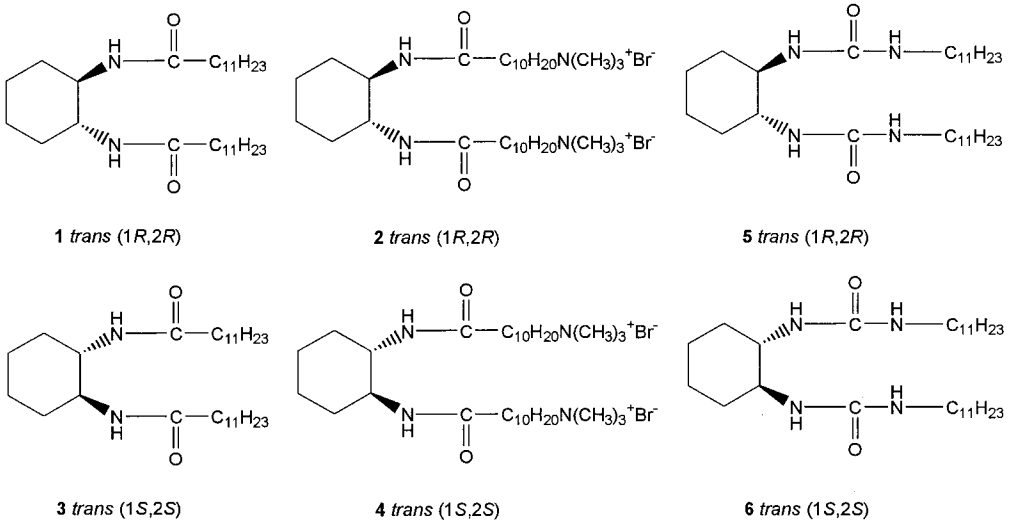
calcination, result in an hollow tube.[12, 13] This organic–inorganic transcription process is similar to the formation of fossil remains. This fact tempted us to test an idea that an helical organogel fiber structure may be also transcribed into the inorganic silica.[3c, 4c] Although several inorganic materials with some helical structure have been reported,[14] they utilize a specific crystallization method or a mechanical method, which are quite different from our chiral transcription method that utilizes chiral organogel fibers.

It is known that in order to transcribe the organogel structure into the silica structure, the cationic charge is indispensable in the sol-gel polycondensation of TEOS.[12] We have noticed, however, that the cationic gelators by themselves tend to lose the high gelation ability and rarely result in the helical structure. To overcome this dilemma we decided to mix the cationic gelator with the neutral gelator in order to obtain stable organogels supported by the helical fiber structure.

We therefore designed amide-based, neutral gelators **1** and **3**, amide-based cationic geltaors **2** and **4**, and urea-based neutral gelators **5** and **6**; these all have a chiral diaminocyclohexane skeleton and are expected to aggregate into a fibrous helical structure. Herein, we report on novel creation of the chiral structure of silica on the basis of transcription of chiral cyclohexanediamine-based aggregates in organogel systems. The purpose of the present research is to establish a correlative relationship between the silica structure and that of the organogel fiber. Very interestingly, we have found that right- and left-handed helical structures of the silica can be created by transcription of right- and left-handed helical structures of the organogel fibers, respectively.[13e]



Results and Discussion

Characterization of organogels by circular dichroism (CD): The gelation ability of **2**, **4**, **5**, and **6** was estimated for ten different organic solvents (5.00×10^{-2} mol L^{-1}) and compared with that of **1** and **3**.[4c] As summarized in Table 1, neutral **1** and **3** can gelate all the solvents tested, and neutral **5** and **6** can gelate nine out of twelve solvents, indicating that they can act as versatile gelators of organic solvents. In particular, it is seen from Table 1 that the gelation ability for aprotic solvents is excellent. On the other hand, cationic **2** and **4** can gelate only five out of ten solvents, indicating that the gelation ability is deteriorated by introduction of cationic charges. Since the presence of the cationic charge in the organogel fibers is indispensable to efficient sol-gel transcription,[12, 13] mixtures of **1**+**2**, **3**+**4**, **5**+**2**, or **6**+**4** were used as gelators in order to maintain the high gelation ability and moderate cationic charge density.

Table 1. The gelation ability of **1**–**6** in organic solvents.[a]

	1[b]	**2**	**3**[b]	**4**	**5**	**6**
methanol	G	S	G	S	S	S
ethanol	G	S	G	S	G[c]	G[c]
1-butanol	G	S	G	S	G	G
acetone	G	G	G	G	I	I
acetonitrile	G	G	G	G	I	I
tetrahydrofurane	G	G	G	G	G	G
dimethylforamide	G	G	G	G	G	G
dimethylsulfoxide	G	S	G	S	G[c]	G[c]
ethylacetate	G	C	G	C	G	G
acetic acid	G	S	G	S	G	G
cyclohexane	G	G	G	G	G	G
n-hexane	G	I	G	I	G	G

[a] Gelator = 5.0 wt %; G = stable gel formed at room temperature; S = solution; I = insoluble; C = crystallize. [b] Reported in ref. [4c]. [c] Reported in ref. [3c].

In order to obtain an insight into the chiral orientation of gelators in an acetonitrile organogel system, circular dichroism (CD) spectra of mixtures **1**+**2** and **3**+**4** were measured (Figure 1). The λ_{max} values in the absorption spectra appear at around 210–220 nm. In the CD spectra, the $\lambda_{\theta=0}$ values

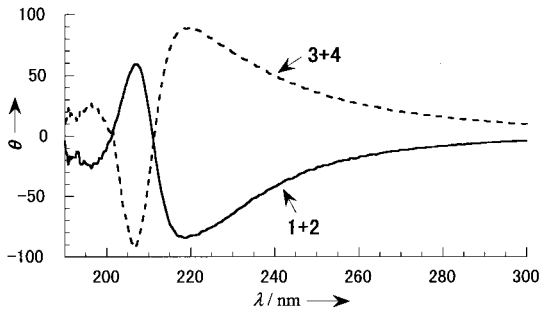


Figure 1. CD spectra of **1**+**2** (1:1 wt %) and **3**+**4** (1:1 wt %) organogels obtained from acetonitrile: 25 °C, total gelator concentration: 4.18×10^{-3} mol L^{-1}.

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appear at 214 nm. One can therefore assign the CD spectra to the exciton coupling bands. The CD spectrum of the amide-based **1**+**2** mixture (*R* enantiomer) exhibits a negative sign for the first Cotton effect, indicating that dipole moments orientate in an anticlockwise direction in the aggregate of these gelators. On the other hand, an **3**+**4** mixture (*S* enantiomer) exhibits a positive sign for the first Cotton effect, indicating that they are oriented in a clockwise direction. Also, it was confirmed that the contribution of linear dichroism (LD) spectra to the true CD spectra is negligible. These CD spectral data support the view that the aggregates formed from **1**+**2** and **3**+**4** are cooperatively organized into the aggregates with left- and right-handed helical structures, respectively.

The λ_{max} values for **5**+**2** (1:1 wt%) and **6**+**4** (1:1 wt%) mixtures in the ethanol organogel system shifted to shorter wavelength (190 nm), and the CD spectra in the shorter wavelength region became unreliable. In the longer wavelength region, the **5**+**2** and **6**+**4** mixtures have values of $\lambda_{\theta=0} = 187.0$ nm and $\lambda_{max} = 189.2$ nm ($\theta = -1.16 \times 10^{-4}$ deg cm^2 dmol^{-1}) and $\lambda_{\theta=0} = 187.5$ nm and $\lambda_{max} = 192.5$ nm ($\theta = 3.50 \times 10^{-4}$ deg cm^2 dmol^{-1}), respectively. Provided that these longer wavelength components are assignable to one side of a pair of exciton-coupling bands (i.e., the first Cotton effect), it follows that the aggregates formed from **5**+**2** and **6**+**4** are also organized into the aggregates with left- and right-handed helical structures, respectively. Since cationic gelators **2** or **4** does not afford CD-active aggregates by themselves, these CD signs should be generated by the influence of urea-based gelators **5** or **6**.

Superstructures of xerogels as examined by SEM observation: To look for such helical morphological structures in organogels, the xerogels obtained by a freezing-and-pumping method[11] from the gel-phase acetonitrile solutions below the sol-gel phase transition temperature ([**1**+**2** or **3**+**4**] = 0.12 wt% (1:1 wt%)) were observed by scanning electron microscopy (SEM: Figures 2a and 2b). It is clearly seen from these pictures that the aggregates are composed of helical fibers with 20–60 nm width. The helicity of the fibers was always left-handed for the mixture **1**+**2** (*R* enantiomer) and always right-handed for the mixture **3**+**4** (*S* enantiomer). These results indicate, together with the CD spectral data in Figure 1, that the exciton-coupling band originates from the chiral orientation of these gelators in the fibrous structure.

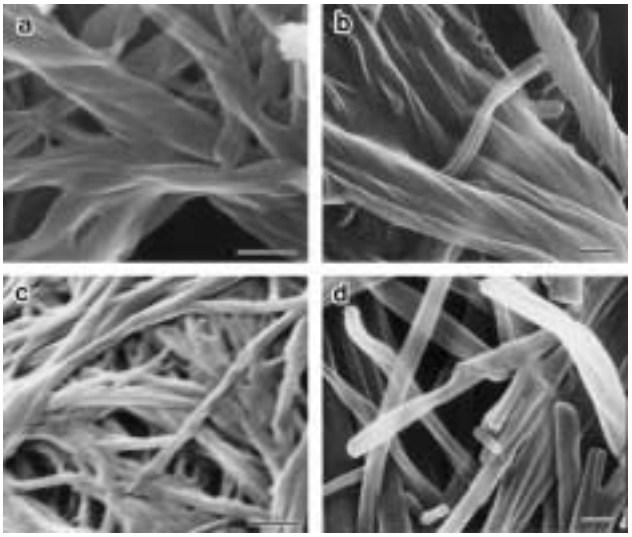

Figure 2. SEM pictures of xerogels of a) **1**+**2** (1:1 wt%), b) **3**+**4** (1:1 wt%), c) **5**+**2** (1:1 wt%), and d) **6**+**4** (1:1 wt%) obtained from acetonitrile or ethanol (bar = 200 nm).

In the mixed systems of urea- and amide-based organogels, the xerogel samples were prepared in ethanol. In the SEM pictures of urea- and amide-based organogels, **5**+**2** (*R* enantiomer, Figure 2c, total concentration: 0.25 wt%, 1:1 wt%) has a right-handed helical structure, whereas **6**+**4** (*S* enantiomer, Figure 2d, total concentration: 0.25 wt%, 1:1 wt%) has a left-handed helical structure. Although the fibers have grown up as large bundles, each component has a fiber diameter of 50–100 nm. The helicity of these organogel systems was not changed by a change in the ratio of cationic gelators **5** or **6** versus neutral gelator **2** or **4**. These results indicate that the helical structure constructed in the organogels is not related to the cationic organogel structure, but dominated by the helical structure of neutral urea-based gelators.

The foregoing findings show that in the systems **1**+**2** and **3**+**4** (*S* and *R*, respectively) the CD sign is consistent with the fiber helicity, whereas in **5**+**2** and **6**+**4** (*S* and *R*, respectively) the CD sign is contrary to the fiber helicity (*R* and *S*, respectively). According to a hierarchy of the helical structure, the fiber grows up in the order of fiber → yarn → strand → rope → cable and the right-handed helicity and the left-handed helicity are replaced alternately (presumably, the primitive fiber is very rigid). We therefore considered that the mismatch between the CD sign and the fiber helicity present in **5**+**2** and **6**+**4** systems might be due to this hierarchical problem. Hence, we changed the concentration of mixed gelators (0.12, 0.25, and 2.5 wt%) and carefully observed the gelator fibers bearing the different diameters by transmission electron microscopy (TEM). We reconfirmed, however, that the system **5**+**2** (*R* enantiomer) always has the right-handed fiber structure, whereas the system **6**+**4** (*S* enantiomer) always exhibits the left-handed fiber structure. These results support the view that the helical direction of the organogel fibers is not necessarily subjected to the hierarchy of the helical structure.

Sol-gel polycondensation of tetraethoxysilane (TEOS) for transcription: The sol-gel polycondensation of TEOS was carried out in the gel-phase solutions of **1**+**2**, **3**+**4**, **5**+**2**, and **6**+**4**. A typical mixture consists of acetonitrile or ethanol, TEOS, water, and benzylamine as a catalyst (for the further details see Experimental Section). The solution was gelated at this stage. The sample was left at room temperature for 3–7 days. Subsequently, they were heated at 200 °C for 2 h and then at 500 °C for 2 h under a nitrogen atmosphere, and finally at 500 °C for 4 h under aerobic conditions.

As shown in Figure 3, when neutral (1*R*,2*R*)-**1** was mixed with cationic (1*R*,2*R*)-**2** [**1**/(**1**+**2**) = 10–85% (weigh ratio = *r*)], the organogel resulted in a left-handed helical silica structure, which has an outer diameter of 100–150 nm (Figure 3a). At $r < 10$%, the resultant silica shows a conven-

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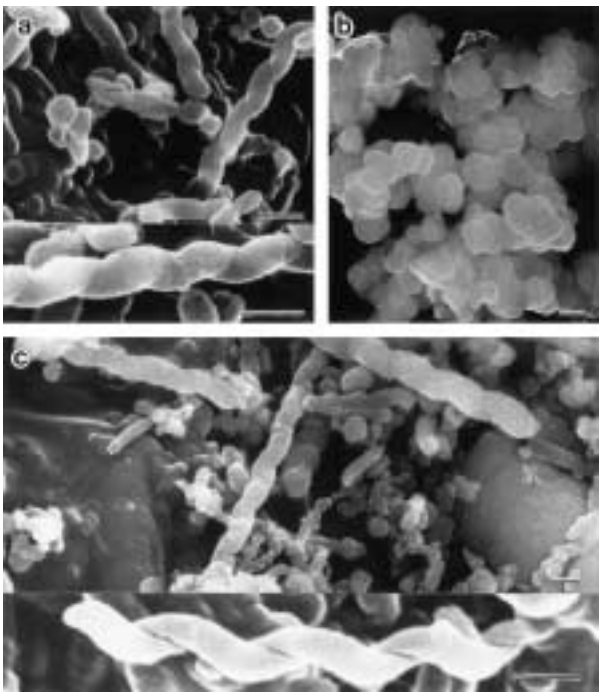

Figure 3. SEM pictures of the silica obtained from a) **1**+**2** (1:1 wt %), b) **1**+**2** (9:1 wt %), and c) **3**+**4** (1:1 wt %) after calcination (bar = 200 nm).

tional granular structure (Figure 3b). As shown in Table 2, the solution was not gelated at $r > 85\,\%$, and the resultant silica again showed the conventional granular structure. The silica obtained from the mixture **3**+**4** (*S* enantiomer) at $10\,\% < r < 85\,\%$ always showed a right-handed structure (Figure 3c).

When urea-based, neutral (1*R*,2*R*)-**5** was mixed with amide-based cationic (1*R*,2*R*)-**2** [**5**/(**5**+**2**) = 20–80 % (*r*)], the organogel resulted in a clearer right-handed helical silica structure (Figure 4a) than that observed for **1**+**2** and **3**+**4** systems. The outer diameter of this fine helical structure is of 90–120 nm. When urea-based neutral (1*S*,2*S*)-**6** was mixed with amide-based cationic (1*R*,2*R*)-**4** [**6**/(**6**+**4**) = 20–80 % (r)], the organogel resulted in a clear left-handed helical silica structure. The consistency between the organogel fiber helicity and the silica fiber helicity indicates that the silica is created under the template effect of the organogel fibers. These results clearly support the view that i) the presence of the adequate amount of the cationic charge is indispensable to transcription of the organogel structure into the silica structure, ii) the helicity of the silica can be conscientiously transcribed from that of the organogel fiber, and iii) this method will be applicable for the efficient transcription of organic supermolecular structures into inorganic materials through the organogel phase.

To further corroborate whether the organogel fibers really acted as a template for the growth of the helical silica, TEM pictures were taken after removal of organic gelators by calcination.[12, 13] Very interestingly, we found that in the right-handed silica obtained from the **3**+**4** organogel, the right-handed inner tubular structure with an inner diameter of 20–60 nm is clearly recognized (Figure 5b). Careful examination of the TEM picture of the left-handed silica obtained from the

Table 2. Results and conditions for the sol-gel polycondensation.

run	**1**+**2** [wt %][a]	silica structure	**3**+ **4** [wt %][a]	silica structure	**5**+**2** [wt %][a]	silica structure	**6**+**4** [wt %][a]	silica structure
1	90/10	granular	90/10	granular	90/10	granular	90/10	granular
2	70/30	left-handed	70/30	right-handed	70/30	right-handed	70/30	left-handed
3	50/50	left-handed	50/50	right-handed	50/50	right-handed	50/50	left-handed
4	40/60	left-handed	40/60	right-handed	40/60	right-handed	40/ 60	left-handed
5	30/70	left-handed	30/70	right-handed	30/ 70	right-handed	30/70	left-handed
6	15/85	left-handed	15/85	right-handed	20/80	right-handed	20/80	left-handed
7	0/100	granular	0/100	granular	–	–	–	–

[a] The total amount of the gelators used under conditions for the sol-gel process of TEOS was 3–4 mg.

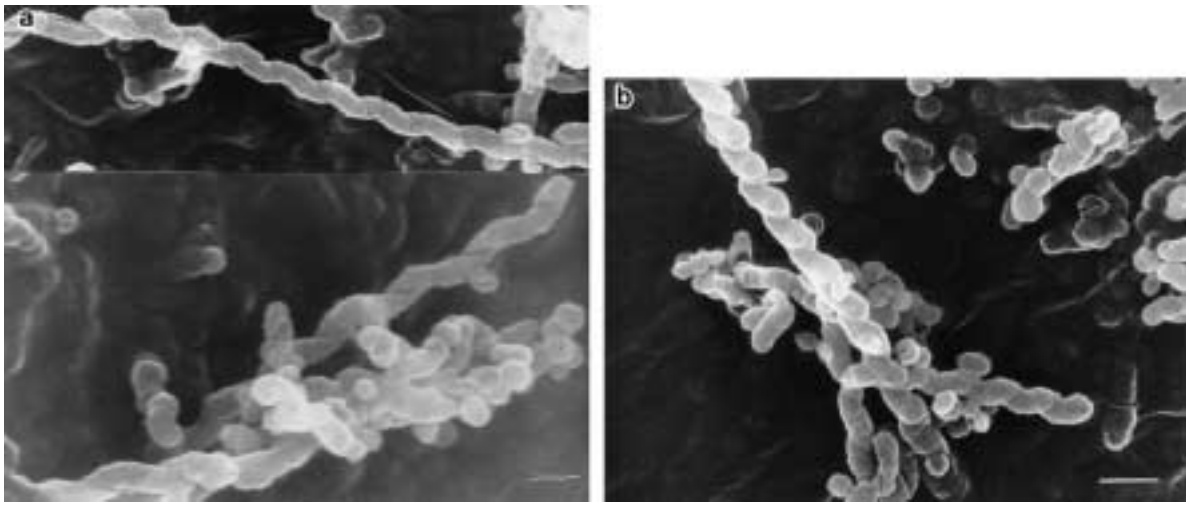

Figure 4. SEM pictures of the silica obtained from a) **5**+**2** (1:1 wt %) and b) **6**+**4** (1:1 wt %) after calcination (bar = 200 nm).

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1+**2** organogel reveals that the observed inner tubular structure with an inner diameter of 20–60 nm is also left-handed (Figure 5a). In addition, examination of the silica fibers obtained from the organogels of **5**+**2** and **6**+**4** mixtures reveals that the observed inner tubular structures with inner diameters of 50–70 nm also have left- and right-handed helical structures, respectively. The results clearly support the view that anionic oligomeric siloxanes are adsorbed onto the cationic helical organogel fibers and chirality of the silica thus grown reflects the that present in the original fibers.

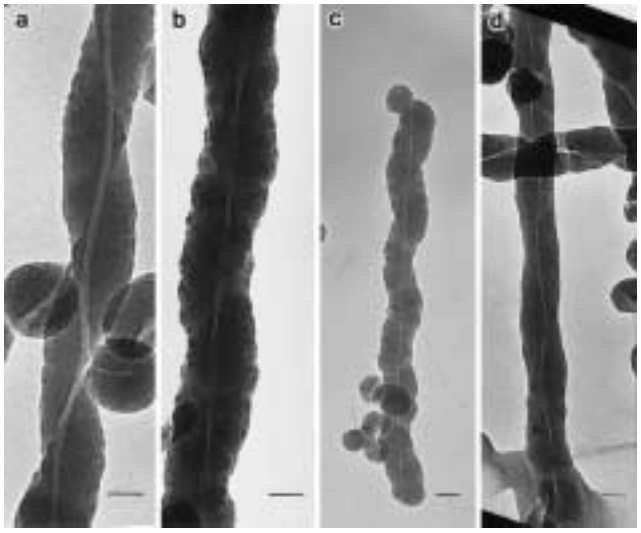


Figure 5. TEM pictures of the silica obtained from a) **1**+**2** (1:1 wt%), b) **3**+**4** (1:1 wt%), c) **5**+**2** (1:1 wt%), and d) **6**+**4** (1:1 wt%) after calcination (bar = 50 nm).

Conclusion

The present paper has demonstrated for the first time that both "right- and left-handed chiralities" that are characteristic of chiral organic compounds and assemblies can also be created in inorganic compounds. For example, the **1**+**2** and **3**+**4** mixtures result in the left- and right-handed helical structures of the silica, respectively. The key point is to transcribe the chirality in organogel fibers into silica fibers utilizing the electrostatic interaction. The results indicate the versatility of the template method in the creation of various silica structures.

In general, organic materials are capable of construction of a variety of supramolecular structures that reflect their own molecular shape, whereas such "shape design" is very difficult for inorganic materials. The present findings suggest 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.

Experimental Section

Apparatus for spectroscopic measurements: ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX300 apparatus. IR spectra were obtained in KBr pellets by using a Shimadzu FT-IR 8100 spectrometer, and MS spectra were obtained on a Hitachi M-250 mass spectrometer.

Transmission and scanning electron microscopy (TEM and SEM): 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, they were shadowed with OsO_4 (10 mg, 2.0 wt% aqueous solution). Then they were dried for 1 h at low pressure. The specimens were examined with an Hitachi H-7100 microscope with an accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron microscopy (SEM) measurments were carried out with an Hitachi S-4500 microscope. The thin gel was prepared in a 1–2 mL bottle and frozen in liquid nitrogen or dry ice/acetone. The frozen specimen was dried with a vacuum pump for 24 h. The dry sample was coated with palladium-platinum. The accelerating voltage of used was 5–15 kV and the emission current was 10 μA.

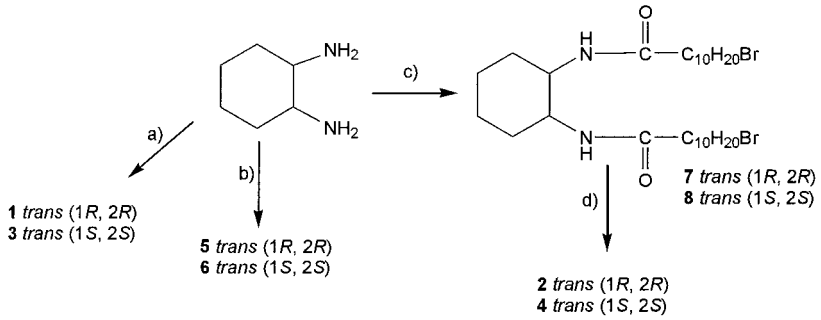
Gelation test of organic fluids: The gelator and the solvent were put in a septum-capped test tube and heated in an oil bath until the solid dissolved. The solution was cooled to room temperature. If the stable gel was observed at this stage, it was classified as G in Table 1.

Sol-gel polycondensation of tetraethoxysilane (TEOS): The gelators (total: 3.0–4.0 mg) were dissolved in acetonitrile or ethanol (100–200 mg). TEOS (8.0–16.0 mg), water (4.0–5.5 mg), and benzylamine (4.0–5.5 mg) were added to the gel sample and warmed until a transparent solution was obtained. The reaction mixture was placed at room temperature under the static conditions for 3–7 days. The product was dried by a vacuum pump at room temperature. Finally, the gelator was removed by calcination at 200 °C for 2 h and then at 500 °C for 2 h under a nitrogen atmosphere, and 500 °C for 4 h under aerobic conditions.

Preparation of the cyclohexanediamine-based organo gelators: The organogelators (**1**–**6**) were synthesized as shown in Scheme 1, and detail methods are following.

***trans*-(1*R*,2*R*)-1,2-Bis(dodecylamido)cyclohexane (1)**: This compound was synthesized by previously reported method.[4c] Yield: 35%; m.p. 164.5–165.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (s, 2H), 3.65 (s, 2H), 3.40 (t, J = 5.3 Hz, 4H), 2.05–1.26 (m, 44H), 0.85 (t, J = 6.3 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 3375, 2970, 1675 cm^{-1}; MS (SIMS): m/z: 479.85 $[M+H]^+$; elemental analysis calcd (%) for $C_{30}H_{58}N_2O_4$ (478.79): C 75.26, H 12.21, N 5.85; found C 74.52, H 12.25, N 5.75.

***trans*-(1*S*,2*S*)-1,2-Bis(dodecylamido)cyclohexane (3)**: This compound was synthesized by the method used for compound **1**.[4c] Yield: 55%; m.p. 164.2–165.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (s, 2H), 3.65 (s, 2H), 3.40 (t, J = 5.3 Hz, 4H), 2.05–1.26 (m, 44H), 0.85 (t, J = 6.3 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 3375, 2970, 1675 cm^{-1}; MS (SIMS): m/z: 479.85 $[M+H]^+$;



Scheme 1. Reagents and conditions for synthesis of organic gelators **1**–**6**. a) Lauroyl chloride, Et_3N, THF, reflux, 8 h. b) Dodecylisocynate, toluene, RT: 24 h, reflux: 2 h. c) 11-Bromoundecanoic acid, DCC, DMAP, THF, 50 °C, 24 h. d) Me_3N, THF/DMF, RT, 24 h.

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elemental analysis calcd (%) for $C_{30}H_{58}N_2O_4$ (478.79): C 75.26, H 12.21, N 5.85; found C 75.25, H 12.50, N 5.70.

***trans*-(1*R*,2*R*)-1,2-Bis(11-bromoundecanoylamino)cyclohexane (7)**: A solution of (1*R*,2*R*)-cylohexanediamine (1.0 g, 9.35 mmol), 11-bromoundecanic acid (10.0 g, 37.70 mmol), dicyclohexylcarbodiimide (DCC, 7.2 g, 34.89 mmol), and dimethylaminopyridine (DMAP, 0.4 g, 3.48 mmol) were stirred at 50 °C for 24 h in dry THF (90 mL). The reaction mixture was filtered, and the filtrate was washed with acidic and basic aqueous solutions. The organic layer was evaporated to dryness. The residue was purified by a silica-gel column with THF/*n*-hexane as the eluant to give compound **7** in 45% yield as white solid. M.p. 106.5–107.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.15$ (s, 2H), 3.65 (s, 2H), 3.40 (t, $J = 5.6$ Hz, 4H), 2.05–1.26 (m, 44H); IR (KBr): $\tilde{\nu} = 3360, 2962, 1655\ cm^{-1}$; MS (SIMS): m/z: 609.50 $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{52}Br_2N_2O_2$ (608.50): C 56.19, H 9.71, N 4.60; found C 56.05, H 9.70, N 4.50.

***trans*-(1*S*,2*S*)-1,2-Bis(11-bromoundecanoylamino)cyclohexane (8)**: This compound was synthesized by the method described above for **7**. Yield: 50%; m.p. 106.5–107.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.15$ (s, 2H), 3.65 (s, 2H), 3.40 (t, $J = 5.6$ Hz, 4H), 2.05–1.26 (m, 44H); IR (KBr): $\tilde{\nu} = 3360, 2962, 1655\ cm^{-1}$; MS (SIMS): m/z: 609.50 $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{52}Br_2N_2O_2$ (608.50): C 56.19, H 9.71, N 4.60; found C 56.39, H 9.62, N 4.55.

***trans*-(1*R*,2*R*)-1,2-Bis(11-*N*,*N*,*N*-trimethylammonium-1-undecylcarbamoyl)-cyclohexanediamine dibromide (2)**: An excess of trimethylamine (10 g, 169 mmol) was slowly added to the compound **7** (1.0 g, 1.64 mmol) in THF/DMF (2:1, 15 mL) at −5 °C. The reaction mixture was maintained at room temperature for 24 h, then evaporated under reduced pressure. The product was purified with recrystallization in THF. Yield: 73%; m.p. 225.5–227.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$ (s, 2H), 3.72 (s, 2H), 3.60 (s, 2H), 3.32–3.12 (m, 8H), 3.03 (s, 18H), 2.01 (t, $J = 5.3$ Hz, 4H), 1.96–1.26 (m, 26H); IR (KBr): $\tilde{\nu} = 3350, 2962, 1650\ cm^{-1}$; MS (SIMS): m/z: 725.45 $[M+H]^+$; elemental analysis calcd (%) for $C_{34}H_{70}Br_2N_4O_2$ (724.40): C 56.19, H 9.71, N 7.71; found C 57.02, H 9.61, N 7.50.

***trans*-(1*S*,2*S*)-1,2-Bis(11-*N*,*N*,*N*-trimethylammonium-1-undecylcarbamoyl)cyclo-hexanediamine dibromide (4)**: This compound was synthesized by the method described above for **2**. Yield; 85%; m.p. 225.5–226.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$ (s, 2H), 3.72 (s, 2H), 3.60 (s, 2H), 3.32–3.12 (m, 8H), 3.03 (s, 18H), 2.01 (t, $J = 5.3$ Hz, 4H), 1.96–1.26 (m, 26H); IR (KBr): $\tilde{\nu} = 3350, 2962, 1650\ cm^{-1}$; MS (SIMS): m/z: 725.45 $[M+H]^+$; elemental analysis calcd (%) for $C_{34}H_{70}Br_2N_4O_2$ (724.40): C 56.19, H 9.71, N 7.71; found C 57.05, H 9.65, N 7.65.

***trans*-(1*R*,2*R*)-1,2-Bis(dodecylureido)cyclohexane (5)**: This compound was synthesized according to a previously reported method.[3c] A solution of dodecylisocyanate (2.75g, 13 mmol) in dry toluene (20 mL) was slowly added to a solution of (1*R*,2*R*)-1,2-cyclohexyldiamine (0.7g, 6.1 mmol) in toluene (100 mL). The reaction mixture, which immediately became viscous, was stirred for 24 h at room temperature and heated for 2 h under reflux. After cooling to room temperature, the gel-like reaction mixture was filtered to give the white waxy solid. The crude product was stirred for 24 h with dichloromethane and collected by filtration. This procedure was repeated with diethyl ether. Finally, the white solid was dried for 24 h at room temperature. Yield: 70%; m.p. 234.5–235.2 °C ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.93$ (d, $J = 6.6$ Hz, 2H), 4.32 (t, $J = 5.3$ Hz, 2H), 3.45 (br, 2H), 3.07 (m, 4H), 2.05 (d, $J = 12.0$ Hz, 2H), 1.80–1.20 (m, 46H), 0.85 (t, $J = 6.6$ Hz, 6H); IR (KBr): $\tilde{\nu} = 3360, 1650, 1560\ cm^{-1}$; MS (SIMS): m/z: 537.8 $[M+H]^+$; elemental analysis calcd (%) for $C_{32}H_{64}N_4O_2$ (536.8): C 71.60, H 12.00, N 10.40; found C 70.90, H 12.05, N 10.25.

***trans*-(1*S*,2*S*)-1,2-Bis(dodecylureido)cyclohexane (6)**: This compound was synthesized by the method described above for **5**, starting from dodecylisocyanate (2.75 g, 13 mmol) and (1*S*,2*S*)-1,2-cyclohexyldiamine (0.7 g, 6.1 mmol). Yield: 85%; m.p. 234.5–235.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): 4.93 (d, $J = 6.6$ Hz, 2H), 4.32 (t, $J = 5.3$ Hz, 2H), 3.45 (br, 2H), 3.07 (m, 4H), 2.05 (d, $J = 12$ Hz, 2H), 1.80–1.20 (m, 46H), 0.85 (t, $J = 6.6$ Hz, 6H); IR (KBr): $\tilde{\nu} = 3360, 1650, 1560\ cm^{-1}$; MS (SIMS): m/z: 537.8 $[M+H]^+$; elemental analysis calcd (%) for $C_{32}H_{64}N_4O_2$ (536.8): C 71.60, H 12.00, N 10.40; found C 71.20, H 11.99, N 10.35.

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