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Creation of Both Right-Handed and Left-Handed Silica Structures by Sol−Gel Transcription of Organogel Fibers Comprised of Chiral Diaminocyclohexane Derivatives

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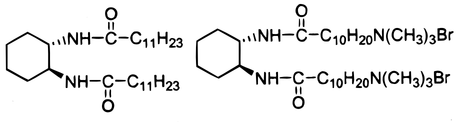
A diversity of supramolecular structures can be created, not only in nature but also in artificial systems, by self-assembly of designed “organic” building blocks.[1] One may consider that this phenomenon is inherent to organic materials. In contrast, creation of such diverse supramolecular structures from “inorganic” materials seems to be very difficult or nearly impossible. The sole method, if any, would be to design such inorganic materials under a template effect of organic supramolecular aggregates.[2]

Recently, exploitation of new organic gelators which can gelate various organic solvents has become an active area of research endeavor.[3−7] 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 applications. More recently, it was found that certain cholesterol derivatives can gelate even tetraethoxysilane (TEOS) which can be used to produce silica by sol−gel polymerization.[8] Very interestingly, it was shown that sol−gel polymerization of gelated TEOS solutions affords silica with a novel hollow fiber structure, because the organogel fibers act as a template in the TEOS polymerization process which, after calcination, result in an hollow tube.[8,9] This organic−inorganic transcription process forms an interesting analogy the formation of fossil remains. The finding tempted us to test whether the helical structure in organogel fibers may be also transcribed into inorganic silica, which would be a completely new way to transcribe chiral information into an inorganic material.

Here, we report on a novel creation method of helically structured silica by sol−gel transcription in chiral diaminocyclohexane-based organogel systems. Very interestingly, we have found that right- and left-handed helical silica structures can be created by transcription of right- and left-handed structures in the organogel fibers, respectively. Although several inorganic materials with some helical structure have been reported,[2a,10] these have been produced utilizing a specific crystallization method or a mechanical method. These methods are quite different from our fine chiral transcription method utilizing chiral organogel fibers. To the best of our knowledge, this is the first example of the creation of both “right- and left-handed helical silica structures” by a sol−gel transcription method.

Compounds **1**−**4** were synthesized using methods which are similar to described previously.[3,8] The gelation ability of **2** and **4** was estimated for 10 different organic solvents (5.00×10^{-2} mol dm^{-3}).[5] Neutral **1** and **3** can gelate alcohols, aprotic, and apolar solvents, indicating that they act as versatile gelators of organic solvents. On the other hand, cationic **2** and **4** can gelate acetonitrile, THF, DMSO, and DMF, indicating that the gelation ability is deteriorated by introduction of cationic charges. However, it can be seen that the gelation ability for aprotic solvents is excellent. Since the presence of the cationic charge in organogel fibers is indispensable to efficient sol−gel transcription,[8,9] mixtures of **1** and **2** or **3** and **4** were used as gelators.



1 trans (1R, 2R)
3 trans (1S, 2S)

2 trans (1R, 2R)
4 trans (1S, 2S)

To characterize the chirality in the organogel systems, CD (circular dichroism) spectra of the organogels, formed by **1**+**2** and **3**+**4** mixtures were measured as shown in Figure 1. The λ_{max} values in the UV absorption spectra appear at around 210−220 nm. In the CD spectra, the $\lambda_{\theta=0}$ values appear at 214 nm. One can thus assign the CD spectra to the exciton-coupling bands. The CD spectrum of an (*R*)-enantiomer mixture, **1**+**2**, exhibits a negative sign for the first Cotton effect, indicating that the dipole moments orientate into an anticlockwise direction in the aggregate of these gelators. On the other hand, an (S)-enantiomer mixture, **3**+**4** exhibits a positive sign for the first Cotton effect, indicating that they are oriented into a clockwise direction. Also, it was confirmed that the contribution of linear dichroism (LD) 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 aggregates with left- and right-handed helical structures, respectively.

To observe such helical morphological structures, the xerogels obtained by a freezing-and-pumping method[5a] were inspected by a scanning electron microscope (SEM). It can be seen that aggregates are comprised of helical fibers with 20−60 nm width. The helicity of the fibers was always left-handed for the (R)-enantiomeer mixture, **1**+**2** and always right-handed for the (*S*)-enantiomer mixture, **3**+**4**. These results show that the exciton-

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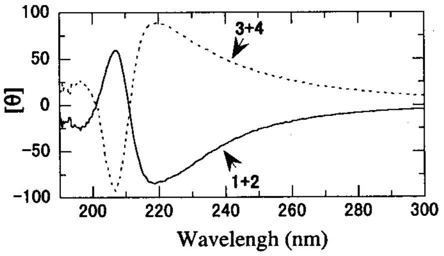

Figure 1. CD spectra of **1**+**2** (1:1 wt %) and **3**+**4** (1:1 wt %) in acetonitrile, respectively.

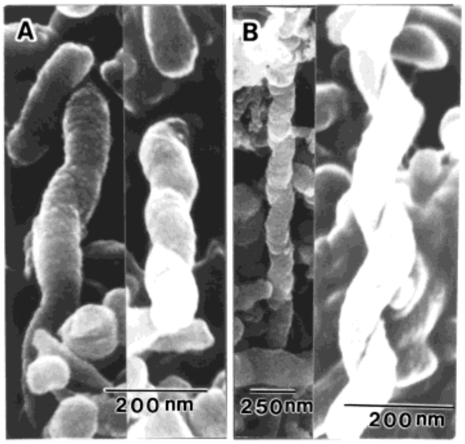

Figure 2. SEM pictures of the silica obtained by sol−gel transcription in (A) left-handed **1**+**2** (1:1 wt %), and (B) right-handed **3**+**4** (1:1 wt %) organogels.

coupling bands in the CD spectra originate from the chiral orientation of these gelators in the fibrous structure.

Sol−gel polymerization of TEOS was carried out according to method which are similar to ones previously described.[8,9]

When neutral **1** was mixed with cationic **2** [**2**/(**1**+**2**) = 30−85%(*r*)], the organogel resulted in the formation of left-handed helical silica, which had an outer diameter of 100−150 nm. At *r* < 30%, the resultant silica showed a conventional granular structure, whereas the solution was not gelated at *r* > 85% and the resultant silica again showed the conventional granular structure. On the other hand, the silica obtained from the (S)-enantiomer mixture, **3**+**4** at *r* [= **4**/(**3**+**4**)] = 30−85% always resulted in a right-handed structure (Figure 2B). In addition, the helical pitch length (340−345 nm) of the organogel fibers and the helical silica are comparable. These results clearly support the view that (i) the presence of an adequate amount of cationic charge is indispensable to the transcription of the organogel structure into the silica structure and (ii) the helicity of the organogel fiber is consistently transcribed into the silica.

Figure 3. TEM pictures of the silica obtained by sol−gel transcription in (A) left-handed **1**+**2** (1:1 wt %), and (B) right-handed **3**+**4** (1:1 wt %) organogels.

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 the organic gelators by calcination.[8,9] Very interestingly, we found that in the right-handed helical silica, a right-handed helical inner tube with a 20−60 nm inner diameter can clearly be recognized (Figure 3B). Careful examination of the TEM picture of the left-handed silica obtained from the (*R*)-enantiomer mixture reveals that the observed inner tubular structure with 20−60 nm inner diameter is also left-handed (Figure 3A). These results support the view that anionic oligomeric siloxanes are adsorbed onto the cationic helical organogel fibers and that the chirality of the silica thus grown reflects the chiral factor present in the organogel fibers.

In conclusion, the present paper demonstrates that “right- and left-handed chirality” which has been characteristic of organic materials can be readily created also in inorganic materials by the sol−gel transcription method. The key point of the present research is to transcribe the chirality in organogel fibers into the silica utilizing electrostatic interactions.[8,9] The results indicate the versatility of the template method in the creation of various inorganic superstructures.

Supporting Information Available: Synthetic scheme, gelation ability of **1**−**4**, SEM pictures of xerogels, and morphology of the resultant silica obtained from **1**/**2**, and **3**/**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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