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Preparation of Ultrastable Mesoporous Silica Using a Phenanthroline-Appended Cholesterol Organogelator as a Template

Jong Hwa Jung, Kazuaki Nakashima, and Seiji Shinkai*

Chemotransfiguration Project, Japan Science and Technology Corporation (JST),
2432 Aikawa, Kurume, Fukuoka 839-0861, Japan

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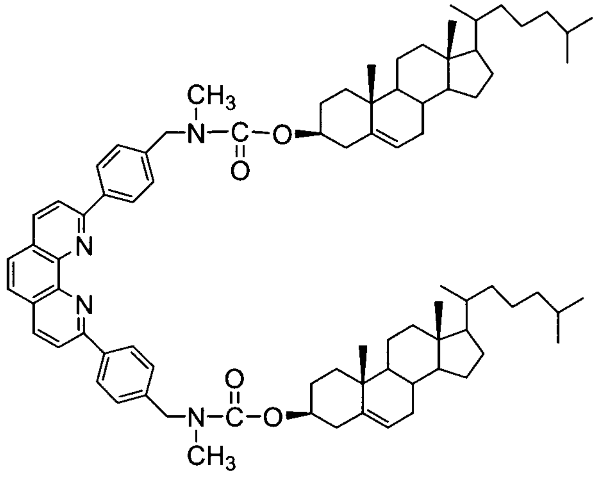
ABSTRACT

New phenanthroline-appended cholesterol organic gelator 1 was synthesized. It was shown from the gelation test that it acts as a versatile gelator of organic fluids such as DMSO, DMF, 1-propanol, acetic acid, etc. The sol–gel polymerization of tetraethoxysilane (TEOS) was carried out using the 1 + acetic acid gel. The silica obtained from the 1 + acetic acid gel resulted in a tubular structure with ca. 4.5 nm inner diameter, which showed the 7.08 value for Q^4/Q^3. These results indicate that the ultrastable mesoporous-sized silica structure can be created by transcription of the organogel superstructure as a template.

The sol−gel synthesis of well-ordered inorganic materials offers a new and wide-ranging approach to new useful materials with controlled architecture and porosity across a range of length scales.[1,2] The direct synthesis of discrete inorganic architectures necessitates the use of dispersed organic supramolecular structures with commensurate dimensionality; for example, hollow fibers of the silica have been prepared by self-assembled phospholipid fibers,[3] viroid cylinders,[4] or organic crystals[2] as templates.

Recently, numerous thermoreversible physical gels formed with low-molecular weight organic molecules have been reported.[5−7] The interest shown by these gels lies in the numerous potential applications envisaged for these materials such as hardeners of solvents, drug delivery systems, membranes, and sensors. More particularly, cholesterol-based organogel templates have created various hollow silica fibers with linear,[8] helical,[9] and multilayered structures[10] by sol−gel polymerization. The findings indicate that the cholesterol-based organogel fibers can act as an efficient template to create an inside hollow tube in the silica polymerization process.[8−12] However, all fiber structures of the silica obtained utilizing the electrostatic interaction between cationic orgngogel templates and anionic TEOS oligomers had macroporous sizes with 30−200 nm of inner diameters. These results indicate that the organogel fibers acting as templates retain the size of 30−200 nm diameters during sol−gel polymerization of TEOS. However, Whitten and coworkers recently found that the "rigid" gel strands with increasing temperature become increasingly "mobile" via solvent-induced swelling of the internal fibril bundles and/or breakup into smaller, more flexible fiber bundles.[6b,c] These results support the view that mesoporous-sized silica would be created by sol−gel polymerization of TEOS using an organogel template that has a T_{gel} (sol−gel phase transition temperature) value very close to room temperature. Therefore, we have designed a new phenanthroline-appended organogelator **1** as a template in order to create mesoporous-sized silica. One can expect for **1** that the phenanthroline nitrogens not only generate the cationic charge necessary to



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* Corresponding author. E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp.

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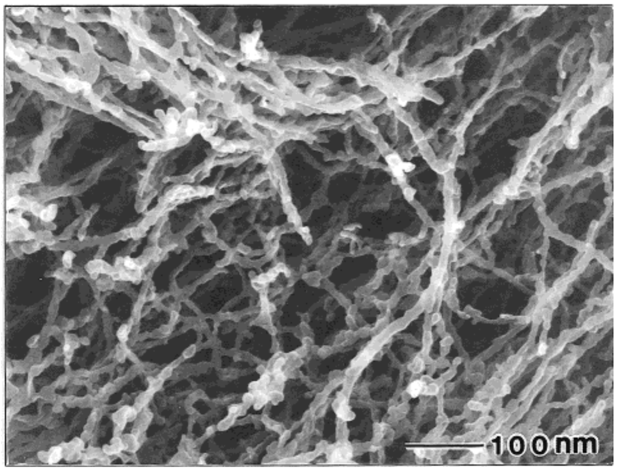

Figure 1. SEM picture of xerogel **1** obtained from the acetic acid gel.

sol−gel transcription but also act as a binding site for metal ions.[13] We have found that **1** affords a fibrous structure with small fiber diameters and the superstructure is successfully transcribed into mesoporous-sized silica under the specific sol−gel polymerization conditions. Moreover, the degree of the framework SiO_4 unit is unprecedented among mesoporous-sized silica, making this material ultrastable in comparison to previously reported mesostructures.

Compound **1** (mp: 73.5−75.0 °C) was synthesized according to the method similar to that reported previously[14] and identified by IR and ^1H NMR spectral evidence and elemental analysis.

The gelation ability of compound **1** was estimated in various organic solvents.[5,15] It can gelate DMSO, DMF, 1-propanol, methylcyclohexane, acetic acid, and propionic acid, indicating that **1** acts as a versatile gelator of organic solvents. To obtain visual insights into the aggregation mode, we observed the xerogel structure of the **1** + acetic acid gel by SEM.[5,7] Figure 1 shows the typical picture of the fibrous structure obtained from the xerogel **1**. It is seen from Figure 1 that the **1** + acetic acid gel forms a frizzled fibrous structure with small 5−30 nm diameters and a few micrometers of length. This result indicates that the xerogel structure of the **1** + acetic acid gel would act as a good template to obtain the mesoporous silica with ca. 5 nm inner diameter under the specific sol−gel polymerization conditions.

To transcribe the superstructure formed in the organogel into the silica structure, sol−gel polymerization of TEOS was carried out using the **1** + acetic acid gel which has a T_{gel} value (23.1−25.3 °C) close to room temperature according to the method described previously.[8−12] For example **1** (1.0−5.0 wt %) was dissolved in a medium for sol−gel polymerization: the medium consists of acetic acid (2.0 g), TEOS (0.2−0.5 g), and water (0.1−0.2 g). The sample was sealed in a glass tube and left at room temperature for 3 days. After calcination, we observed the SEM picture of the silica obtained from the acetic acid gel (Figure 2a). The silica obtained from **1** shows the fibrous structure with 30−70 nm outer diameters and a few micrometers length. The yield for the fiber structure of the silica obtained from acetic acid gel **1** was not 100%. The granular silica was also induced during sol−gel polymerization using the acetic acid gel **1** as a template. However, we consider that this granular silica is produced without the template effect of the organogel **1**. These results indicate, therefore, that the fibrous structure of the silica is created by transcription of the organogel superstructure owing to the electrostatic interaction between the cationic charges of **1** (protonated phenanthroline) and TEOS (or anionic oligomeric silica particles).[8−12]

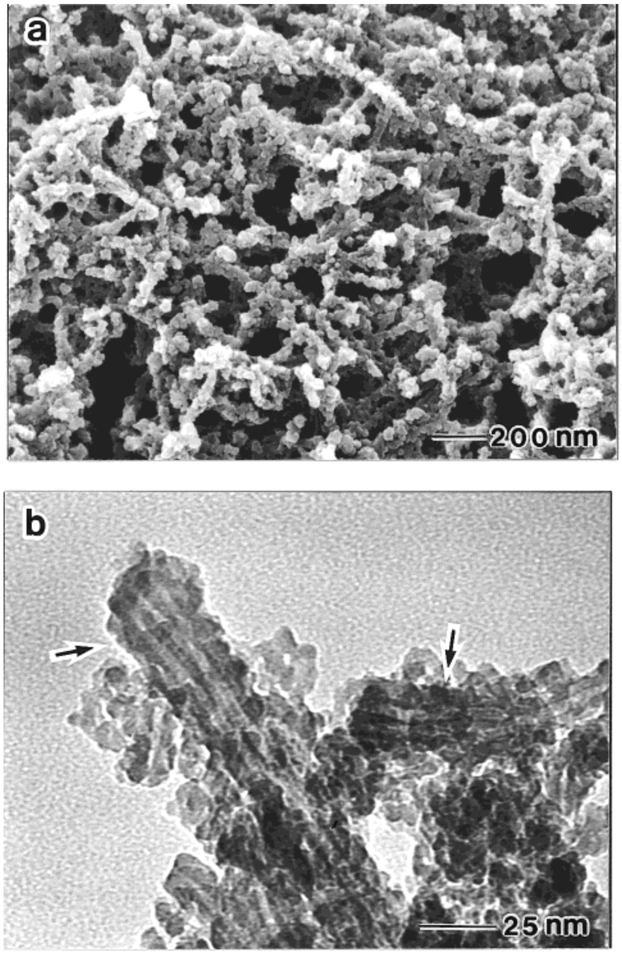

Figure 2. (a) SEM and (b) TEM pictures of the silica (after calcination) obtained by sol−gel polymerization of TEOS in the **1** + acetic acid gel.

To further corroborate that the organogel fibers really acted as a template for the growth of the tubular silica, we took the TEM pictures after removal of **1** by calcination. Very interestingly, we found that the silica obtained from **1** has an inner tube structure with 4−5 nm diameters (Figure 2b). One may expect a slight shrinkage of the silica during the calcination process. The results again support the view that oligomeric silica particles are adsorbed onto the cationic organogel fibers by the electrostatic interaction.[8−12] One may thus regard that this is a new class of mesoporous-sized silica with a tubular structure.

Why can the **1** + acetic acid gel result in the mesoporous-sized silica? The organogel formed from **1** has a T_{gel} value (23.1−25.3 °C) close to room temperature, and therefore the gel strands should be relatively "flexible" and retain the

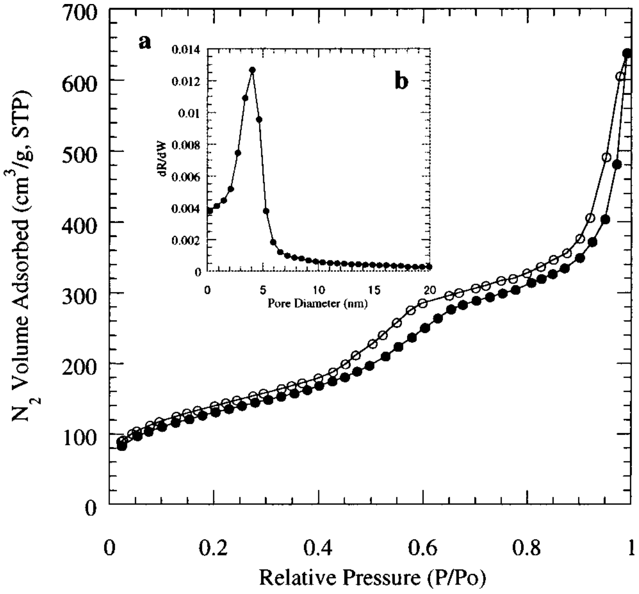

Figure 3. (a) Nitrogen adsorption−desorption isotherms and (b) pore size of the silica obtained from the **1** + acetic acid gel after calcination.

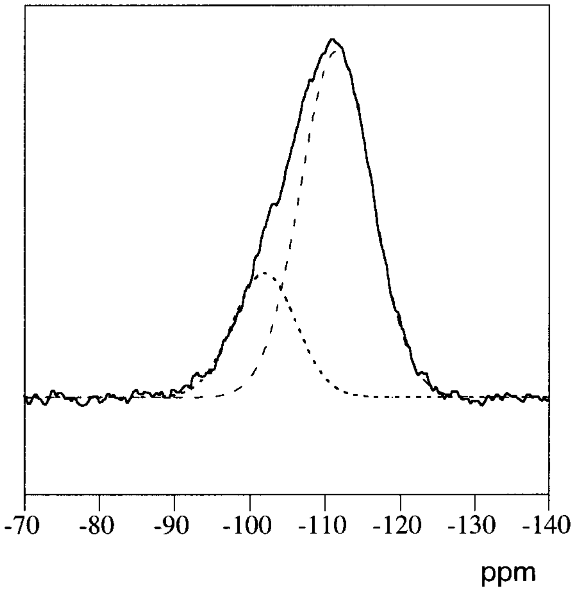

Figure 4. ^{29}Si MAS NMR spectrum of the silica obtained from the **1** + acetic acid gel after calcination.

smaller fiber size during the sol−gel transcription process. On the other hand, the organogels used in the previous studies have T_{gel} values much higher than room temperature[10] and the gel strands should be relatively "rigid", which tend to aggregate into the large fiber size. We now consider that this difference is reflected in the size of the inner tube diameter.

Figure 3 illustrates N_2 adsorption−desorption isotherms and a BJH pore size distribution plot (insert) calculated from the adsorption branch of the N_2 isotherms for calcined silica obtained from the **1** + acetic acid gel. The N_2 adsorption−desorption isotherms of this material exhibit a typical type IV, which is characteristic of mesoporosity. A narrow pore size distribution with a mean value of 4.5 nm is also obtained from both the adsorption and desorption processes. This material has a Brunauer−Emmett−Teller (BET) surface area of 460 m^2/g.

More important between the silica obtained from the **1** + acetic acid gel and previously reported mesoporous silica materials are the high degree of SiO_4 unit cross-linking in the framework and the structural stability that results from this cross-linking. As shown by the deconvoluted ^{29}Si MAS NMR spectra in Figure 4, the silica framework consists of a major fraction of the fully cross-linked Q^4 unit; $Si(OSi)_4$ (as shown by a resonance near −110 ppm) and a minor fraction of the incompletely cross-linked Q^3 unit; $(OH)Si(OSi)_3$ (as shown by a resonance near −98 ppm). Generally, surfactant-containing silica mesostructures exhibit Q^4/Q^3 ratios less than 2.0, and their calcined derivatives exhibit the values near 3.0.[16] However, the Q^4/Q^3 ratio for the silica obtained from the **1** + acetic acid gel gives 7.08, suggesting that the SiOH groups may be site-isolated and buried in the framework. This very high Q^4/Q^3 value is comparable with those of the vesicular silica structures obtained from gemini-type surfactants reported by Pinnavaia et al. (6.2−7.4).[16] It is undoubted that this high Q^4/Q^3 value in our system is associated with the small organogel fiber structure used as a template.

In conclusion, the present paper has demonstrated a new method to prepare the mesoporous-sized and ultrastabilized silica using the phenanthrolin-appended cholesterol organic gelator. This mesoporous-sized silica is created by the electrostatic interaction with the fine fiber structure characteristic of this gelator. We believe that this concept will be more generally applicable to the new silica preparation using various organogel superstructures as templates.

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