

The Role of the Neutral and Cationic Gelators from (1S,2S)-(-)-Diphenylethylenediamine for the Preparation of Silica Nano Tubes

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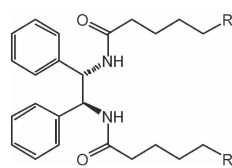
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Many scientists have recently been interested in the synthesis of helical silica nano tubes by using the self assemblies of chiral organic gelators as templates. As organic gelators, for example, sugar-integrated gelators¹ or cholesterol-based gelators² based on chiral compounds readily available from natural environments in an optically active form have been used for the preparation of silica nano tubes. Chiral *trans*-1,2-cyclohexanediamine derivatives have also been known as excellent gelators that can harden a wide variety of organic fluids. *Trans*-(1*R*,2*R*)- or *trans*-(1*S*,2*S*)-1,2-di(undecylcarbonylamino)cyclohexane derivatives were reported to self-assemble into left-handed and right-handed helical organogel fibers, which are stabilized by inter molecular hydrogen-bonds through amide groups.³ The chiral self-assemblies based on these organic gelators have been successfully utilized as excellent templates for the sol-gel polycondensation of tetraethoxysilane (TEOS) into helical silica nano tubes.⁴ In order to transcribe the organogel structure into the silica structure, it was noticed that the cationic charge in the gelators is indispensable in the sol-gel polycondensation of TEOS, but the cationic gelators tend to lose the high gelation ability and rarely result in the helical structure.⁵ To overcome this dilemma, the mixture of the neutral and the cationic gelators have been utilized to form stable organogels supported by the helical fiber structure.⁵ However, it is not clear how the neutral and cationic gelators are integrated into the organogels while it is known that cationic charge is necessary for the sol-gel transcription in order to adsorb anionic silica particles onto the organogels.¹

In order to explore how the neutral and cationic gelators are integrated into the organogels and to explore the role of the neutral and cationic gelators in forming silica tubes, in this study, we prepared two organic gelators **1** and **2** starting from



1 R = CH₃
2 R = N(CH₂)₂⁺Br

(1*S*,2*S*)-(-)-diphenylethylenediamine via the method utilized for the preparation of organic gelators from optically active *trans*-diaminocyclohexane.⁵ The structures of the two gelators prepared in this study were confirmed by the ¹H-, ¹³C-NMR, FT-IR spectral data and melting points.

Gelation abilities of neutral and cationic gelators (**1** and **2**) were tested in various solvents and the results are summarized in Table 1. Neutral gelator **1** can gelate ethanol, acetonitrile, *n*-butanol, tetrahydrofuran and ethyl acetate among eight solvents tested while cationic gelator **2** can partially gelate *n*-butanol only. However, when gelator **2** was mixed with gelator **1**, the mixed gelator (**1** + **2**, 1:1 wt% mixture) was found to gelate ethanol, acetonitrile and *n*-butanol.

In order to see the morphological structures of organogels prepared in ethanol, the organogels prepared from gelator **1** and the mixed gelator were diluted with ethanol. The ethanol solution of gelator **2** was also diluted with ethanol. And then the partially dissolved organogels and the ethanol solution of gelator **2** were taken on the carbon grids five times. The carbon grids were frozen in liquid nitrogen and then were lyophilized. The resulting carbon grids were subjected to scanning electron microscopy (SEM). SEM results are shown in Figure 1. In the case of neutral gelator **1**, rod-shaped structure is shown (Figure 1a), the thickness of the rods being in the range of 70 ~ 90 nm. In the case of cationic gelator **2**, does not have any regular morphology (Figure 1b) even though gelator **2** does not gelate ethanol under usual condition as shown Table 1.

Table 1. The gelation ability of gelator **1**, gelator **2** and the mixed gelator (**1** + **2**, 1:1 wt% mixture).^a

Solvent	Gelator 1	Gelator 2	1 + 2 (1:1 wt%)
Ethanol	G	S	G
Acetonitrile	G	S	G
<i>n</i> -Butanol	G	Gp	G
Tetrahydrofuran	G	I	I
Chloroform	S	I	I
Hexane	I	I	I
Ethyl acetate	G	I	I
Methanol	C	S	C

^aGelator concentration: 5.0 wt%/vol. G = stable gel at room temperature, S = solution, I = insoluble, C = crystallize, Gp = partial gel.

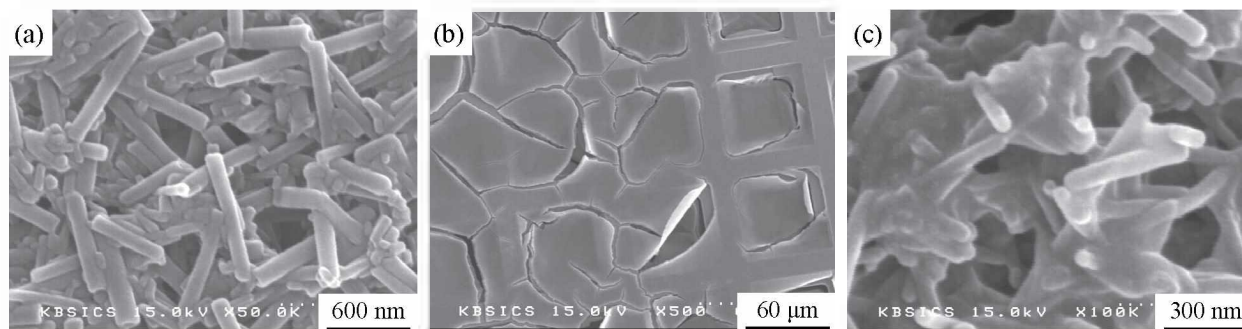


Figure 1. SEM images of organogels of (a) **1** (bar = 600 nm), (b) **2** (bar = 60 μm) and (c) **1 + 2** (1:1 wt%) in ethanol.

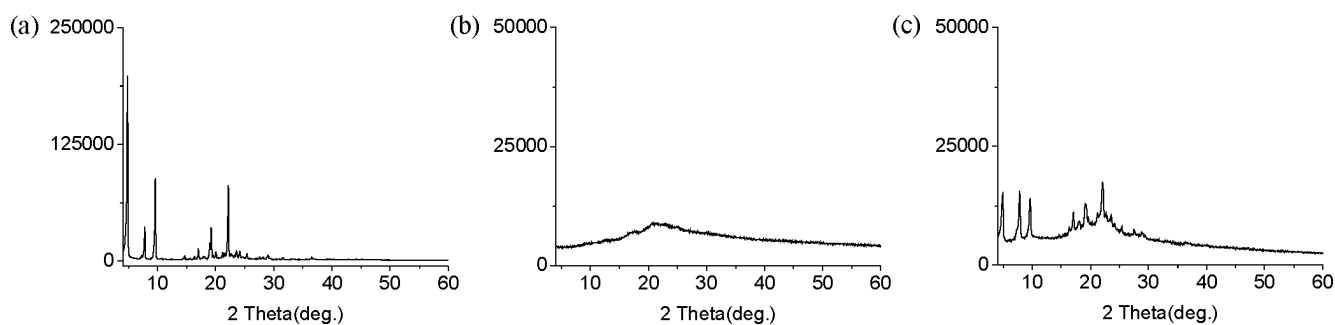


Figure 2. The XRD spectra of organogels of (a) **1**, (b) **2** and (c) **1 + 2** (1:1 wt%) in ethanol.

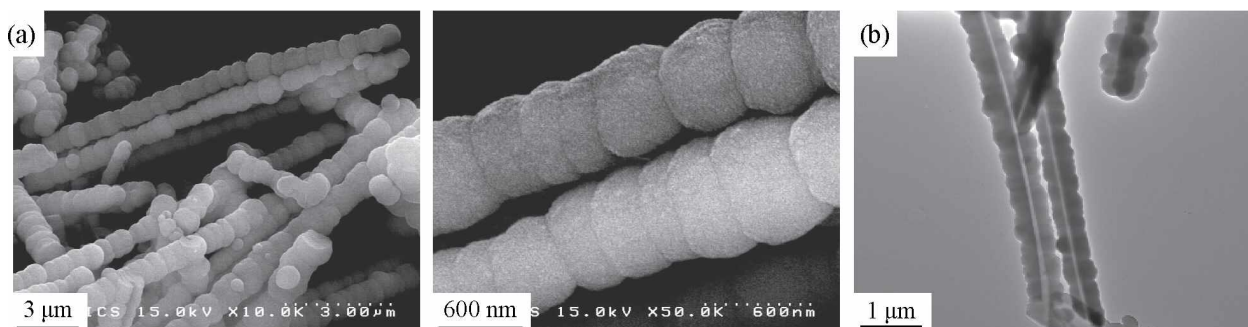


Figure 3. SEM (a) (bar = 3 μm and 600 nm) and TEM (b) (bar = 1 μm) images of the silica obtained from the mixed gelator (**1 + 2**, 1:1 wt%) in ethanol after calcination.

Interestingly, the organogel prepared from the mixed gelator looks like that the rod-shaped gel is relatively evenly covered by the non-shaped gel. These results indicate that the neutral and cationic gelators are not integrated in the single organogel structure, but they act independently in gelation.

The independent action of the neutral and cationic gelators of the mixed gelators in gelation can be supported by XRD spectrums. The XRD spectrums for the organogels of gelator **1**, gelator **2** and the mixed gelator (**1 + 2**, 1:1 wt%) obtained from ethanol are shown in Figure 2. The organogel of gelator **1** shows a distinct crystal unity (Figure 2a) while the organogel of gelator **2** does show amorphous pattern (Figure 2b). Interestingly, the XRD spectrum of the organogel of the mixed gelator is just the mixture of the two patterns (Figure 2c). These results indicate that the neutral and cationic gelators consisting of the mixed gelator do not act cooperatively in gelation. Consequently, two different organogels seem to be formed independently from the neutral and cationic gelators.

one organogel being covered by the other organogel. These results are exactly consistent with those observed by the SEM images of organogels.

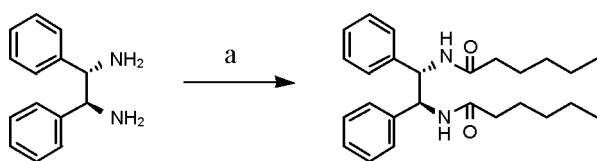
In order to form silica, the sol-gel polycondensation of TEOS was carried out with gelator **1**, gelator **2** and the mixed gelator (**1 + 2**, 1:1 wt%) in ethanol, respectively, *via* the known procedure. The sol-gel polycondensation of TEOS with a single gelator as the neutral gelator, **1** or the cationic gelator, **2** in ethanol was found to produce only silica particles. In contrast, the sol-gel polycondensation of TEOS with the mixed gelator in ethanol was found to produce silica nano tubes with an inner diameter of about 50 ~ 70 nm after calcination as shown by the SEM and TEM images in Figure 3. From these results, it is concluded that both of gelator **1** and gelator **2** are required for the formation of silica nano tubes by the sol-gel polycondensation of TEOS, but the rod-shaped organogel originated from the neutral gelator should be evenly covered by the cationic gelator for the formation of silica nano tubes.

The same experiment was performed starting from (1*R*,2*R*)-(-)-diphenylethylenediamine and the results including the formation of the silica nanotubes were identical to those obtained with the use of (1*S*,2*S*)-(-)-diphenylethylenediamine. Unfortunately, the helicity of the silica nano tubes was not clearly observed in either case.

In short, in this study, we demonstrated that the neutral gelator determines the shape of organogel morphology, and the cationic gelator influences the polymerization of TEOS after covering the surface of the organogel originated from the neutral gelator using derivatives of (1*S*,2*S*)-(-)-diphenylethylenediamine. From these results it is concluded that the neutral and cationic gelators play different roles in forming silica nano tubes.

Experimental Section

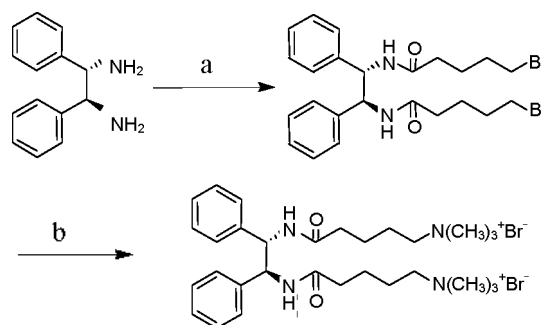
Synthesis of the neutral gelator 1. Add 0.20 g (0.94 mmol) of (1*S*,2*S*)-(-)-diphenylethylenediamine, 5 mL of distilled dichloromethane, and 0.30 mL (2.15 mmol) of triethylamine into a 50 mL one neck round bottom flask and stir well. Add 0.29 mL (2.11 mmol) of hexanoyl chloride slowly by using a dropping funnel and stir the solution for 1 day. Use 2 N-HCl (aq) and 2 N-NaOH (aq) to extract organic layer from the water layer. Dry the organic layer with sodium sulfate then recrystallize to obtain 0.27 g (yield: 70.0%) of the white solid compound.: ¹H-NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.6 Hz, 6H), 1.27 ~ 1.33 (m, 8H), 1.60 (m, 4H), 2.18 (t, *J* = 7.2 Hz, 4H), 5.24 ~ 5.27 (dd, *J* = 5.3, 2.4 Hz, 2H), 6.81 (s, 2H), 7.09 ~ 7.17 (m, 10H); ¹³C-NMR (CDCl₃, ppm): δ 14.07, 22.57, 25.56, 31.62, 36.80, 59.73, 127.71, 128.03, 128.80, 138.94, 174.57; FT-IR (KBr): ν_{\max} 3312, 3064, 3034, 2954, 2928, 2859, 1642, 1540, 1455, 701 cm⁻¹; mp 224.0 ~ 224.5 °C. Elemental analysis: C₂₆H₃₆N₂O₂ (Mw: 395.27), calcd (%): C, 76.43; H, 8.88; N, 6.86. Found: C, 76.53; H, 8.96; N, 6.96.



a. Hexanoyl chloride, Et₃N, CH₂Cl₂, rt, 24 hrs

Synthesis of the cationic gelator 2. Add 0.20 g (0.94 mmol) of (1*S*,2*S*)-(-)-diphenylethylenediamine, 5 mL of distilled dichloromethane, and 0.60 mL (4.30 mmol) of triethylamine into a 50 mL one neck round bottom flask and stir the solution at the room temperature for 30 minutes. Add 0.30 mL (2.24 mmol) of 5-bromovaleryl chloride slowly into the reaction solution by using a dropping funnel and stir at the room temperature for 1 day. Use 6 N-HCl (aq) and 6 N-NaOH (aq) to extract organic layer from the water layer. Dry the organic layer with sodium sulfate then remove the organic solvent at low pressure and recrystallize to obtain 0.25 g (yield: 50.5%) of the white solid intermediated compound.: ¹H-NMR (CDCl₃, ppm): δ 1.73 ~ 1.89 (m, 8H), 2.23 (t, *J* = 7.5 Hz, 4H), 3.39 (t, *J* = 6.3 Hz, 4H), 5.24 (dd, *J* = 5.3, 2.4 Hz, 2H), 6.68 (s, 2H), 7.09 ~ 7.21 (m, 10

H); ¹³C-NMR (CDCl₃, ppm): δ 24.36, 32.34, 33.34, 35.84, 59.75, 127.66, 128.11, 128.87, 138.86, 173.29; FT-IR (KBr): ν_{\max} 3445, 3290, 3062, 2936, 1641, 1538, 1454, 1376, 1232, 701 cm⁻¹; mp 142.2 ~ 142.7 °C. Elemental analysis: C₂₄H₃₀Br₂N₂O₂ (Mw: 536.07), calcd (%): C, 53.55; H, 5.62; N, 5.20. Found: C, 53.63; H, 5.59; N, 5.32.



a. 5-Bromovaleryl chloride, Et₃N, CH₂Cl₂, rt, 1 day
b. Trimethylamine, THF:Ethanol (2:1), rt, 4 days

Add 0.27 g (0.49 mmol) of the synthesized intermediate, 10 mL of the 2:1 mixture of THF and ethanol, and 7 mL (75.32 mmol) of trimethylamine into a 5 mL one neck round bottom flask and stir at the room temperature for 4 days. Then, remove the organic solvent at low pressure and recrystallize to obtain 0.27 g (yield: 70.5%) of the grey solid compound.: ¹H-NMR (CD₃CN, ppm): δ 1.51 (m, 8H), 2.32 (m, 4H), 3.00 (s, 18H), 3.23 ~ 3.46 (m, 4H), 5.46 (d, *J* = 9.0 Hz, 2H), 7.25 ~ 7.28 (m, 2H), 7.31 ~ 7.37 (m, 4H), 7.56 ~ 7.60 (m, 4H), 9.06 (d, *J* = 9.0 Hz, 2H); ¹³C-NMR (CD₃OD, ppm): δ 22.04, 22.34, 34.78, 52.37, 57.79, 66.12, 127.30, 127.38, 128.20, 139.80, 173.54; FT-IR (KBr): ν_{\max} 3430, 3282, 3062, 3029, 2952, 1640, 1537, 1489, 1455, 701 cm⁻¹; mp 200.6 ~ 201.0 °C. Elemental analysis: C₃₀H₄₈Br₂N₄O₂ (Mw: 654.21), calcd (%): C, 54.88; H, 7.37; N, 8.53. Found: C, 54.84; H, 7.21; N, 8.49.

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