

ORIGINAL PAPER

Helical silica nanotubes: Nanofabrication architecture, transfer of helix and chirality to silica nanotubes

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A series of neutral gelators and cationic amphiphiles derived from 1,2 diphenylethylenediamine (I) and 1,2-cyclohexanediamine (II) was synthesised. Helical silica nanotubes were prepared utilising these organic gelators through sol–gel polycondensation of tetraethoxy silane, (TEOS–silica source). Right- and left-handed helical nanotubes respectively were obtained from a 1 : 1 mass mixture of optically active, (1S,2S)-III–(1S,2S)-VI neutral gelator and (1S,2S)-IV–(1S,2S)-VI cationic amphiphile and a 1 : 1 mass mixture of optically active, (1R,2R)-III–(1R,2R)-VI cationic amphiphile, indicating that the handedness of the helical nanotubes varied with the change in the neutral gelator precursors used. The nanotubes were characterised by SEM images.

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Keywords: organogels, silica nanomaterials, chirality, handedness, crossover experiments

Introduction

Silica nanostructure materials have received much attraction recently due to their potential applications in many fields such as catalysis or chiral catalysis in organic synthesis (Sayari, 1996), chiral adsorbent in chromatographic separation (Bruzzoniti et al., 2000), and in the controlled release of drugs (Zhu et al., 2005). Silica-titania nanorods-nanotubes composite membranes with multi-functional properties such as photo-catalysis and membrane property have been innovative in water purification, i.e. removal of sodium dodecylbenzene sulphonate (SDBS) from water (Zhang et al., 2006). Using silica-titania nanotubes, researchers have also demonstrated the possibility of the delivery of proteins into living cells and their functions within the cell. These nanotube– protein drug delivery systems have led to significant advances in different fields of medicine (Cho et al., 2010).

Chiral organic-inorganic hybrid 4,4-biphenylenesilica nanotubes were prepared using a pair of chiral anionic enantiomers (Wang et al., 2010). Silica nanotubes have been prepared by using hard templates, such as anodic alumina membranes, polycarbonate membranes (Bian et al., 2009; Yang et al., 2003; Liang & Susha, 2004), and soft organic templates such as surfactants (Yu et al., 2008; Kleitz et al., 2001;. Delclos et al., 2008; Kim et al., 1998; Yang et al., 1997; Asefa et al., 1995; Huo et al.,

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1994; Stupp & Braun, 1997; Tanev & Pinnavaia, 1996; Tanev et al., 1997), polymers (Mecerreyes et al., 2001; Zhao et al., 1998), sugar-related (Yoza et al., 1999) and amine-based (Jung et al., 2000b) gelators, etc. It is well known that the chirality transfer can be made from high-molecular mass compounds to lowmolecular mass compounds through non-covalent interactions and that single-handed helical silica nanotubes have been prepared by using the self-assemblies of optically active organic gelators or surfactants as templates including sugar-integrated gelators (Yoza et al., 1999), cholesterol-based gelators (Jung et al., 2003, 2001; Piepenbrock et al., 2010; Qiao et al., 2009), chiral surfactants, amino acid-based gelators (Yang et al., 2006; Paik et al., 2010), or amino acid-based surfactants (Che et al., 2004; Qiu et al., 2008) derived from optically active chiral compounds readily available from nature.

Chiral *trans*-1,2-cyclohexanediamine-derived gelators have also been used for the preparation of single-handed helical silica nanotubes (Jung et al., 2000a, 2000b). Optically active amide or ureide derivatives of *trans*-1,2-cyclohexanediamine were reported to self-assemble into left-handed or right-handed helical organogels and were transcribed into left- or righthanded helical silica nanotubes through the sol-gel polycondensation of tetraethoxy silane (TEOS). In transcribing the organogel structure into the silica structure, it was noted that the cationic charge in the gelators was indispensable in the sol-gel polycondensation of TEOS as a silica source, but that the cationic gelators tended to lose the high gelation ability. Consequently, a mixture of neutral and cationic gelators of identical stereochemistry prepared from *trans*-1,2-cyclohexanediamine was used to form stable organogels. However, it was not clear how the neutral and cationic gelators were integrated into the organogels and their role in sol-gel polycondensation, even though it was known that cationic charge was necessary for the sol-gel transcription in order to adsorb anionic silica particles onto the organogels.

We recently demonstrated that the neutral gelator (with the shorter alkyl side-chain) determined the shape of the organogel, and the cationic amphiphile influenced the polymerisation of TEOS after covering the surface of the organogel originating from the neutral gelator (Hyun et al., 2009). Continuing our research interest in nanomaterials (Kim et al., 2011; Roopan et al., 2010; Roopan & Nawaz Khan, 2010a, 2010b, 2011), this paper is concerned with nanofabrication architecture, the transfer of helix and chirality to silica nanotubes.



Fig. 1. Synthesis of neutral organic gelators and cationic amphiphiles: a) lauroyl chloride, Et₃N, CH₂Cl₂, r.t.; b) (*i*) 11bromoundecanoic acid, 2-ethoxy-1-ethoxycarbonyl-1,2-dihidroquinoline (EEDQ), trimethyl amine, r.t., (*ii*) trimethyl amine, THF–ethanol ($\varphi_r = 2:1$), r.t., 4 days.

Table 1. Characterisation data of prepared compounds

Compound	Formula	$M_{ m r}$ –	$w_{ m i}({ m calc.})/\% \ w_{ m i}({ m found})/\%$			Yield	M.p.
Compound			С	Н	Ν	%	$^{\circ}\mathrm{C}$
(1S,2S)-III	$C_{38}H_{60}N_2O_2$	576.9	$79.11 \\ 79.32$	$\begin{array}{c} 10.48\\ 10.56\end{array}$	$4.86 \\ 4.96$	65.0	137.0–137.7
Bromine intermediate	$\mathrm{C}_{36}\mathrm{H}_{54}\mathrm{Br}_{2}\mathrm{N}_{2}\mathrm{O}_{2}$	706.63	$61.19 \\ 61.27$	$7.70 \\ 7.59$	$3.96 \\ 3.83$	70.0	146.8 - 147.5
(1S,2S)-IV	$\mathrm{C}_{42}\mathrm{H}_{72}\mathrm{Br}_{2}\mathrm{N}_{4}\mathrm{O}_{2}$	824.85	$\begin{array}{c} 61.16\\ 61.24\end{array}$	8.80 8.76	$6.79 \\ 6.85$	60.0	116.8–117.4

Table 2. Spectral data of prepared compounds

Compound	Spectral data
(1 <i>S</i> ,2 <i>S</i>)- <i>III</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 3316, 3062, 3032, 2920, 2850, 1642, 1535, 1455, 701 ¹ H NMR (CDCl ₃), δ : 0.87 (t, $J = 6.6$ Hz, 6H), 1.24 (m, 32H), 1.59 (m, 4H), 2.18 (t, $J = 7.2$ Hz, 4H), 5.24 (dd, $J = 4.8$ Hz, $J = 2.4$ Hz, 2H), 6.81 (s, 2H), 7.09–7.20 (m, 10H) ¹³ C NMR (CDCl ₃), δ : 14.26, 22.88, 26.01, 29.51, 29.54, 29.59, 29.73, 29.85, 32.12, 36.75, 59.72, 125.40, 127.70, 128.01, 128.77, 138.87, 174.81
Bromine intermediate	IR, $\tilde{\nu}/cm^{-1}$: 3433, 3306, 3059, 2925, 2851, 1642, 1543, 1458, 1381, 1252, 701 ¹ H NMR (CDCl ₃), δ : 1.26 (m, 20H), 1.41 (m, 4H), 1.58 (m, 4H), 1.89 (m, 4H), 2.17 (t, $J = 7.2$ Hz, 4H), 3.40 (t, $J = 6.9$ Hz, 4H), 5.24 (dd, $J = 4.8$ Hz, $J = 2.4$ Hz, 2H), 6.64 (s, 2H), 7.09–7.19 (m, 10H) ¹³ C NMR (CDCl ₃), δ : 25.90, 28.40, 28.89, 29.10, 29.51, 29.55, 29.60, 29.61, 33.05, 34.27, 37.07, 59.59, 127.74, 128.00, 128.81, 139.10, 174.09
(1 <i>S</i> ,2 <i>S</i>)- <i>IV</i>	IR, $\tilde{\nu}/cm^{-1}$: 3419, 3299, 3030, 2924, 2853, 2074, 1641, 1541, 1490, 701 ¹ H NMR (CD ₃ CN), δ : 1.08–1.43 (m, 28H), 1.71 (m, 4H), 2.21 (t, $J = 6.3$ Hz, 4H), 3.04 (s, 18H), 3.24–3.30 (m, 4H), 5.37 (d, $J = 8.7$ Hz, 2H), 7.22 (t, $J = 5.1$ Hz, 2H), 7.31 (t, $J = 5.4$ Hz, 4H), 7.54 (d, $J = 7.2$ Hz, 2H), 8.98 (d, $J = 10.2$ Hz, 2H) ¹³ C NMR (CD ₃ CN), δ : 23.93, 27.04, 27.35, 30.14, 30.19, 30.37, 30.41, 30.43, 37.22, 53.52, 53.57, 59.06, 67.87, 128.39, 128.58, 129.27, 140,80, 175.91

Experimental

The silica nanomaterials were characterised using the conventional X-ray diffractometer (XRD, Rigaku D-2400, Rigaku, Japan). The scanning electron microscope (SEM) images of samples were recorded on a Hitachi S-4200 (Hitachi, Japan), a field emission SEM. The transmission electron microscope (TEM) images were collected using a Jeol JEM 2010 microscope (Jeol, Japan) at 200 kV.

The neutral organic gelators and cationic amphiphile required in the present studies were synthesised as per the scheme depicted below (Fig. 1) and were characterised by different analytical techniques (Tables 1 and 2).

Neutral gelator, (1S,2S)-III: to a mixture of (1S, 2S)-(-)-diphenylethylenediamine (0.20 g, 0.94 mmol), dichloromethane (5 mL) and triethylamine (0.53 mL, 3.80 mmol) stirred in a 50 mL round bottom flask, dodecanoyl chloride (lauroyl chloride) (0.49 mL, 2.07 mmol) was slowly added through a dropping funnel and continued to be stirred at room temperature until the completion of the reaction, which was monitored by thin layer chromatography (TLC), was

reached. Then the reaction mixture was diluted with dichloromethane, washed first with 1 M HCl solution to remove un-reacted amine (triethylamine) impurity, then by using 1 M NaOH solution to remove any excess acid impurity. The organic layer was then washed thoroughly with water and dried using anhydrous sodium sulphate. Next, the solvent was removed by distillation to yield the crude neutral gelator. The pure neutral gelator was obtained as a white solid by re-crystallisation from the mixture of dichloromethane and hexane.

The other neutral gelators required in the investigations, namely (1R,2R)-III and (\pm) -III were prepared following the same procedure and were characterised by NMR, IR, and elemental analysis.

Cationic amphiphile, (1S,2S)-*IV*: to a mixture of 11-bromoundecanoic acid (3.0 g, 11.32 mmol) and 2-ethoxy-1-ethoxycarbonyl-1,2-dihidroquinoline,

(EEDQ) (3.1 g, 12.54 mmol) stirred in a 250 mL round bottom flask, (1S,2S)-(-)-diphenylethylenediamine (1.0 g, 4.71 mmol) was slowly added through a dropping funnel and continued to be stirred at room temperature until the completion of the reaction, which was monitored by thin layer chromatography (TLC),



Fig. 2. Synthesis of right- and left-handed helical silica nanotubes.

was reached. Then the reaction mixture was diluted with dichloromethane, washed first with 1 M HCl solution to remove un-reacted amine impurity, then by using 1 M NaOH solution to remove any excess acid impurity. The organic layer was washed thoroughly with water, dried using anhydrous sodium sulphate, and the solvent removed by distillation to yield the crude halide intermediate. The pure intermediate was then re-crystallised from the mixture of dichloromethane and hexane as a pale yellow solid.

To the mixture of the halide intermediate (1.0 g, 1.42 mmol) in THF–ethanol ($\varphi_r = 2 : 1$) (24 mL) in a 50 mL round bottom flask, trimethyl amine (12 mL, 129.12 mmol) was added and the mixture stirred at room temperature for 4 days. The completion of the reaction was monitored by thin layer chromatography (TLC). The organic solvent was removed under reduced pressure to yield the crude cationic amphiphile. The pure cationic amphiphile was then re-crystallised from the mixture of methanol and diethyl ether as a white solid.

The other cationic amphiphiles required in the investigations, namely, (1R,2R)-IV and (\pm) -IV were prepared following the same procedure and were characterised by NMR, IR, and elemental analysis. The other neutral gelators (1S,2S)-V, (1R,2R)-V and cationic amphiphiles (1S,2S)-IV and (1R,2R)-IV based on 1,2-cyclohexanediamine, required in the present study, were prepared following the reported procedure (Jung et al., 2000a, 2000b).

The sol-gel polycondensation of tetraethoxy silane, (TEOS), in the presence of benzyl amine and water under the influence of the organogel template, was adopted for the synthesis of helical silica nanotubes as depicted in the figure below (Fig. 2). A mixture of 1 : 1 neutral and cationic amphiphile (2 mg each) was added to ethanol (100 μ L) in a 2 mL vial and heated until dissolved and allowed to form an organogel at room temperature. To the organogel, TEOS (16 μ L), benzyl amine (10 μ L), and water (10 μ L) were added and heated until a transparent solution was obtained and then allowed to rest for seven days. Then, the mixture was heated under argon atmosphere initially up



Fig. 3. SEM images of the organogels obtained in ethanol from (1S,2S)-III (A), (1S,2S)-IV (B), and mixture (1 : 1) of (1S,2S)-III and (1S,2S)-IV (C).

to 200 °C within 3 h at a heating rate of $1 ^{\circ}$ C min⁻¹, maintained at 200 °C for 2 h, then further increased to 500 °C at a heating rate of $1.7 ^{\circ}$ C min⁻¹ within 3 h and maintained at 500 °C for 3 h. Finally, the reaction mixture was cooled to 25 °C and then reheated under aerobic conditions initially up to 200 °C, maintained at that temperature for 2 h and then increased to 500 °C and maintained at 500 °C for 3 h to yield the silica nanotubes. The formation processes of the silica nanotubes were elucidated by monitoring the shape and size of the structures with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM and TEM images were recorded before calcinations and after calcinations; the images were found to be similar.

Results and discussion

The gel formations of the neutral gelators and cationic amphiphiles (Fig. 3) were investigated using various organic solvents. The morphology of different gels was also investigated using crossover experiments and by recording the SEM and TEM images. The neutral or cationic gelators (2 mg each) or 1 : 1 mixture of neutral gelators and cationic amphiphiles (2 mg each) were added to 100 μ L of each of ethanol, acetonitrile, and butan-1-ol solvents; however, they were all only soluble upon heating. It was observed that when the neutral gelator solution was left at room temperature for 10 min the gelation was completed. However, the cationic amphiphiles failed to form the organogel, whereas the 1:1 mass mixture of neutral gelators and cationic amphiphiles formed the organogel. In order to understand the morphology of the gels, SEM images of the gels were recorded, i.e. a piece of organogel was placed on a carbon-coated copper grid and removed after 1 min, leaving some small patches of the



Fig. 4. SEM image of a helical silica product before calcination.

gel on the grid. Then they were dried under vacuum and analysed by SEM. For example, the SEM images



Fig. 5. SEM (A) and TEM (B) images of the right-handed helical silica nanotubes obtained from the 1:1 mass mixture of (1S,2S)-III and (1S,2S)-IV (after calcination).



Fig. 6. SEM (A) and TEM (B) images of the left-handed helical silica nanotubes obtained from the 1:1 mass mixture of (1S,2S)-III and (1S,2S)-IV (after calcination).



Fig. 7. SEM (A) and TEM (B) images of the non-helical silica tubes obtained from the 1:1 mass mixture of (\pm) -*III* and (\pm) -*IV* (after calcination).



Fig. 8. SEM images of right-handed helical silica nanotubes obtained from the 1 : 1 mixture of (1S,2S)-III and (1S,2S)-IV (A), (1R,2R)-IV (B), or (\pm) -IV (C) (after calcination).

of the organogels formed from (1S,2S)-*III*, (1S,2S)-*IV* and the 1 : 1 mass mixture of (1S,2S)-*III* and (1S,2S)-*IV* in ethanol were investigated. The neutral gelator, (1S,2S)-*III*, produced slightly helical-type organogel, but the cationic amphiphile, (1S,2S)-*IV*, formed a viscous fluid, with no regular morphology. By contrast, the 1 : 1 mass mixture of (1S,2S)-III and (1S,2S)-IV produced right-handed helical organogel with a diameter of few nanometers, (Fig. 3).

The chiral silica nanotubes were obtained by



Fig. 9. SEM images of left-handed helical silica nanotubes obtained from the 1 : 1 mixture of (1R,2R)-III and (1R,2R)-IV (A), (1S,2S)-IV (B), or (\pm) -IV (C) (after calcination).

the sol-gel polycondensation of tetraethoxy silane, (TEOS), in the presence of benzyl amine and water under the influence of organogel templates, by heating the whole mixture and then cooling it to room temperature for seven days. The SEM images of the resulting silica materials were recorded to explore the chirality and thickness of the helical silica materials (Fig. 4). The helical silica materials obtained were calcinated to prepare helical silica nanotubes. The SEM and TEM images of the silica nanotubes obtained after the calcinations (Figs. 5–7) were examined for their chiral structure. Interestingly, it was observed that when a 1 : 1 mixture of neutral gelator (1S, 2S)-III and cationic amphiphile (1S, 2S)-IV was used, right-handed helical silica nanotubes were obtained (see Fig. 5). Similarly, a 1 : 1 mixture of (1R,2R)-III and (1R,2R)-IV resulted in left-handed helical silica nanotubes (Fig. 6); however, a 1 : 1 mixture of (\pm) -III and (\pm) -IV resulted in non-helical silica tubes (Fig. 7) and the calibre of the tube was generally larger (from 600 nm to $2 \mu m$) than

the helical silica nanotubes (50–70 nm).

In order to understand and establish the optimum conditions for the synthesis of chiral nanotubes, a crossover experiment to explain the role of neutral organic gelators and cation amphiphiles was performed.

At the start of the crossover experiment, the neutral gelator (1S,2S)-III was constant the cationic amphiphiles varied from (1S,2S)-IV, (1R,2R)-IV, and (\pm) -IV and the silica nanotubes were obtained from 1 : 1 mixture of neutral gelator and cationic amphiphile. The handedness of the helical silica nanotubes obtained is presented in the figures; when (1S,2S)-III was used as a neutral gelator, in every case the morphology of the silica nanotubes was a right-handed helical structure (Fig. 8). Similarly, when the neutral gelator (1R,2R)-III was constant and the cationic amphiphiles varied, the resulting silica nanotubes were of a lefthanded helical structure, (Fig. 9). However, when the racemic neutral gelator (\pm) -III was used instead, the resulting silica tubes were non-helical (Fig. 10). From



Fig. 10. SEM images of non-helical silica nanotubes obtained from the 1 : 1 mixture of (\pm) -III and (1S,2S)-IV (A), (1R,2R)-IV (B), or (\pm) -IV (C) (after calcination).

these observations it may be assumed that it was not the cationic amphiphile but the absolute configuration of the neutral gelator that played a major role in determining the chirality of the silica nanotube. Similar observations, identical to the earlier report, were made in the crossover experiments performed using a 1:1 mixture of neutral V and cationic VI gelators derived from 1,2-cyclohexanediamine (Fig. 11) i.e. the right-handed helical silica nanotubes were obtained using organogel formed from the mixture of (1S, 2S)-V and (1S,2S)-VI whereas the left-handed helical silica nanotubes were formed from the 1 : 1 mixture of (1R,2R)-V and (1R,2R)-VI. However, a comparison of the SEM images of silica nanotubes obtained using gelators derived from 1,2-cyclohexanediamine and 1,2diphenylethylenediamine revealed that a higher purity and yield of helical silica nanotubes were only obtained in the case of gelators derived from 1,2diphenylethylenediamine, due to the inter-molecular interactions between the two phenyl groups which resulted in the effective hydrophobic interaction essential to the self-assembly gelation process. It was also established that the 1 : 1 mixture of neutral gelator and cationic amphiphile played an essential role in the handedness of helical silica nanotubes. We may conclude from these results that the handedness of helical silica nanotubes is controlled solely by the stereochemistry of the neutral gelator and is independent of the stereochemistry of the cationic amphiphile.

Conclusion

Silica nanotubes were prepared through the solgel polycondensation of TEOS, using organogels as templates. When 1 : 1 mass mixtures of optically active or racemic neutral gelator and cationic amphiphile prepared from 1,2-diphenylethylenediamine or 1,2-diaminocyclohexane were used as templates, the resulting silica nanotubes were found to show singlehanded helicity or non-helicity according to the stereochemistry of the neutral gelators used, irrespective of the stereochemistry of the cationic amphiphiles. From



Fig. 11. SEM images of the right- and left-handed helical silica nanotubes obtained from the 1:1 mixture of (1S,2S)-V and (1S,2S)-VI (A) or (1R,2R)-VI (B) and from the 1:1 mixture of (1R,2R)-V and (1S,2S)-VI (C) or (1R,2R)-VI (D) (after calcination).

these results, it may be concluded that the neutral gelators play an important role in determining the handedness of helical silica nanotubes according to their stereochemistry.

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