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Double helical silica fibrils by sol–gel transcription of chiral aggregates of gemini surfactants†

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Silica fibrils with a novel double stranded helical structure are prepared by sol–gel transcription of twisted bilayer ribbons formed by cationic gemini surfactants.

Both in natural and artificial systems, the self-assembly of *organic* building blocks give rise to supramolecular structures of various sizes, shapes, chemical composition and function. In order to develop novel *inorganic* materials closely corresponding to these organic assemblies, one approach is to transcribe them to produce inorganic replicas, thus mimicking biomineralization processes. Amphiphilic molecules for example, exhibit one of the richest polymorphism of structures and mesophases.[1] Among these, vesicles,[2] ultra-thin membranes,[3] and others,[4] have been utilized as templates to create mesoporous inorganic materials.[5] In order to 'design' the sizes and shapes of such materials (as organic compounds and assemblies can be 'designed'), it is essential to explore and elucidate the mechanisms of transcription of various organic precursors.

Recently, increasing attention has been paid to low molecular-weight compounds that can efficiently gelate various organic solvents upon forming networks of fibrillar aggregates.[6] In studies devoted to cholesterol-based gelators, we found that even liquid silanol derivatives can be gelated.[7] It thus occurred to us that if the sol–gel polycondensation of silanol proceeds in the organogel phase, the fibrillar aggregate should act as a template that, after calcination, would leave a void in the resulting silica. After trial-and-error, we found that the fibers of certain 'cationic' cholesterol derivatives gelate a tetraethoxysilane (TEOS) solution and are efficiently transcribed to give a novel mesoporous silica with a tubular, macaroni-like structure.[8] Condensation of anionic silica occurs preferentially at the surface of the cationic aggregate. Under some limited conditions, a unique, right-handed 'helical' silica was obtained.[8]

Meanwhile, the French group of this paper reported that 'cationic' gemini surfactants having chiral tartrate counter ions assemble into twisted ribbons both in chlorinated and aromatic organic solvents, and in water.[9] The handedness of the ribbons and their helical pitch can be tuned continuously upon varying the ratio between L and D tartrate (*e.g.* the pitch increases for decreasing % ee).[10] This kind of 'fine tuning' is nearly impossible in other gelators. Here, we report on the sol–gel transcritpion of this system and the observation of novel double helical silica fibers with a tunable pitch.

We first seeked for a transcription medium capable of dissolving TEOS, containing water, and compatible with the formation of the twisted ribbons of L-**1** and D-**1**. A mixture of water and pyridine (1:1 v/v) satisfies these requirements. Indeed L-**1**, D-**1** and L-**1**/D-**1** mixtures assemble in this mixture as they do in pure water or pyridine.[9] A typical TEM image of the xerogel prepared from gels containing L-**1** and D-**1** is shown in Fig. 1. Additionaly, the twist pitch (*T*) and the width (*W*) of these ribbons were shown to vary with the ee in water/pyridine, a feature previously observed in pure water[10] but not in organic solvents. The dimensionless parameter *T*/*W* characterises the aspect ratio of the twisted structures.[10] In water/pyridine (1:1 v/v) *T*/*W* = 7.1 for 100% ee, 12.0 for 50% ee (Fig. 1) and 18.7 for 33% ee. These values are comparable to those reported in water.

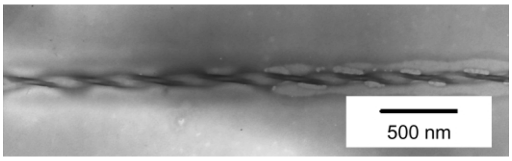

Fig. 1 TEM image of a right handed twisted ribbon in a xerogel prepared from a L-**1**/D-**1** mixture (3:1 mol/mol, 50% ee) in water/pyridine (1:1 v/v).

Sol–gel polycondensation of silica was carried out as follows: L-**1** and D-**1** (total 2.0 mg, 2.6×10^{-6} mol) were added to water (100 μl)/pyridine (100 μl)/TEOS (10 μl)/benzylamine (5 μl) and the mixture was warmed until a transparent solution was obtained. The reaction mixture was placed at room temperature under static condition for 3 days. The product was dried under vacuum at room temperature. Finally, the gelator was removed by calcination at 100 °C for 1 h, 200 °C for 1 h, 500 °C for 2 h under a nitrogen atmosphere, and 500 °C for 4 h under aerobic conditions.

A typical TEM image of a fiber *before* calcination (*e.g.* composed of both silica and the dimeric amphiphiles) obtained by sol–gel transcription is shown in Fig. 2. One can recognize two intertwined fibrils. The handedness could not clearly be determined. The helical pitch (300–500 nm) is a little shorter than that of the corresponding purely organic ribbon (about 400–800 nm). These observations suggest that the condensation of silica does not alter very significantly the concomitant aggregation of amphiphiles.

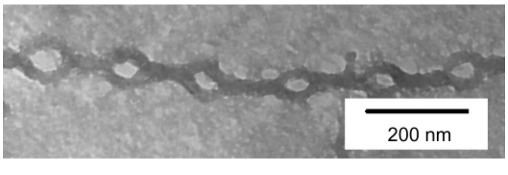

Fig. 2 TEM image of the fibers obtained by sol–gel transcription of a L-**1**/D-**1** mixture (3:1 mol/mol, 50% ee) before calcination.

Fig. 3 shows a SEM image of the silica *after* calcination obtained from a gel of pure L-**1** (100% ee). One can observe a network of rope-like right-handed helical fibrils. This is the expected handedness from the L enantiomer of **1**. Judging from the inclination of the ropes with respect to the axis of the fibers, one may presume that they consist of a double stranded structure.‡ When the ee is decreased from 100 to 20%, double helices with increasing pitch are observed (Fig. 4). The aspect ratio of these inorganic fibers was found to be *T*/*W* = 1.6 for 100% ee, 4.3 for 50% ee, 5.1 for 33% ee and 9.8 for 20% ee These values are somewhat smaller than those of the precursor

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† Electronic supplementary information (ESI) available: Fig. S1: TEM image of double stranded silica obtained by sol–gel transcription of L-**1**/D-**1** gel (2:1 mol/mol, 33% ee L-**1** excess). See http://www.rsc.org/suppdata/cc/b2/b202799m/

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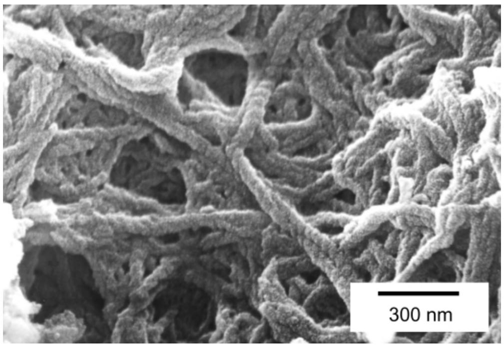

Fig. 3 SEM image of the silica obtained by sol–gel transcription of a L-**1** gel (2.0 wt%, after calcination).

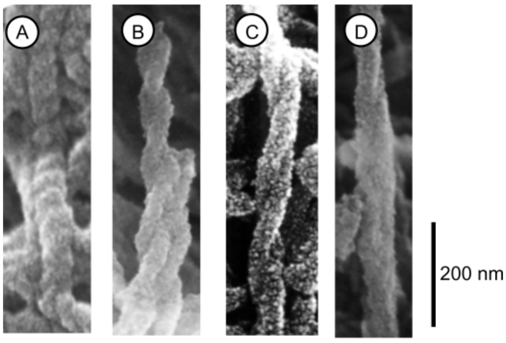

Fig. 4 Influence of the ee (L-**1** in excess) on the helical pitch of double stranded silica: A, 100% ee; B, 50% ee; C, 33% ee; D, 20% ee.

twisted ribbons, but one may rationalize this discrepancy from a possible shrinkage of silica fibrils during the calcination process. The double stranded helical structure appears particularly clearly for silica fibrils obtained at 50% ee and 33% ee (Fig. 4B and C).

Thus, the helical shape, the handedness and even the tunable chirality of the organic twisted ribbons are efficiently transcribed to the inorganic replicas. But the question remains of how these surprising inorganic double helices arise from flat twisted structures. When a prolonged sol–gel polycondensation is performed (7 days; the regular condition is a period of 3 days), inorganic twisted tapes form which are very similar to the original organic ribbons (Fig. 5). This suggests that the organic structures do act as templates, and that the double helical silica fibrils form during early stages of the polycondensation. One important observation is that the silica fibers are not hollow: the electron density across the fibers does not decrease in their center (Fig. S1, ESI†). This implies that they form at the surface of the organic template but do not completely surround it. Two possible rationales come to our mind to explain double helix formation. TEOS polycondensation may proceed preferentially along the gutter-shaped faces of the twisted ribbons where the density of positive charge is larger. Alternatively, it may proceed preferentially along the edges of the ribbons, where the density of positive charge is smaller but which are more exposed to the solvent. Since the ribbons have two edges and two faces, two intertwined silica fibrils would be expected in both rationales. However the distance between the fibrils would be expected to be of the order of a ribbon thickness when condensation occurs on the faces, and of the order of a ribbon width when condensation occurs on the edges. If the fibrils observed before calcination (Fig. 2) are indeed the final silica fibrils, the distance between them (50 nm) corresponds to the width of a twisted ribbon, suggesting condensation along the edges. On the other hand, the fibrils in the double helices observed after calcination are not separated by any gap. If condensation occurs preferentially at the edges, considerable shrinkage of the structure during calcination must be invoked to bring the fibrils in close contact. Further studies on the mechanism are currently continued in these laboratories. In particular, concentration, stoichiometry and reaction times are expected to significantly affect the transcription process.

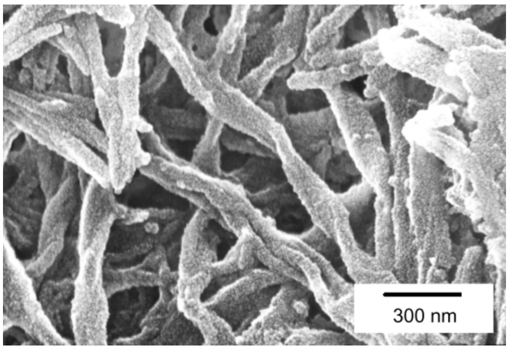

Fig. 5 SEM image of the silica obtained after a prolonged sol–gel polycondensation time from a L-**1**/D-**1** gel (2 : 1 mol/mol, 33% ee L-**1** excess).

As a final remark, chiral silica phases generally refer to organic moieties bearing asymmetric centers tethered to achiral silica particles. In contrast, chirality in the helical fibers described here belongs to the silica itself. It will be worth exploring how this chiral silica performs in applications such as chiral separation or enantioselective catalysis.

Notes and references

‡ Fig. 4 shows a perspective view; the inclination of the ropes with respect to the axis of the fibers is measured on those fibers which lay flat in the plane of the micrograph.

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