The increase of JA production in the Lima bean plants prompted us to test ALA in tendril-coiling experiments. Tendrils of *Bryonia dioica* respond to JA, MeJA, and 12-OPDA with a coiling reaction comparable to the free coiling reaction of mechanically stimulated tendrils.[19] Tendrils of *Bryonia dioica*, *Pisum sativum*, and *Lathyrus* sp. were treated with solutions of ALA (5 μM) through the transpiration stream and, after 20 h, the degree of coiling was measured. Alternatively, tendrils were subjected to the coiling assay described in the literature.[20] All tested plant species exhibited a rapid coiling response towards ALA. Surprisingly, inhibition of the octadecanoid cascade with phenidone did not hamper the coiling reaction, which indicates that signaling systems independent of the lipid-based pathway, such as ion fluxes, have to be considered as elements of mechanotransduction.[20]

Besides ALA, many other peptaibols and peptides endowed with pore-forming or ion-transporting properties are known. To establish whether pore formation within a membrane or ion transport through a membrane is the underlying principle for the induction of volatile compound biosynthesis, other pore-forming peptaibols and some typical ion transporters were tested. The results are compiled in Table 1. The entire group of peptaibols induced the same pattern of volatile compounds in Lima bean leaves, suggesting a common mode of action. Although the basic peptide melittin is known as a pore-forming compound,[21] it failed to induce volatile biosynthesis in Lima bean leaves. A typical ion transporter, K$^+$ selective valinomycin[22] (9 μM), was also found to be inactive. Other biologically active small peptides which act through specific receptors, such as the undecapeptide "substance P",[23] the nonapeptide bradykinin,[22] and systemin, a signal peptide of tomato plants,[24] did not induce volatile compound biosynthesis, supporting the pore-forming capability of peptaibols as the essential property for the elicitation process.

Channel-forming peptides, such as alamethicin, may be used as valuable tools to unravel the early events of plant defense under well defined conditions. First analyses of insect salivary secretions have already demonstrated the presence of pore-forming compounds,[26] suggesting that membrane depolarisation also has to be considered as an important element of insect-induced plant defense.

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Sol–Gel Polycondensation of Tetraethoxysilane in a Cholesterol-Based Organogel System Results in Chiral Spiral Silica

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Exploitation of new organic gelators that can gelate various organic solvents has become an active area of research.[1–11] These organogels are of particular interest because they are different from polymer gels. Fibrous aggregates of low molecular weight compounds formed by noncovalent interactions are responsible for such gelation phenomena. Hence, the xerogels exhibit various superstructures, reflecting the monomeric structure of each gelator. This is why the study of organogels is considered to be a new field of supramolecular chemistry.[11]

Recently, it was found that certain cholesterol derivatives can gelate even tetraethoxysilane (TEOS), which results in

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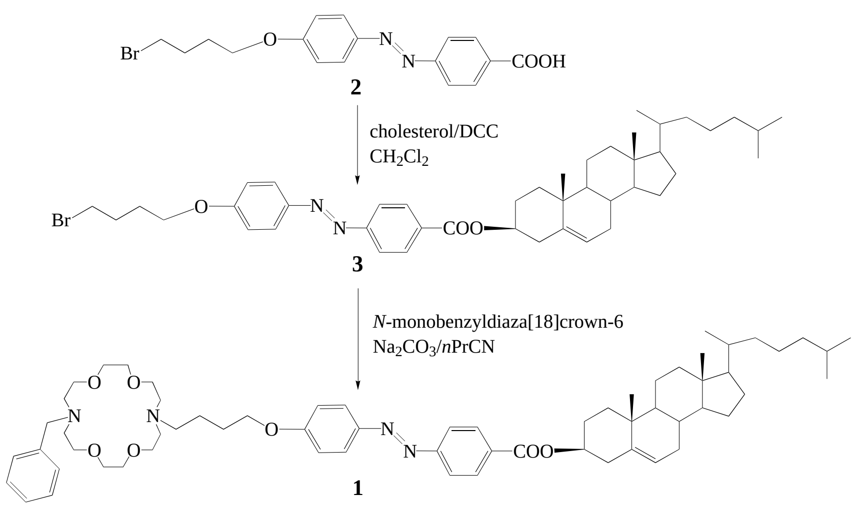
silica by sol–gel polycondensation.[12, 13] Sol–gel polycondensation of gelated TEOS solutions affords novel silica with a hollow fiber structure, because the organogel fibers act as a template to create an inner tube in the TEOS polycondensation process.[12, 13] One may therefore consider that the unique superstructures of organogel fibers can be transcribed in the silica structure: Superstructures of organic aggregates temporarily formed by noncovalent interactions can be permanently fixed in inorganic silica. It was later proven that the presence of the positive charge in the organogel fibers is indispensable for transcribing the organogel superstructure into the silica structure.[13] This prerequisite is rationalized in terms of an electrostatic interaction between oligomeric "anionic" silica and "cationic" organogel fibers during the sol–gel polycondensation process.

Organogel fibers formed from cholesterol-based gelators frequently result in a helical structure.[3, 7] This fact tempted us to transcribe the helical organogel fiber structure into the inorganic silica. We have noticed, however, that the presence of a cationic group tends to reduce the gelation ability and that these systems rarely result in the formation of a helical structure.[12] An idea to overcome this dilemma came to mind: The positive charge can be readily incorporated by a metal–crown interaction. We therefore designed compound **1** (see Scheme 1), which has a cholesterol skeleton as a chiral aggregate-forming site and an azacrown moiety as a metal binding site.[14] We found that **1** not only gelates various organic solvents, but in the presence of metal cations also acts as a template for sol–gel polycondensation of TEOS to produce the novel "chiral spiral silica". To the best of our knowledge, this is a very rare example of "chirality" being induced in the inorganic silica by the organogel template method.[15]

Compound **1** (m.p. 113.3–115.2 °C) was synthesized according to Scheme 1 and identified by IR and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The gelation ability was estimated for 17 different organic solvents containing **1** (5.00×10^{-2} mol L^{-1}).[16] As summarized in Table 1, **1** can gelate 8 out of the 17 solvents, and therefore acts as a versatile gelator of organic solvents. The gelation ability for alcohols in general is excellent.



Scheme 1. Synthesis of **1**. DCC = dicyclohexyl carbodiimide.

Table 1. The gelation ability[a] of **1** in organic solvents.

Solvent	Result[b]	Solvent	Result[b]
methanol	I	acetone	I
ethanol	I	acetonitrile	I
1-propanol	G	cyclohexane	PG
1-butanol	G	methylcyclohexane	PG/R
tert-butyl alcohol	G	acetic anhydride	G
isobutanol	G	acetic acid	S
1-octanol	G	dichloromethane	S
dimethyl sulfoxide	G		
1,2-diaminoethane	PG		
1,3-diaminopropane	G		

[a] The concentration of the gelator was 5.0 wt %. [b] G = stable gel formed at room temperature; I = insoluble; PG = partially gelatinized; R = recrystallization; S = solution.

To characterize the chirality of the organogel, the circular dichroism (CD) spectrum of the organogel formed by **1** in the presence and absence of $AgNO_3$ or $CsClO_4$ was measured (Figure 1). Since the λ values for $\theta = 0$ (θ = ellipticity) in the CD spectra (365 and 358 nm in the presence of $CsClO_4$ (3.15×10^{-3} mol L^{-1}) and $AgNO_3$ (3.15×10^{-3} mol L^{-1}), respectively) are very close to the λ_{max} of the absorption spectrum (360 nm), one can regard these bands as positive exciton-coupling bands: Compound **1** forms aggregates and the dipoles in the chromophoric azobenzene moieties are orientated in a clockwise direction (i.e., with an *R* configuration). Although the gel formed in the absence of a metal salt was CD-active, the spectrum did not show a clear exciton-coupling band.

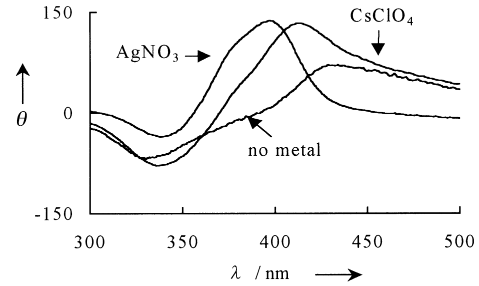


Figure 1. CD spectra of **1** (5.00×10^{-2} mol L^{-1}) in 1-butanol in the absence and presence of $CsClO_4$ (5.00×10^{-2} mol L^{-1}) or $AgNO_3$ (5.00×10^{-2} mol L^{-1}; concentration in the gel phase). The concentration of **1** required to gelate the 1-butanol solution was so high that the CD spectra could not be measured with conventional optical cells. They were obtained by sandwiching the gel between two glass plates to make a thin layer. Hence, the ellipticity θ is given in arbitrary units.

The scanning electron microscopy (SEM) pictures of the xerogels obtained by a freeze-and-pump method from gel-phase solutions of **1** in *tert*-butyl alcohol below the sol–gel phase-transition temperature ([**1**] = 5.00×10^{-2} mol L^{-1}) are shown in Figure 2.[17] In the absence of a metal salt, the major structures are film-like lamella, some of which show a pseudocylindrical structure (Figure 2 A).

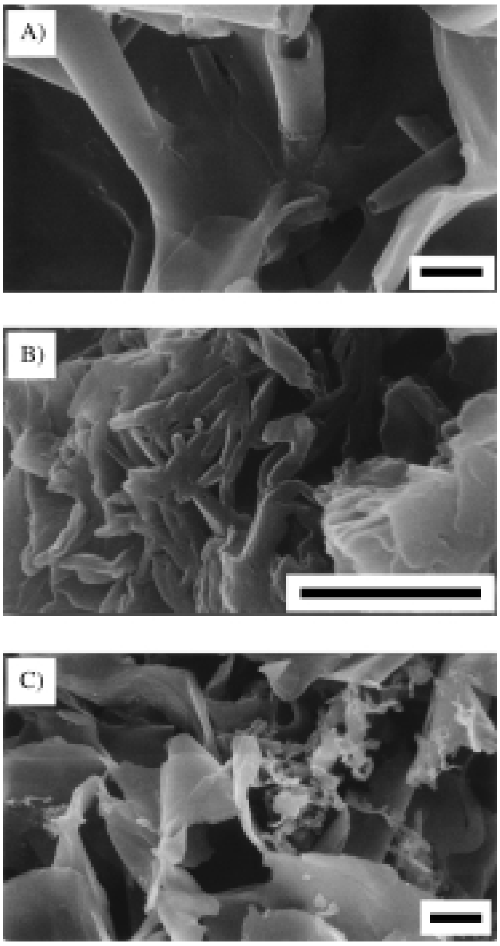


Figure 2. SEM pictures of the xerogels obtained from the gel-phase solution of **1** (5.00×10^{-2} mol L^{-1}) in *tert*-butyl alcohol A) in the absence of and B) in the presence of $AgNO_3$ (5.00×10^{-2} mol L^{-1}) or C) $CsClO_4$ (5.00×10^{-2} mol L^{-1}). The gel was first cooled in liquid nitrogen and then the solvent was removed under vacuum at 15 °C. In each case the bar corresponds to 1.5 µm.

In the presence of $AgNO_3$ or $CsClO_4$, on the other hand, both the fibrous structure and the lamellar structure can be recognized (Figure 2B and C, respectively). These results, together with the CD spectra, suggest that the exciton-coupling band originates from the chirality present in the fibrous structure.

Sol–gel polycondensation of TEOS was carried out in the gel phase of **1** in the absence and the presence of $AgNO_3$ or $CsClO_4$. A typical mixture consists of 1-butanol (98 mg), TEOS (16 mg), water (5.7 mg), and benzylamine (5.6 mg) as a catalyst. This mixture was left at room temperature for one day. The SEM pictures taken at this stage are shown in Figure 3. The silica obtained in the absence of metal salt showed the nonimpressive granular structure, which is also obtained from conventional TEOS polycondensation in solution (not shown). This result indicates that 1) the presence of the positive charge is indispensable for transcribing the organogel structure into the silica structure[12, 14] and 2) as shown by the CD spectrum in Figure 1, the aggregates formed in the absence of a metal salts are not so highly orientated that they affect the silica structure.

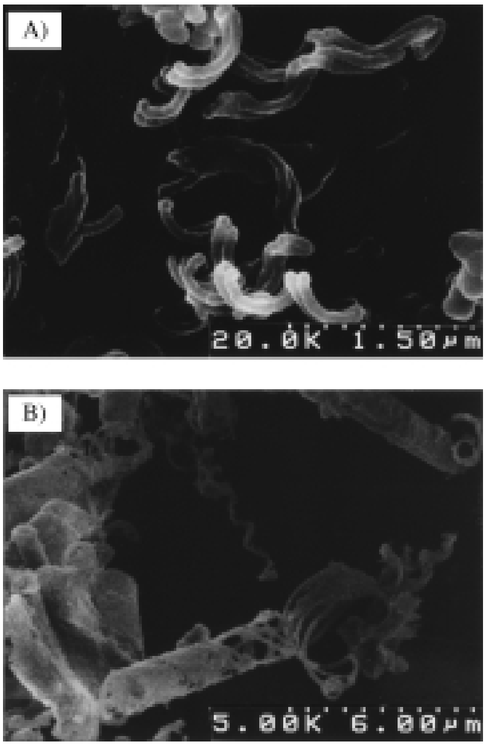


Figure 3. SEM pictures of the spiral silica obtained from **1** (5.00×10^{-2} mol L^{-1}) in the presence of A) $AgNO_3$ (5.00×10^{-2} mol L^{-1}) and B) $CsClO_4$ (5.00×10^{-2} mol L^{-1}) before calcination. A similar structure was also observed after calcination, indicating that the organogel fibers are surrounded by the silica.

In contrast, the silica obtained in the presence of $AgNO_3$ shows a novel spiral structure (Figure 3A). As far as can be recognized, all the spirals possess a right-handed helical motif. Since the exciton-coupling band of the organogel also shows *R* helicity in the presence of $AgNO_3$, we consider that microscopic helicity to be reflected by a macroscopic spiral helicity. Figure 3B shows the SEM picture of the silica obtained in the presence of $CsClO_4$—again the well-grown spiral structure is seen, which features a right-handed helical motif. In this picture, one can also recognize a filmlike structure, which is presumably constructed by transcription of the lamellar structure of the organogel (which is also seen in Figure 2C). The silica obtained in the presence of $NaClO_4$ or $KClO_4$ showed a hollow fiber structure as observed previously,[12, 14] but the spiral structure was not recognized (not shown).

To further corroborate that the organogel fibers really acted as a template for the growth of spiral silica, transmission electron microscopy (TEM) pictures were taken after removal of **1** by calcination.[12, 14] We found that the spirals have a tubular structure with an inner diameter of 25–50 nm (Figure 4). These results support the view that anionic oligomeric siloxanes are adsorbed onto metal-containing cationic organogel fibers, and the silica spirals thus grown reflect the chiral factor present in the organogel fibers.

In conclusion, sol–gel polycondensation of TEOS in the gel phase supported by an azacrown-appended cholesterol gelator results in a unique spiral silica with a right-handed helical motif. This is a very rare example of chirality being created in

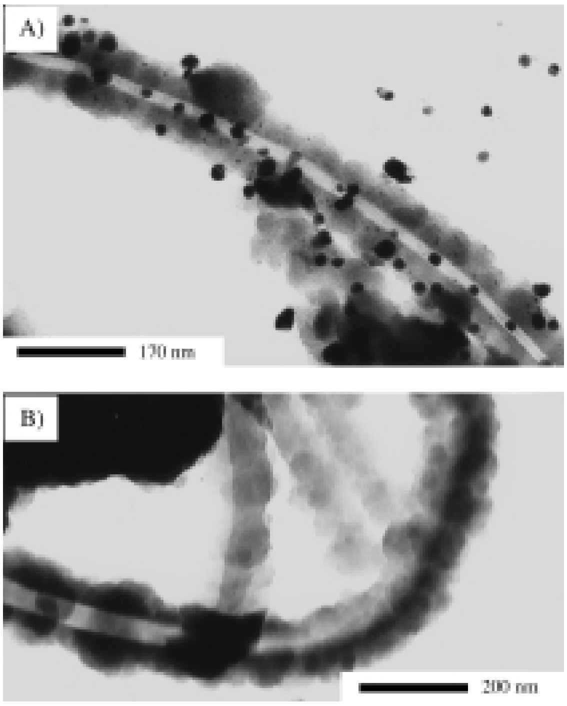


Figure 4. TEM pictures of the spiral silica obtained from **1** in the presence of A) $AgNO_3$ (the dots are silver particles) and B) $CsClO_4$ after calcination. The final calcination was carried out at 500 °C for 4 h under aerobic conditions. The silica obtained from the experiment in the presence of $CsClO_4$ was confirmed with a electron probe microanalyzer (Si: 45.45, O: 44.34, Cs: 9.32 wt %).

the inorganic material. The results indicate the versatility of the template method for the creation of various silica structures.[15]

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