# Nematic silsesquioxanes—towards nanocrystals dispersed in a nematic liquid crystal matrix

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**The reaction of suitable organic groups in combination with well defined inorganic silsequioxane cores leads to covalently bound organic–inorganic hybrid materials, which exhibit nematic and smectic C phase behaiour close to room temperature.**

Much attention has been paid to the investigation of nanoscopic organic–inorganic hybrids which are amorphous, crystalline or which exhibit bicontinuos, columnar or lamellar morphologies.[1–4] This makes the investigation of systems where a covalently attached inorganic core is dispersed homogeneously in a nematic matrix a fascinating proposition.

Our approach is based on molecular designed LC materials where it has been established that the linkage of polyphilic groups to nematogenic molecules leads to layered structures.[5,6] This requires a systematic approach to arrive at the targeted nematic materials based on crystalline silsesquioxane cores **A**, shown in Fig. 1 as a model system for a monodisperse inorganic crystal of defined stereochemistry. The linkage of the liquid-crystalline rod-shaped mesogenic moieties to the inorganic cores is effected by spacers consisting of organic methylene groups bonded *via* 1,1,3,3-tetramethyldisiloxane groups to the core. Eight mesogenic groups are appended from the cuboid core leading to a molecular structure, where in the LC phase the nematic director field is responsible for the deformation of the spatially isotropic molecules to assemble into the nematic phase structure.

In order to assure the formation of liquid-crystalline phases above ambient temperature aromatic core structures of the mesogenic units were selected containing three and four aromatic rings, linked by C–C single bonds or ester groups shown in Scheme 1. In order to assure a suitable stability range of the liquid-crystalline phase terminal alkyl chains of eight or eleven methylene groups were selected. The lateral attachment of the mesogens to the central core was chosen to favour side-on interactions of the mesogens following an established concept.[7] A spacer of five methylene groups and a siloxane unit was used to obtain a suitable degree of decoupling of the rigid aromatic mesogens and the silsesquioxane crystalline core.

The synthesis of the functionalised monomer **5** is shown in Scheme 1. Alkylation of 2,4-dihydroxymethylbenzoate **1** with 1-bromooctane in the *p*-position of the aromatic ring and subsequently with 5-bromopent-1-ene in the *o*-position followed by removal of the protective methyl group leads to the intermediate **2**. Compound **4** containing four aromatic rings was obtained by esterification of **2** with **3**, the product of the esterification of octyloxybenzoic acid with one of the phenol groups of 4,4′-biphenol. The attachment of a 1,1,3,3-tetramethyldisiloxane group **B** to **4** in a hydrosilylation reaction using Karstedt's catalyst leads to the functionalised monomer **5**.

The structurally related mesogen **6** containing only three aromatic rings was synthesised as published earlier and hydrosilylated as described for **4** leading to the material **7**.[2]

In order to assess whether the phase behaviour is determined by microphase separation or by the size of the relatively bulky methyl groups of the siloxane units, **4** was reacted with 1,1,3,3,3-pentamethyldisiloxane **C** leading to material **8**, an anologue to compound **5**. The reaction of **6** with **C** in a similar manner yields compound **9**, structurally similar to material **6**.

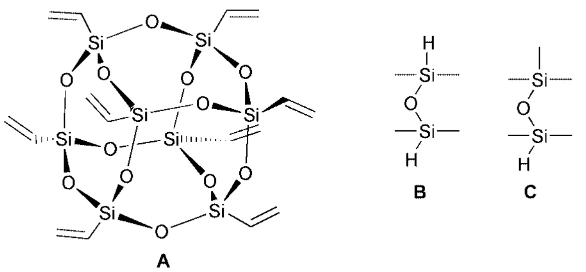
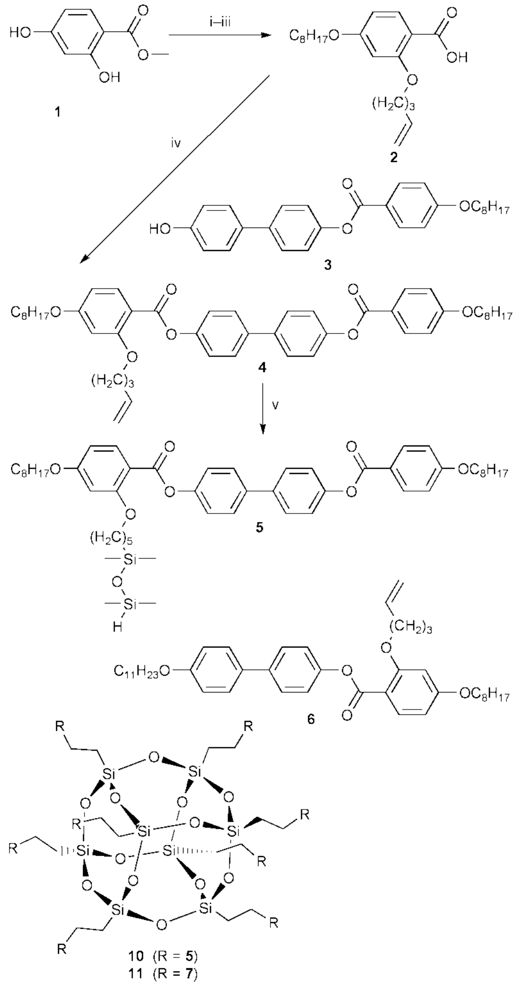


**Fig. 1** Structures of the siloxane and silsequioxane cores.



**Scheme 1** *Reagents and conditions*: i, $K_2CO_3$, KI, butanone, 1-bromooctane; ii, $K_2CO_3$, KI, butanone, 5-bromopent-1-ene; iii, NaOH–MeOH, HCl–$H_2O$; iv, DCC–DMAP, **3**; v, 1,1,3,3-tetramethyldisiloxane, Karstedt's catalyst.

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**Table 1** Transition temperatures as determined by DSC

| Compound | Structure | Phase transitions/°C |
|---|---|---|
| **4** | **4** | cr 99.4 N 173.2 Iso |
| **5** | **4-B** | cr 67.1 [SmC 51.3] N 123.8 Iso |
| **6** | **6** | cr 53.8 N 72.7 Iso |
| **7** | **6-B** | cr 18.0 N 39.1 Iso |
| **8** | **4-C** | cr 76.6 [SmC 58.2] N 122.0 Iso |
| **9** | **6-C** | cr 24.8 N 39.5 Iso |
| **10** | [**4-B**]$_8$-**A** | cr 59.5 [SmX 33.1] SmC 111.3 N 145.8 Iso |
| **11** | [**6-B**]$_8$-**A** | $T_g$ −19.3 SmX 37.6 N 50.5 Iso |

The organic–inorganic hybrid materials containing a central silsesquioxane core were obtained by reacting octavinylsilsesquioxane **A** with **5** in a hydrosilylation reaction leading to material **10**. The bond formation could be monitored by the occurrence of the signals for the ethylene bridge in the $^1$H NMR spectrum and unambiguously in this context by the appearance of peaks at $\delta$ 4.1 and 9.8 in the $^{13}$C NMR spectra. The fusion of the inorganic core **C** in a similar manner with the functionalised mesogenic side-chain **7** containing three aromatic rings resulted in compound **11**. The materials were purified by column chromatography, indicating that the incorporation of siloxane groups in the spacer alters the solubility of these materials, when compared to related structures.[8,9] The eluent for material **11** was dichloromethane–hexane with the mixture gradient changed from 1:1 to 4:1 during the elution.

The transition temperatures of the liquid-crystalline materials **4**–**11** are listed in Table 1. All of these materials exhibit a nematic phase as the highest stable liquid-crystalline phase, characterised by a typical *schlieren* texture when observed using optical polarising microscopy.

For the four-ring system **4** the side-on attachment of the microphase seperating tetramethylsiloxane group leads to a marked decrease of the isotropisation temperature from 173.2 °C for **4** to 123.8 °C for compound **5**, a fall of 49.4 °C.

For the three-ring system **6** with an isotropisation temperature of 72.7 °C fusion to be tetramethylsiloxane group, leading to compound **7**, results in a decrease of the clearing temperature to 39.1 °C, a fall of 33.6 °C.

This modification of the mesogenic moieties by siloxane groups is additionally accompanied by a strong fall in the melting temperatures to 67.1 °C for **5** (99.4 °C for **4**) and to 18.0 °C for **7** (53.8 °C for **6**) when compared to the starting materials. An interesting feature is the occurrence of a low temperature smectic C phase characterised by broken focal conics and a *schlieren* texture for material **5**, a feature very unusual in rod shaped materials with a lateral side-chain.[10–12]

The structurally related materials containing a pentamethyldisiloxane endgroup, **8** and **9**, have similar isotropisation temperatures as observed for **5** and **7** containing tetramethyldisolaxane groups, indicating that the liquid-crystal phase behaviour is governed mainly by microphase separation of the organic and siloxane groups. The increase in the melting points for **8** (76.6 °C *cf.* 67.1 °C for **5**) and **9** (24.8 °C *cf.* 18 °C for **7**) can be attributed to the more bulky siloxane groups, leading to more stable crystalline phases.

The material **10** containing an inorganic core has an isotropisation temperature of 145.8 °C, a rise by 22 °C compared to the monomer **5**, indicating that the incorporation of a suitably functionalised inorganic core can promote the stability of the mesomorpic state. The increase of the stability range of the smectic C phase by 60 °C to 111.3 °C observable for material **10** is remarkable. This is accompanied by a fall of the crystallisation temperature to 59.5 °C of this structure. Additionally a monotropic highly ordered LC phase of undetermined structure was observed below 33.1 °C.

A special feature of the cuboid material **11**, where the inorganic core is decorated with eight mesogens containing three aromatic is the absence of a crystalline state, only a low glass transition temperature of −19.3 °C could be observed. The material clears from the nematic phase to the isotropic state at 50.5 °C and shows an underlying smectic phase (smectic X) at 37.6 °C, confirming thus the versatility of the selected systematic approach, geared towards low temperature organic–inorganic anisotropic fluids incorporating nanocrystalline cores.

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