

## Supporting Information

### Synthesis and Mesomorphic Properties of "Side-on" Hybrid Liquid Crystalline Silsesquioxanes

Kosuke KANEKO <sup>1,2\*</sup>, Atsuhiko MANDAI <sup>1</sup>, Benoît HEINRICH <sup>2</sup>,  
Bertrand DONNIO <sup>2</sup> and Tomonori HANASAKI <sup>1</sup>

*1) Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University,  
1-1-1, Nojihigashi, Kusatsu, Shiga 525-8577, JAPAN*

*2) Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS),  
UMR 7504 (CNRS-Université de Strasbourg)  
23, rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France*

E-mail: [kaneko@fc.ritsumei.ac.jp](mailto:kaneko@fc.ritsumei.ac.jp)

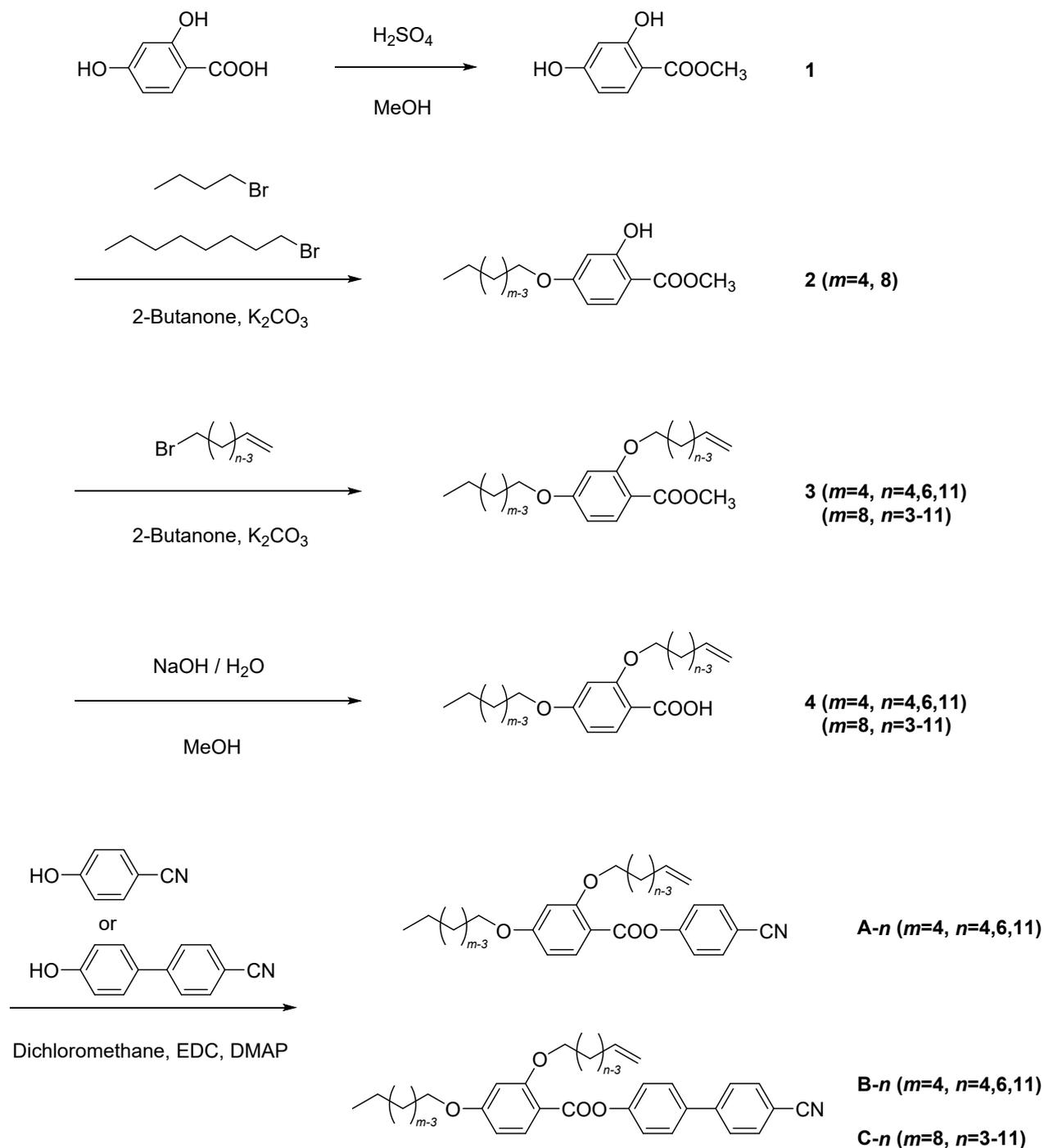
- 1. Materials and Experimental procedures**
- 2. Synthesis and Characterization**
- 3. GPC**
- 4. DSC and POM**
- 5. SWAXS**
- 6. References**

## 1. Materials and Experimental procedures

2,4-Dihydroxybenzoic acid, 1-bromobutane, 1-bromooctane, all bromoalkene ( $\text{Br}(\text{CH}_2)_{n-2}\text{CH}=\text{CH}_2$ ,  $n=3-11$ ), *N,N*-dimethyl-4-aminopyridine (DMAP) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) were purchased from Tokyo Kasei Kogyo Co., Ltd.. 4-Hydroxybenzotrile and 4'-hydroxy-4-biphenylcarbonitrile were purchased from Nacalai tesque Co., Ltd.. Octakis(dimethylsilyloxy)silsesquioxane was purchased from Sigma-Aldrich Co., Ltd.. Toluene used in this study was dried by sodium wire and then distilled, and other solvents were used without further purification. The synthetic route of the side-on mesogens (**A-*n***, **B-*n***, **C-*n***) and the liquid crystal (LC) silsesquioxanes prepared in this research are shown in Figures S1 and S2, respectively.

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ -NMR measurements were performed with a JEOL ALPHA-400 FT NMR (400MHz) spectrometer using  $\text{CDCl}_3$ ,  $(\text{CD}_3)_2\text{CO}$  and deuterated DMSO solvents. In the final reaction's step, FT-IR spectrometer (PERKIN ELMER) was used to check the completeness of the coupling reaction, by monitoring the disappearance of the Si-H signal at  $2160\text{ cm}^{-1}$ . Gel-permeation-chromatography (GPC) measurements were carried out using Tosoh HLC-8020 instrument with tetrahydrofuran as eluent to check the purity of the samples. Standard polystyrenes were used for calibration. Thermal properties were measured by differential scanning calorimetry (DSC) using a Diamond DSC (PERKIN ELMER) with heating and cooling rates of  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . The textures of the LC phases were observed with a Nikon ECLIPSE E600 polarizing optical microscope (POM) equipped with a METTLER TOLEDO FP-82 hot stage and a METTLER TOLEDO FP-90 central processor.

## 2. Synthesis and Characterization



Figures S1 The synthetic route of the side-on mesogens (A-n, B-n, C-n).

The side-on mesogens (**A-*n***, **B-*n***, **C-*n***) were synthesized using the reported methods<sup>1-3</sup>. As a representative, the synthetic detail for **A-4** is described here. 1-Bromooctane and 4'-hydroxy-4-biphenylcarbonitrile were used for **B-*n*** and **C-*n*** instead of 1-bromobutane and 4-hydroxybenzotrile, respectively.

#### Methyl 2,4-dihydroxybenzoate    **1**

A solution of 2,4-dihydroxybenzoic acid (25.0 g; 0.16 mol) in 300 mL of methanol containing a few drops of concentrated sulfuric acid was refluxed for 24 h, and most of the methanol was removed by distillation. The residue was extracted with ethyl acetate. The organic layer was washed with saturated NaHCO<sub>3</sub> solution and then water. After evaporating the solvent, the residue was purified by means of column chromatography on silica gel using ethyl acetate/hexane (1/1 by volume) as eluent. As a result, 24.3 g of methyl 2,4-dihydroxybenzoate was obtained as a white solid. Yield 90 %.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) :  $\delta$  (ppm) 10.98 (s, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 6.34-6.39 (m, 2H), 5.79 (s, 1H), 3.92 (s, 3H).

#### Methyl 4-butoxy-2-hydroxybenzoate    **2** ( $m=4$ )

A solution containing the obtained methyl 2,4-dihydroxybenzoate (15 g; 0.087 mol), 1-bromobutane (12 g; 0.087 mol), and potassium carbonate (12 g; 0.087 mol) in 200 mL of 2-butanone was refluxed for 24 h. After removing the solid, ethyl acetate was added to the solvent, and washed with water. After the evaporation of the organic solvent, the residue was purified by means of column chromatography on silica gel using dichloromethane as eluent. As a result, 16.2 g of methyl 4-butoxy-2-hydroxybenzoate was obtained as a transparent colorless liquid. Yield 83 %.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) :  $\delta$  (ppm) 10.96 (s, 1H), 7.72 (dd,  $J = 7.3, 2.0$  Hz, 1H), 6.37-6.43 (m, 2H), 3.98 (t,  $J = 6.6$  Hz, 2H), 3.91 (s, 3H), 1.73-1.80 (m, 2H), 1.48 (dt,  $J = 14.9, 7.5$  Hz, 2H), 0.97 (t,  $J = 7.3$  Hz, 3H).

Methyl 2-(but-3-enyloxy)-4-(butoxy)benzoate    **3** ( $m=4, n=4$ )

A solution containing the obtained methyl 4-butoxy-2-hydroxybenzoate (10 g; 0.045 mol), 4-bromo-1-butene (6.1 g; 0.045 mol), and potassium carbonate (6.2 g; 0.045 mol) in 150 mL of 2-butanone was refluxed for 24 h. After removing the solid, ethyl acetate was added to the solvent, and washed with water. After the evaporation of the organic solvent, the residue was purified by means of column chromatography on silica gel using dichloromethane/hexane (1/1 by volume) as eluent. As a result, 4.0 g of methyl 2-(but-3-enyloxy)-4-(butoxy)benzoate was obtained as a transparent colorless liquid. Yield 32%.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 7.82 (d,  $J = 8.6$  Hz, 1H), 6.46 (dd,  $J = 10.1, 3.5$  Hz, 2H), 5.90-6.01 (m, 1H), 5.15 (ddt,  $J = 18.4, 7.3, 3.4$  Hz, 2H), 4.05 (t,  $J = 6.8$  Hz, 2H), 3.98 (t,  $J = 6.6$  Hz, 2H), 3.84 (s, 3H), 2.60 (dt,  $J = 7.0, 5.7$  Hz, 2H), 1.73-1.80 (m, 2H), 1.49 (dt,  $J = 14.9, 7.2$  Hz, 2H), 0.98 (t,  $J = 7.5$  Hz, 3H).

2-(But-3-enyloxy)-4-(butoxy)benzoic acid    **4** ( $m=4, n=4$ )

The obtained methyl 2-(but-3-enyloxy)-4-(butoxy)benzoate (6.5 g; 0.023 mol) was dissolved in 100 mL of methanol. This solution was poured into a solution containing NaOH (1.4 g; 0.035 mol) in 20 mL of water, and the mixture was refluxed for 1.5 h. After the solvent was distilled off, the residue was dissolved in water. Then, hydrochloric acid was added until the solution became acidic, whereupon a white precipitate formed. The resulting white precipitate was filtered and washed with water. The residue was then washed with hexane and dried to obtain 5.3 g of 2-(but-3-enyloxy)-4-(butoxy)benzoic acid as a white solid. Yield 86%.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 10.61 (s, 1H), 8.11 (d,  $J = 9.2$  Hz, 1H), 6.59-6.65 (m, 1H), 6.50 (d,  $J = 2.4$  Hz, 1H), 5.86 (ddt,  $J = 17.4, 10.5, 6.8$  Hz, 1H), 5.20-5.30 (m, 2H), 4.26 (t,  $J = 6.2$  Hz, 2H), 4.02 (t,  $J = 6.4$  Hz, 2H), 2.66 (q,  $J = 6.5$  Hz, 2H), 1.79 (pentet,  $J = 7.1$  Hz, 2H), 1.44-1.56 (m, 2H), 0.99 (t,  $J = 7.6$  Hz, 3H).

4-Cyanophenyl 2-(but-3-enyloxy)-4-(butoxy)benzoate    **A-4** ( $m=4, n=4$ )

The obtained 2-(but-3-enyloxy)-4-(butoxy)benzoic acid (3.8 g; 14 mmol), 4-hydroxybenzotrile (1.7 g; 14 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (5.4 g; 28 mmol), and *N,N*-dimethyl-4-aminopyridine (DMAP) (0.34 g; 2.8 mmol) were dissolved in 150 mL of dichloromethane under argon atmosphere, and the mixture was refluxed for 24 h. Then, dichloromethane (100 mL) was added, and the organic layer was washed with saturated  $\text{NH}_4\text{Cl}$  solution. After the solvent was distilled off, the residue was purified by means of column chromatography on silica gel using dichloromethane as eluent. As a result, 4.7 g of 4-cyanophenyl 2-(but-3-enyloxy)-4-(butoxy)benzoate was obtained as a white solid. Yield 92%.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.01 (d,  $J = 8.3$  Hz, 1H), 7.68-7.76 (m, 2H), 7.30-7.36 (m, 2H), 6.48-6.58 (m, 2H), 5.93 (ddt,  $J = 17.1, 10.3, 6.8$  Hz, 1H), 5.11-5.18 (m, 1H), 5.05-5.10 (m, 1H), 4.09 (t,  $J = 6.8$  Hz, 2H), 4.04 (t,  $J = 6.8$  Hz, 2H), 2.60 (q,  $J = 6.7$  Hz, 2H), 1.80 (pentet,  $J = 7.1$  Hz, 2H), 1.44-1.56 (m, 2H), 1.00 (t,  $J = 7.3$  Hz, 3H).

4-Cyanophenyl 4-(butoxy)-2-(hex-5-enyloxy)benzoate    **A-6** ( $m=4, n=6$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.02 (d,  $J = 8.8$  Hz, 1H), 7.67-7.75 (m, 2H), 7.28-7.38 (m, 2H), 6.44-6.62 (m, 2H), 5.77 (ddt,  $J = 16.9, 10.5, 4.5$  Hz, 1H), 4.89-5.03 (m, 2H), 3.98-4.10 (m, 4H), 2.10 (q,  $J = 7.2$  Hz, 2H), 1.75-1.92 (m, 4H), 1.62 (pentet,  $J = 7.5$  Hz, 2H), 1.45-1.57 (m, 2H), 1.00 (t,  $J = 7.2$  Hz, 3H). Yield 88 %.

4-Cyanophenyl 4-butoxy-2-(undec-10-enyloxy)benzoate    **A-11** ( $m=4, n=11$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.01 (d,  $J = 8.8$  Hz, 1H), 7.68-7.74 (m, 2H), 7.28-7.38 (m, 2H), 6.44-6.62 (m, 2H), 5.81 (ddt,  $J = 17.1, 10.3, 6.8$  Hz, 1H), 4.88-5.05 (m, 2H), 4.04 (t,  $J = 6.6$  Hz, 2H), 3.85-4.20 (t, 4H), 2.02 (pentet,  $J = 7.0$  Hz, 2H), 1.74-1.90 (m, 4H), 1.16-1.62 (m, 14H), 1.00 (t,  $J = 7.3$  Hz, 3H). Yield 73 %.

4'-Cyanobiphenyl 2-(but-3-enyloxy)-4-(butoxy)benzoate **B-4** ( $m=4, n=4$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.05 (d,  $J = 8.7$  Hz, 1H), 7.56-7.76 (m, 6H), 7.31 (d,  $J = 8.2$  Hz, 2H), 6.45-6.59 (m, 2H), 5.96 (ddt,  $J = 17.4, 10.6, 6.8$  Hz, 1H), 5.00-5.20 (m, 2H), 4.10 (t,  $J = 6.9$  Hz, 2H), 4.04 (t,  $J = 6.4$  Hz, 2H), 2.62 (q,  $J = 6.5$  Hz, 2H), 1.80 (pentet,  $J = 7.0$  Hz, 2H), 1.44-1.56 (m, 2H), 1.00 (t,  $J = 7.2$  Hz, 3H). Yield 91 %.

4'-Cyanobiphenyl 4-butoxy-2-(hex-5-enyloxy)benzoate **B-6** ( $m=4, n=6$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.05 (d,  $J = 9.1$  Hz, 1H), 7.65-7.76 (m, 4H), 7.62 (d,  $J = 8.6$  Hz, 2H), 7.31 (d,  $J = 8.6$  Hz, 2H), 6.49-6.58 (m, 2H), 5.77 (ddt,  $J = 16.9, 10.5, 4.5$  Hz, 1H), 4.89-5.03 (m, 2H), 3.98-4.10 (m, 4H), 2.10 (q,  $J = 7.2$  Hz, 2H), 1.75-1.92 (m, 4H), 1.62 (pentet,  $J = 7.5$  Hz, 2H), 1.44-1.57 (m, 2H), 1.00 (t,  $J = 7.2$  Hz, 3H). Yield 89 %.

4'-Cyanobiphenyl 4-butoxy-2-(undec-10-enyloxy)benzoate **B-11** ( $m=4, n=11$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.05 (d,  $J = 9.2$  Hz, 1H), 7.64-7.77 (m, 4H), 7.62 (d,  $J = 8.5$  Hz, 2H), 7.31 (d,  $J = 8.7$  Hz, 2H), 6.48-6.58 (m, 2H), 5.81 (ddt,  $J = 17.2, 10.3, 6.7$  Hz, 1H), 4.88-5.05 (m, 2H), 4.04 (t,  $J = 6.6$  Hz, 2H), 3.85-4.20 (t, 4H), 2.02 (pentet,  $J = 7.0$  Hz, 2H), 1.73-1.91 (m, 4H), 1.16-1.62 (m, 14H), 1.00 (t,  $J = 7.4$  Hz, 3H). Yield 82 %.

4'-Cyanobiphenyl 4-octyloxy-2-(prop-2-enyloxy)benzoate **C-3** ( $m=8, n=3$ )

$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) :  $\delta$  (ppm) 7.89-7.99 (m, 5H), 7.81-7.87 (m, 2H), 7.33-7.39 (m, 2H), 6.66-6.72 (m, 2H), 6.04 (ddt,  $J = 17.4, 11.0, 4.6$  Hz, 1H), 5.49-5.58 (m, 1H), 5.21-5.27 (m, 1H), 4.66-4.72 (m, 2H), 4.08 (t,  $J = 6.6$  Hz, 2H), 1.74 (pentet,  $J = 7.1$  Hz, 2H), 1.21-1.48 (m, 10H), 0.87 (t,  $J = 6.9$  Hz, 3H). Yield 94 %.

4'-Cyanobiphenyl 2-(but-3-enyloxy)-4-(octyloxy)benzoate **C-4** ( $m=8, n=4$ )

$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) :  $\delta$  (ppm) 7.87-7.98 (m, 5H), 7.78-7.87 (m, 2H), 7.31-7.37 (m, 2H), 6.63-6.72 (m, 2H), 5.93 (ddt,  $J = 17.4, 10.5, 6.8$  Hz, 1H), 5.10-5.19 (m, 1H), 5.01-5.07 (m, 1H), 4.04-4.16 (m, 4H), 2.41-2.48 (m, 2H), 1.74 (pentet,  $J = 7.1$  Hz, 2H), 1.21-1.47 (m, 10H), 0.87 (t,  $J = 7.1$  Hz, 3H). Yield 91 %.

4'-Cyanobiphenyl 4-octyloxy-2-(pent-4-enyloxy)benzoate C-5 ( $m=8, n=5$ )

$^1\text{H-NMR}$  (DMSO- $d_6$ ) :  $\delta$  (ppm) 7.89-7.98 (m, 5H), 7.81-7.87 (m, 2H), 7.32-7.37 (m, 2H), 6.63-6.70 (m, 2H), 5.84 (ddt,  $J = 17.4, 10.4, 6.7$  Hz, 1H), 4.91-5.02 (m, 2H), 4.04-4.13 (m, 4H), 2.23 (q,  $J = 7.2$  Hz, 2H), 1.82 (pentet,  $J = 6.9$  Hz, 2H), 1.74 (pentet,  $J = 7.1$  Hz, 2H), 1.21-1.48 (m, 10H), 0.87 (t,  $J = 7.1$  Hz, 3H). Yield 88 %.

4'-Cyanobiphenyl 2-(hex-5-enyloxy)-4-(octyloxy)benzoate C-6 ( $m=8, n=6$ )

$^1\text{H-NMR}$  (DMSO- $d_6$ ) :  $\delta$  (ppm) 7.88-7.99 (m, 5H), 7.80-7.88 (m, 2H), 7.30-7.37 (m, 2H), 6.62-6.71 (m, 2H), 5.76 (ddt,  $J = 17.4, 10.4, 6.7$  Hz, 1H), 4.94-5.02 (m, 1H), 4.88-4.94 (m, 1H), 4.02-4.15 (m, 4H), 2.05 (q,  $J = 7.3$  Hz, 2H), 1.67-1.80 (m, 4H), 1.54 (pentet,  $J = 7.5$  Hz, 2H), 1.20-1.49 (m, 10H), 0.87 (t,  $J = 6.9$  Hz, 3H). Yield 85 %.

4'-Cyanobiphenyl 2-(hept-6-enyloxy)-4-(octyloxy)benzoate C-7 ( $m=8, n=7$ )

$^1\text{H-NMR}$  (DMSO- $d_6$ ) :  $\delta$  (ppm) 7.87-7.98 (m, 5H), 7.81-7.87 (m, 2H), 7.31-7.37 (m, 2H), 6.63-6.70 (m, 2H), 5.73 (ddt,  $J = 17.2, 10.4, 6.8$  Hz, 1H), 4.91-4.99 (m, 1H), 4.85-4.91 (m, 1H), 4.04-4.12 (m, 4H), 1.97 (q,  $J = 7.4$  Hz, 2H), 1.67-1.79 (m, 4H), 1.22-1.51 (m, 14H), 0.87 (t,  $J = 6.9$  Hz, 3H). Yield 82 %.

4'-Cyanobiphenyl 2-(oct-7-enyloxy)-4-(octyloxy)benzoate C-8 ( $m=8, n=8$ )

$^1\text{H-NMR}$  (DMSO- $d_6$ ) :  $\delta$  (ppm) 7.88-7.98 (m, 5H), 7.79-7.87 (m, 2H), 7.30-7.37 (m, 2H), 6.62-6.71 (m, 2H), 5.73 (ddt,  $J = 17.4, 10.4, 6.7$  Hz, 1H), 4.84-4.97 (m, 2H), 4.03-4.12 (m, 4H), 1.94 (q,  $J = 7.4$  Hz, 2H), 1.66-1.79 (m, 4H), 1.21-1.52 (m, 16H), 0.87 (t,  $J = 6.9$  Hz, 3H). Yield 89 %.

4'-Cyanobiphenyl 2-(non-8-enyloxy)-4-(octyloxy)benzoate C-9 ( $m=8, n=9$ )

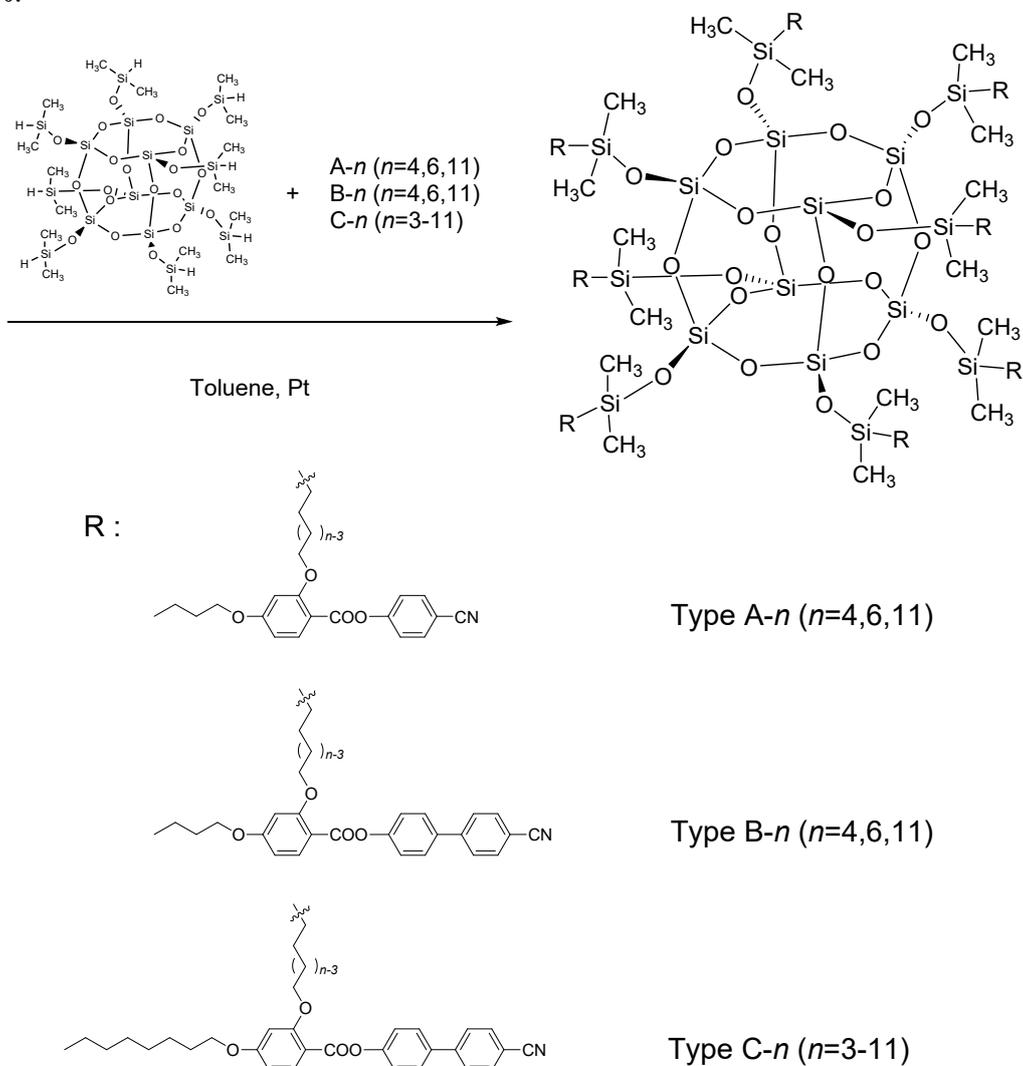
$^1\text{H-NMR}$  (DMSO- $d_6$ ) :  $\delta$  (ppm) 7.87-7.98 (m, 5H), 7.80-7.86 (m, 2H), 7.29-7.37 (m, 2H), 6.61-6.71 (m, 2H), 5.71 (ddt,  $J = 17.4, 10.4, 6.8$  Hz, 1H), 4.83-4.96 (m, 2H), 4.02-4.13 (m, 4H), 1.93 (q,  $J = 7.0$  Hz, 2H), 1.65-1.79 (m, 4H), 1.14-1.50 (m, 18H), 0.87 (t,  $J = 6.8$  Hz, 3H). Yield 79 %.

4'-Cyanobiphenyl 2-(dec-9-enyloxy)-4-(octyloxy)benzoate **C-10** ( $m=8, n=10$ )

$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) :  $\delta$  (ppm) 7.87-7.97 (m, 5H), 7.79-7.86 (m, 2H), 7.30-7.36 (m, 2H), 6.61-6.70 (m, 2H), 5.71 (ddt,  $J = 17.2, 10.3, 6.7$  Hz, 1H), 4.84-4.96 (m, 2H), 3.99-4.14 (m, 4H), 1.92 (q,  $J = 7.0$  Hz, 2H), 1.64-1.80 (m, 4H), 1.11-1.51 (m, 20H), 0.87 (t,  $J = 6.8$  Hz, 3H). Yield 75 %.

4'-Cyanobiphenyl 4-octyloxy-2-(undec-10-enyloxy)benzoate **C-11** ( $m=8, n=11$ )

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 8.05 (d,  $J = 8.7$  Hz, 1H), 7.57-7.77 (m, 6H), 7.29-7.34 (m, 2H), 6.49-6.57 (m, 2H), 5.78 (ddt,  $J = 17.2, 10.4, 6.7$  Hz, 1H), 4.93-5.01 (m, 1H), 4.88-4.93 (m, 1H), 3.98-4.08 (m, 4H), 2.00 (q,  $J = 7.3$  Hz, 2H), 1.76-1.89 (m, 4H), 1.18-1.53 (m, 22H), 0.90 (t,  $J = 7.0$  Hz, 3H). Yield 77 %.



Figures S2 The synthetic route of the silsesquoxane derivatives (Type A, B, C).

### Side-on Liquid Crystalline silsesquioxane Type A (n=4)

The side-on liquid crystalline silsesquioxane was prepared by means of a typical hydrosilylation of an allyl-bearing substituted compound **A-4** [4-cyanophenyl 2-(but-3-enyloxy)-4-(butoxy)benzoate] with the silsesquioxane having Si-H groups using a platinum catalyst. Octakis(dimethylsilyloxy)-silsesquioxane (0.58 g;  $5.7 \times 10^{-4}$  mol) and 4-cyanophenyl 2-(but-3-enyloxy)-4-(butoxy)benzoate (2.5 g;  $5.7 \times 10^{-3}$  mol) were dissolved in 100 mL of dried toluene. Hydrogen hexachloroplatinate (IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), dissolved in a few milliliters of 2-propanol, was poured into the solution, and the mixture was refluxed for 24 h. The reaction mixture was poured into an excess of methanol to precipitate the sample. The sample obtained was reprecipitated twice from its toluene solution into an excess of methanol and dried in vacuum. The purity of the compound was identified by means of gel permeation chromatography (GPC) by checking the disappearance of the peak due to non-reacted mesogens.  $^1\text{H-NMR}$  analysis revealed a completeness of the reaction between the silsesquioxane and the mesogen, indicating the complete absence of the vinyl protons ( $\text{CH}_2=\text{CH-}$ ) of the corresponding mesogen at 5.16 ppm and 5.08 ppm, and the loss of Si-H peak at 4.5 ppm.  $^{29}\text{Si-NMR}$  analysis revealed two different silicon peaks at 13.4 ppm and -108.4 ppm that represent  $\text{OSi}(\text{CH}_3)_2$  and  $\text{SiO}_4$ , respectively. The IR spectra of the silsesquioxane showed the complete disappearance of the Si-H stretching band at  $2160 \text{ cm}^{-1}$ .

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 7.93-8.01 (m, 8H), 7.79-7.87 (m, 16H), 7.38-7.46 (m, 16H), 6.58-6.68 (m, 16H), 4.01-4.14 (m, 32H), 1.66-1.88 (m, 32H), 1.38-1.53 (m, 32H), 0.90-1.02 (m, 24H), 0.52-0.68 (m, 16H), 0.02-0.13 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.4 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.4 (s,  $\text{SiO}_4$ ). Yield 66 %.

### **Type A (n=6)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.93-7.98 (m, 8H), 7.80-7.86 (m, 16H), 7.39-7.46 (m, 16H), 6.58-6.66 (m, 16H), 4.01-4.12 (m, 32H), 1.68-1.88 (m, 32H), 1.43-1.57 (m, 32H), 1.29-1.42 (m, 32H), 0.96 (t,  $J = 7.6 \text{ Hz}$ , 24H), 0.53-0.68 (m, 16H), 0.07-0.19 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.4 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.4 (s,  $\text{SiO}_4$ ). Yield 52 %.

**Type A (n=11)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.96 (d,  $J = 8.7$  Hz, 8H), 7.81-7.89 (m, 16H), 7.40-7.49 (m, 16H), 6.58-6.68 (m, 16H), 4.01-4.15 (m, 32H), 1.71-1.84 (m, 32H), 1.44-1.57 (m, 32H), 1.18-1.44 (m, 112H), 0.97 (t,  $J = 7.3$  Hz, 24H), 0.60-0.70 (m, 16H), 0.12-0.22 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.4 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.4 (s,  $\text{SiO}_4$ ). Yield 67 %.

**Type B (n=4)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.95 (d,  $J = 8.7$  Hz, 8H), 7.62-7.84 (m, 48H), 7.21-7.34 (m, 16H), 6.53-6.66 (m, 16H), 3.94-4.12 (m, 32H), 1.67-1.86 (m, 32H), 1.39-1.62 (m, 32H), 0.88-1.00 (m, 24H), 0.52-0.69 (m, 16H), 0.01-0.10 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.3 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.4 (s,  $\text{SiO}_4$ ). Yield 58 %.

**Type B (n=6)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.96 (d,  $J = 9.6$  Hz, 8H), 7.78-7.84 (m, 32H), 7.69-7.74 (m, 16H), 7.27-7.34 (m, 16H), 6.59-6.65 (m, 16H), 3.97-4.12 (m, 32H), 1.75 (pentet,  $J = 7.1$  Hz, 32H), 1.41-1.54 (m, 32H), 1.22-1.38 (m, 32H), 0.95 (t,  $J = 7.6$  Hz, 24H), 0.48-0.60 (m, 16H), 0.02-0.10 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.3 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.3 (s,  $\text{SiO}_4$ ). Yield 59 %.

**Type B (n=11)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.96 (d,  $J = 8.2$  Hz, 8H), 7.79-7.89 (m, 32H), 7.69-7.79 (m, 16H), 7.29-7.37 (m, 16H), 6.58-6.67 (m, 16H), 4.01-4.12 (m, 32H), 1.68-1.86 (m, 32H), 1.43-1.57 (m, 32H), 1.15-1.42 (m, 112H), 0.96 (t,  $J = 7.6$  Hz, 24H), 0.52-0.66 (m, 16H), 0.08-0.18 (m, 48H).  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.1 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.3 (s,  $\text{SiO}_4$ ). Yield 48 %.

**Type C (*n*=3)**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) : δ (ppm) 7.86-8.05 (m, 8H), 7.35-7.72 (m, 48H), 7.07-7.27 (m, 16H), 6.25-6.58 (m, 16H), 3.66-4.04 (m, 32H), 1.62-1.90 (m, 32H), 1.07-1.50 (m, 80H), 0.75-0.93 (m, 24H), 0.53-0.74 (m, 16H), 0.00-0.17 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.6, 161.6, 156.7, 151.6, 145.2, 134.5, 132.6, 132.5, 131.2, 128.4, 128.1, 127.7, 127.4, 127.0, 122.6, 122.5, 118.8, 116.0, 110.6, 109.9, 100.1, 68.3, 31.7, 29.3, 29.2, 29.1, 25.9, 22.6, 14.1, 13.5, -0.5. <sup>29</sup>Si-NMR (Acetone-*d*6) : δ (ppm) 13.3 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.4 (s, SiO<sub>4</sub>). Yield 66 %.

**Type C (*n*=4)**

<sup>1</sup>H-NMR (Acetone-*d*6) : δ (ppm) 7.95 (d, *J* = 8.7 Hz, 8H), 7.56-7.84 (m, 48H), 7.19-7.34 (m, 16H), 6.50-6.66 (m, 16H), 3.90-4.10 (m, 32H), 1.66-1.86 (m, 32H), 1.17-1.64 (m, 96H), 0.87 (t, *J* = 6.6 Hz, 24H), 0.50-0.67 (m, 16H), 0.01-0.11 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.5, 163.5, 161.7, 151.6, 144.7, 136.1, 134.4, 132.5, 128.1, 127.5, 122.6, 118.8, 110.6, 110.6, 105.1, 100.1, 68.7, 68.3, 31.7, 29.5, 29.3, 29.1, 29.0, 28.8, 25.9, 22.6, 22.6, 17.4, 14.0, -0.5. <sup>29</sup>Si-NMR (Acetone-*d*6) : δ (ppm) 13.3 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.4 (s, SiO<sub>4</sub>). Yield 56 %.

**Type C (*n*=5)**

<sup>1</sup>H-NMR (Acetone-*d*6) : δ (ppm) 7.95 (d, *J* = 8.7 Hz, 8H), 7.62-7.85 (m, 48H), 7.23-7.34 (m, 16H), 6.52-6.64 (m, 16H), 3.92-4.11 (m, 32H), 1.66-1.84 (m, 32H), 1.19-1.57 (m, 112H), 0.87 (t, *J* = 6.9 Hz, 24H), 0.45-0.60 (m, 16H), 0.01-0.11 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.5, 163.5, 161.7, 151.6, 144.7, 136.1, 134.4, 132.5, 128.1, 127.5, 122.6, 118.8, 110.6, 110.6, 105.1, 100.1, 68.7, 68.3, 31.7, 29.5, 29.3, 29.1, 29.0, 28.8, 25.9, 22.6, 22.6, 17.4, 14.0, -0.5. <sup>29</sup>Si-NMR (Acetone-*d*6) : δ (ppm) 13.3 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.3 (s, SiO<sub>4</sub>). Yield 45 %.

**Type C (n=6)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.96 (d,  $J = 9.2$  Hz, 8H), 7.65-7.86 (m, 48H), 7.25-7.35 (m, 16H), 6.55-6.65 (m, 16H), 3.95-4.11 (m, 32H), 1.69-1.83 (m, 32H), 1.19-1.58 (m, 128H), 0.87 (t,  $J = 6.9$  Hz, 24H), 0.47-0.60 (m, 16H), 0.02-0.12 (m, 48H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 164.5, 163.5, 161.7, 151.6, 144.7, 136.2, 134.4, 132.5, 128.1, 127.5, 122.6, 118.8, 110.7, 110.6, 105.1, 100.1, 68.8, 68.3, 33.0, 31.7, 29.3, 29.1, 29.0, 29.0, 25.9, 25.5, 22.7, 22.6, 17.5, 14.0, -0.5.  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.3 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.3 (s,  $\text{SiO}_4$ ). Yield 60 %.

**Type C (n=7)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.95 (d,  $J = 9.2$  Hz, 8H), 7.68-7.85 (m, 48H), 7.28-7.35 (m, 16H), 6.58-6.65 (m, 16H), 3.97-4.12 (m, 32H), 1.69-1.84 (m, 32H), 1.20-1.55 (m, 144H), 0.88 (t,  $J = 6.9$  Hz, 24H), 0.47-0.59 (m, 16H), 0.02-0.12 (m, 48H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 164.5, 163.6, 161.7, 151.6, 144.8, 136.2, 134.4, 132.5, 128.1, 127.5, 122.6, 118.8, 110.7, 110.6, 105.2, 100.1, 81.4, 68.8, 68.3, 33.3, 31.7, 29.3, 29.1, 29.1, 29.1, 25.9, 22.8, 22.6, 17.6, 14.0, -0.4.  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.2 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.3 (s,  $\text{SiO}_4$ ). Yield 55 %.

**Type C (n=8)**

$^1\text{H-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 7.96 (d,  $J = 9.2$  Hz, 8H), 7.62-7.88 (m, 48H), 7.24-7.37 (m, 16H), 6.53-6.68 (m, 16H), 3.94-4.12 (m, 32H), 1.68-1.84 (m, 32H), 1.10-1.58 (m, 160H), 0.88 (t,  $J = 6.3$  Hz, 24H), 0.47-0.63 (m, 16H), 0.03-0.17 (m, 48H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 164.6, 163.7, 161.7, 151.6, 144.8, 136.2, 134.4, 132.5, 128.1, 127.5, 122.7, 118.8, 110.7, 110.6, 105.2, 100.1, 68.8, 68.3, 33.4, 31.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 25.9, 25.9, 22.9, 22.6, 17.6, 14.1, -0.4.  $^{29}\text{Si-NMR}$  (Acetone-*d*6) :  $\delta$  (ppm) 13.2 (s,  $\text{OSi}(\text{CH}_3)_2$ ), -108.4 (s,  $\text{SiO}_4$ ). Yield 69 %.

**Type C (*n*=9)**

<sup>1</sup>H-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 7.96 (d, *J* = 9.6 Hz, 8H), 7.66-7.89 (m, 48H), 7.26-7.37 (m, 16H), 6.56-6.67 (m, 16H), 3.97-4.13 (m, 32H), 1.69-1.86 (m, 32H), 1.16-1.57 (m, 176H), 0.88 (t, *J* = 6.6 Hz, 24H), 0.50-0.62 (m, 16H), 0.06-0.16 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.6, 163.7, 161.7, 151.6, 144.8, 136.2, 134.4, 132.5, 128.1, 127.5, 122.7, 118.8, 110.7, 110.6, 105.2, 100.1, 68.8, 68.3, 33.4, 31.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 25.9, 25.9, 22.9, 22.6, 17.6, 14.1, -0.4. <sup>29</sup>Si-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 13.2 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.3 (s, SiO<sub>4</sub>). Yield 52 %.

**Type C (*n*=10)**

<sup>1</sup>H-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 7.95 (d, *J* = 8.7 Hz, 8H), 7.69-7.88 (m, 48H), 7.28-7.37 (m, 16H), 6.58-6.66 (m, 16H), 3.97-4.14 (m, 32H), 1.69-1.85 (m, 32H), 1.14-1.56 (m, 192H), 0.88 (t, *J* = 6.6 Hz, 24H), 0.51-0.63 (m, 16H), 0.07-0.17 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.5, 163.7, 161.7, 151.6, 144.8, 136.2, 134.4, 132.5, 128.1, 127.5, 122.6, 118.8, 110.7, 110.6, 105.2, 100.1, 68.8, 68.3, 33.4, 31.7, 29.6, 29.6, 29.4, 29.3, 29.1, 29.1, 29.0, 25.9, 25.9, 22.9, 22.6, 17.6, 14.0, -0.4. <sup>29</sup>Si-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 13.1 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.3 (s, SiO<sub>4</sub>). Yield 64 %.

**Type C (*n*=11)**

<sup>1</sup>H-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 8.03 (d, *J* = 8.7 Hz, 8H), 7.51-7.73 (m, 48H), 7.25-7.32 (m, 16H), 6.43-6.56 (m, 16H), 3.90-4.08 (m, 32H), 1.71-1.87 (m, 32H), 1.10-1.51 (m, 208H), 0.88 (t, *J* = 6.9 Hz, 24H), 0.48-0.60 (m, 16H), 0.03-0.14 (m, 48H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ (ppm) 164.5, 163.7, 161.7, 151.6, 144.8, 136.2, 134.4, 132.5, 128.1, 127.5, 122.7, 118.8, 110.7, 110.6, 105.2, 100.1, 68.8, 68.3, 33.4, 31.7, 29.7, 29.6, 29.4, 29.4, 29.3, 29.1, 29.0, 25.9, 22.9, 22.6, 17.6, 14.0, -0.4. <sup>29</sup>Si-NMR (Acetone-*d*<sub>6</sub>) : δ (ppm) 13.1 (s, OSi(CH<sub>3</sub>)<sub>2</sub>), -108.3 (s, SiO<sub>4</sub>). Yield 58 %.

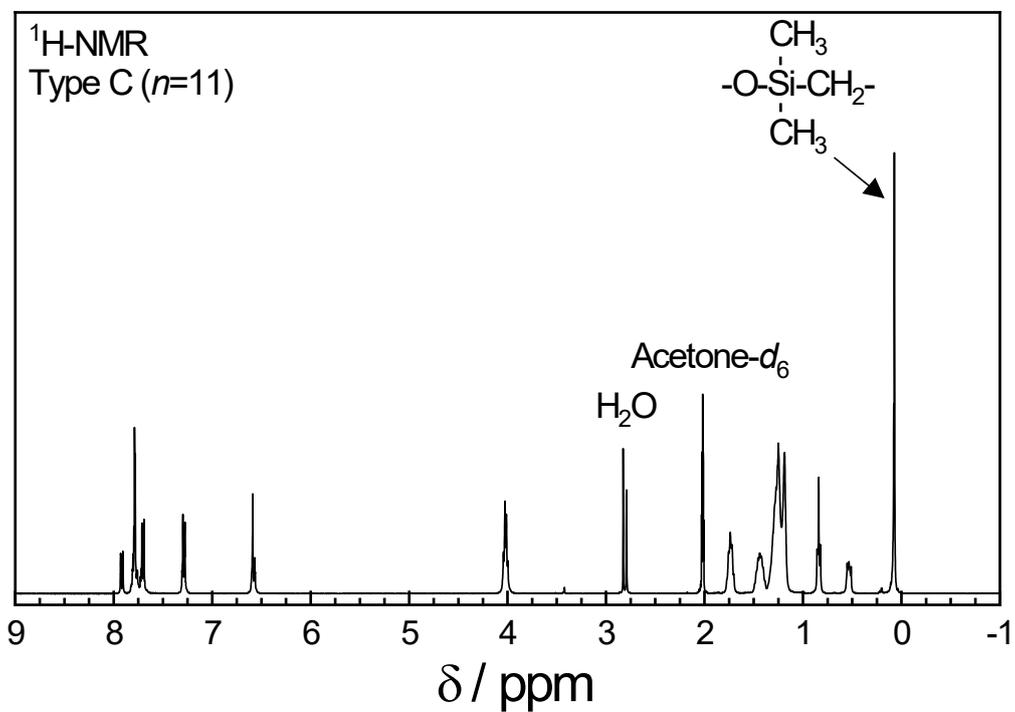
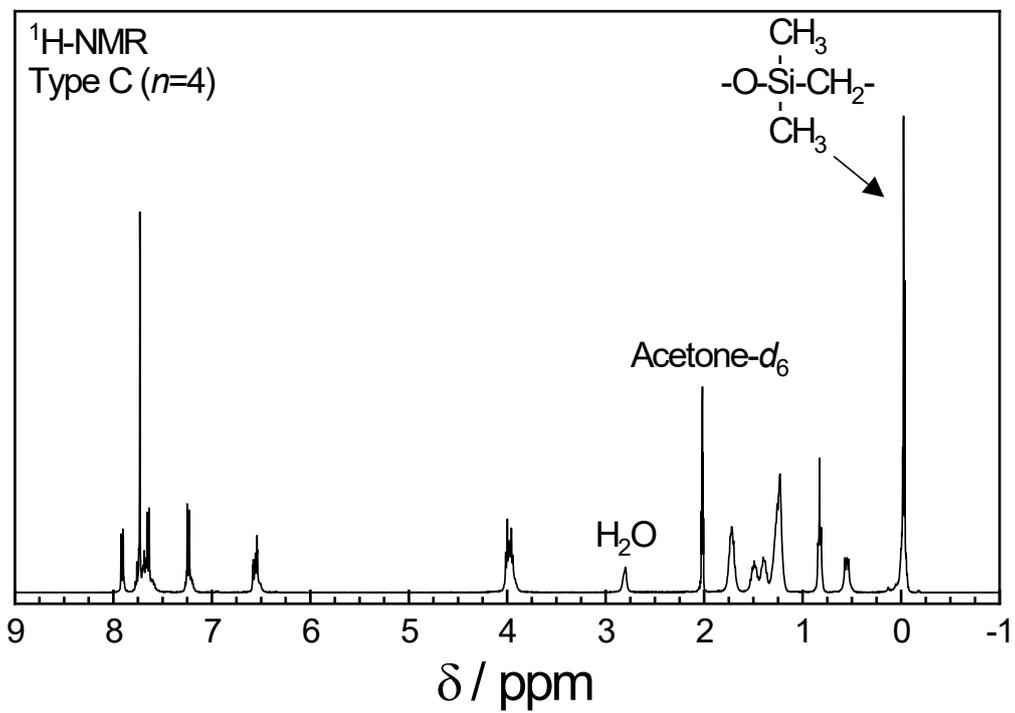


Figure S3 <sup>1</sup>H-NMR spectra of the LC silsesquioxane in Type C (*n*=4, 11).

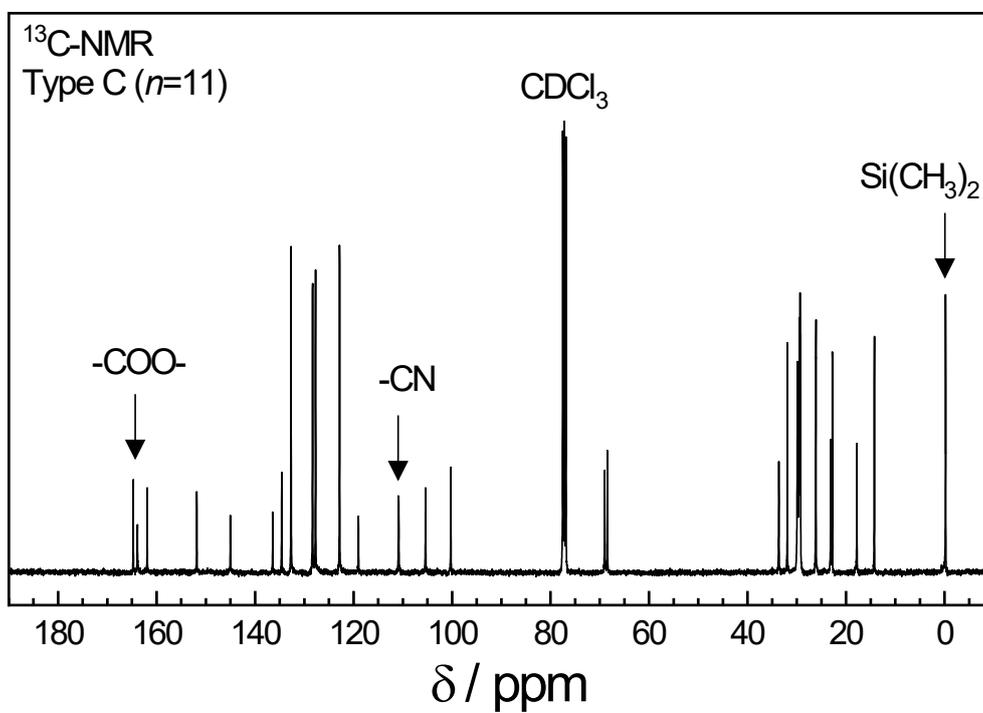
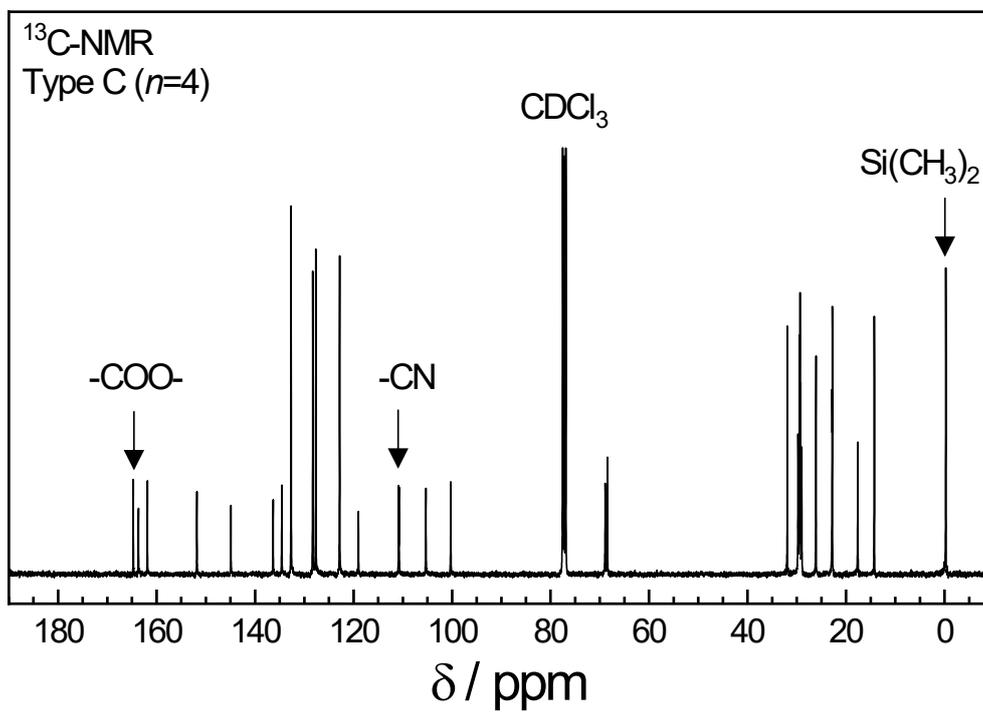


Figure S4 <sup>13</sup>C-NMR spectra of the LC silsesquioxane in Type C (*n*=4, 11).

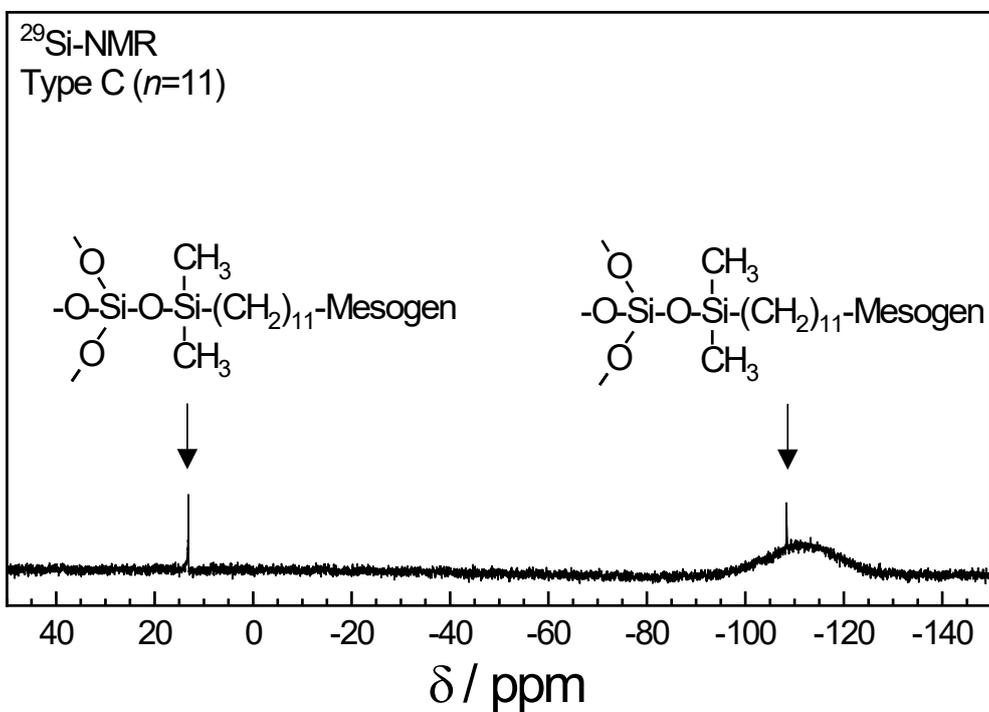
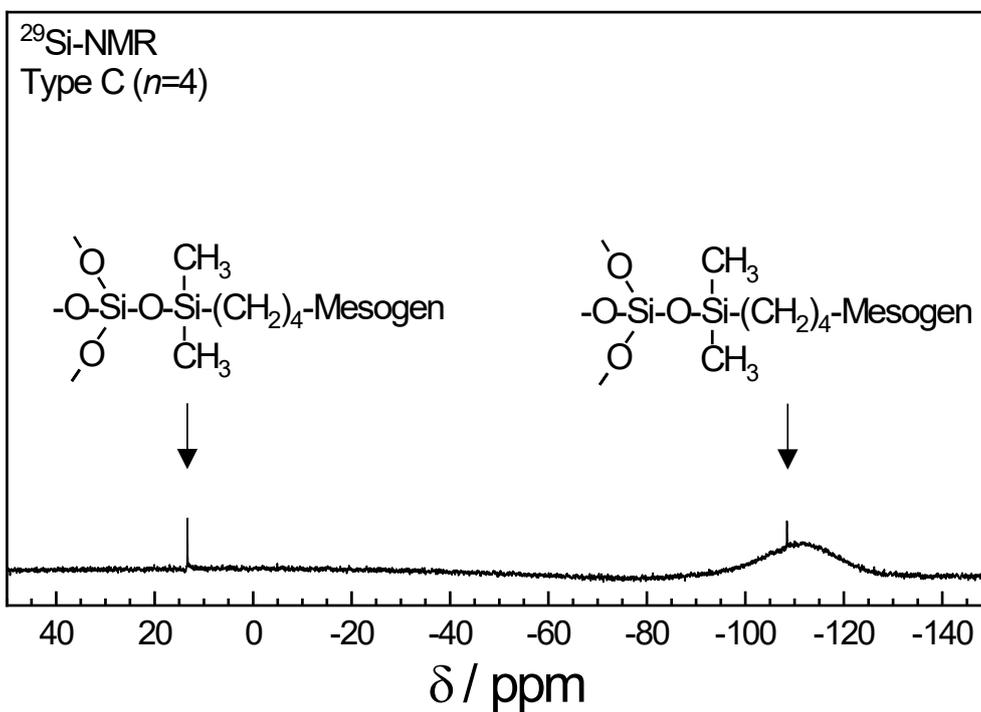


Figure S5 <sup>29</sup>Si-NMR spectra of the LC silsesquioxane in Type C (*n*=4, 11).

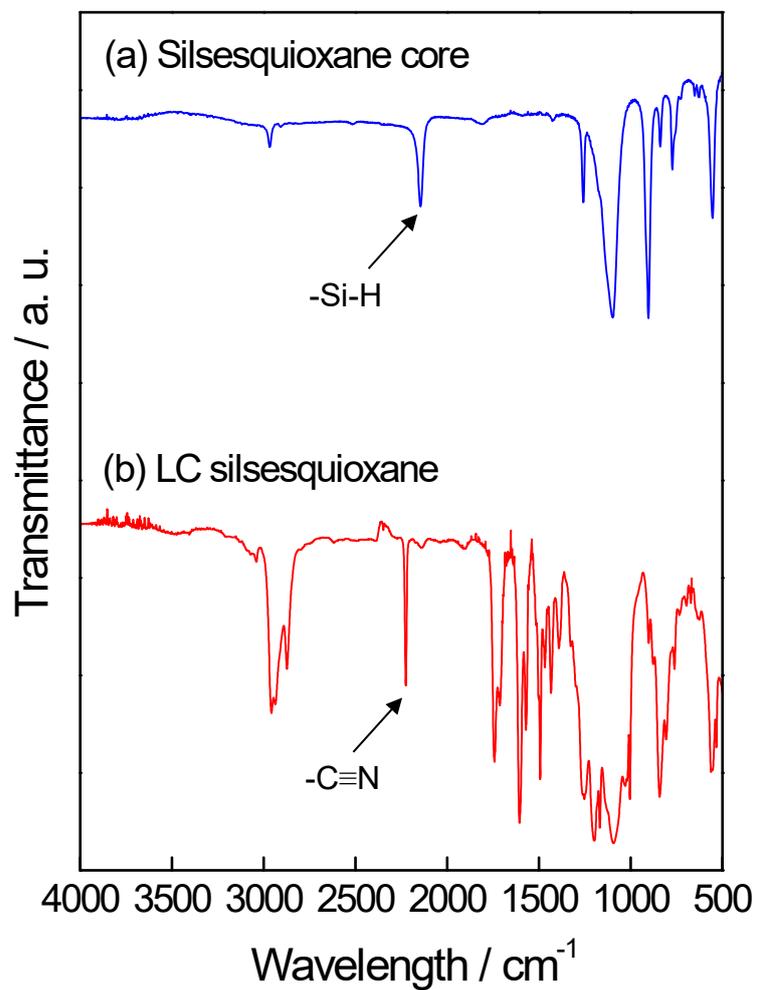


Figure S6 IR spectra of (a) the silsesquioxane core and (b) the LC silsesquioxane (**Type A-4**).

### 3. GPC

Table S1 GPC data of the silsesquioxane derivatives (**Type A, B, C**).

Samples (type, <i>n</i> )	Mn ( $\times 10^3$ )	Mw ( $\times 10^3$ )	Mw/Mn	
<b>A</b>	<b>4</b>	3.98	4.12	1.04
	<b>6</b>	3.83	4.15	1.08
	<b>11</b>	5.63	6.63	1.18
-----				
<b>B</b>	<b>4</b>	4.34	4.53	1.04
	<b>6</b>	4.30	4.74	1.10
	<b>11</b>	4.96	5.32	1.07
-----				
<b>C</b>	<b>3</b>	3.81	4.04	1.06
	<b>4</b>	4.35	4.51	1.03
	<b>5</b>	4.35	4.53	1.04
	<b>6</b>	4.45	4.75	1.07
	<b>7</b>	4.65	4.79	1.03
	<b>8</b>	4.84	5.00	1.03
	<b>9</b>	5.35	5.74	1.07
	<b>10</b>	6.02	6.28	1.04
	<b>11</b>	7.17	7.43	1.04

#### 4. DSC and POM

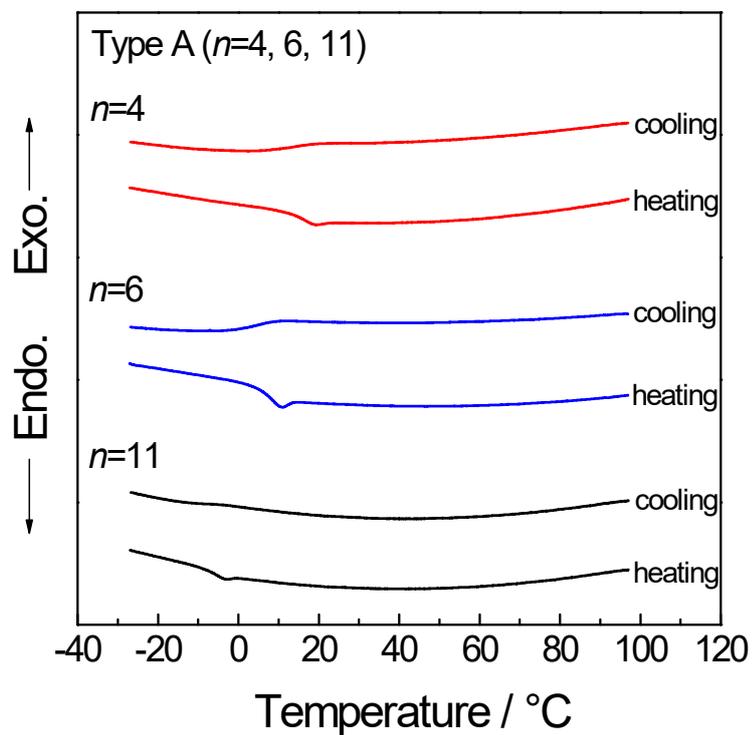


Figure S7 DSC curves of the LC silsesquioxanes in Type A.

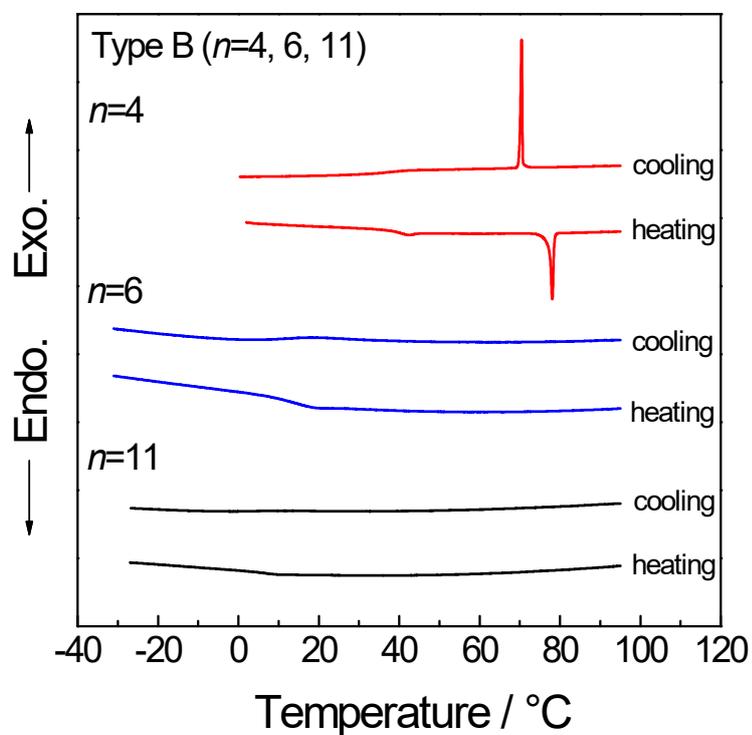


Figure S8 DSC curves of the LC silsesquioxanes in Type B.

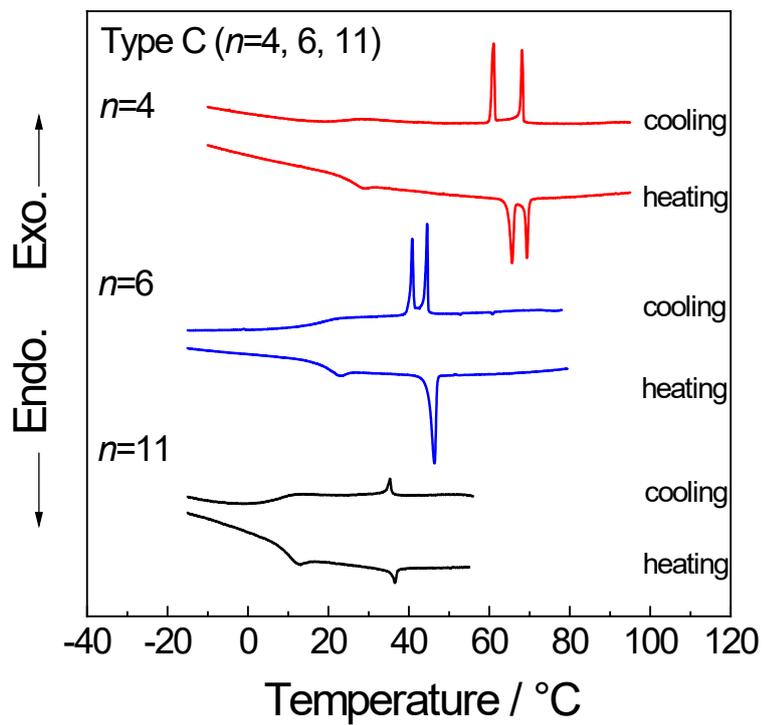


Figure S9 DSC curves of the LC silsesquioxanes in Type C.

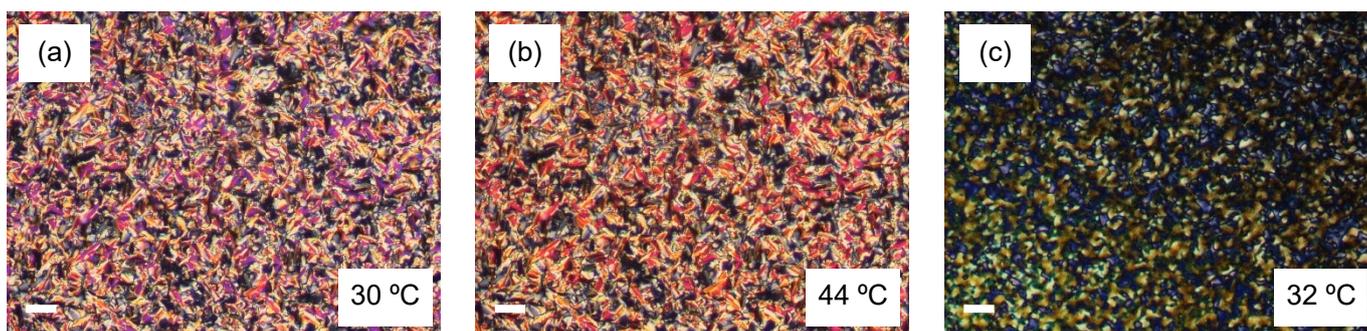


Figure S10 POM images of the LC silsesquioxanes in Type C; (a, b)  $n=6$  and (c)  $n=11$  on cooling.

(Scar bar: 100  $\mu\text{m}$ )

Table S2 Optical, thermal, and thermodynamic data.

Compound	Transition <sup>a</sup>	$T^a$ (°C)	$\Delta H^a$ (J/g)	Transition <sup>b</sup>	$T^b$ (°C)	$\Delta H^b$ (J/g)
<b>Type C (<math>n = 4</math>)</b>	G $\rightarrow$ Col <sub>hex</sub>	24	0	Iso $\rightarrow$ N	68.6	8.4
	Col <sub>hex</sub> $\rightarrow$ N	64.3	13.6	N $\rightarrow$ Col <sub>hex</sub>	61.5	10.0
	N $\rightarrow$ Iso	68.8	8.5	Col <sub>hex</sub> $\rightarrow$ G	23	0
<b>Type C (<math>n = 6</math>)</b>	G $\rightarrow$ N	18.8	0	Iso $\rightarrow$ N	44.8	11.0
	N $\rightarrow$ Iso	44.7	22.6	N $\rightarrow$ Col <sub>hex</sub>	41.3	11.3
				Col <sub>hex</sub> $\rightarrow$ G	17.5	
<b>Type C (<math>n = 11</math>)</b>	G $\rightarrow$ N	9	0	Iso $\rightarrow$ N	35.8	4.6
	N $\rightarrow$ Iso	35.6	3.6	N $\rightarrow$ G	7	0

<sup>a</sup> Phase transitions, transition temperatures and enthalpy changes collected on second heating DSC run with 5°C/min scanning rate; <sup>b</sup> Phase transitions, transition temperature and enthalpy changes collected on cooling DSC run with 5°C/min scanning rate. Phase types: G, glassy state; Col<sub>hex</sub>, hexagonal columnar mesophase; Iso, isotropic liquid. First order transition temperatures are given as peak onsets.

## 5. SWAXS

Table S3 Table of indexations.

$2\theta_{\text{exp}}$	$d_{\text{exp}}$	$I[\xi(\text{nm})]$	$hk$	$2\theta_{\text{cal}}$	$d_{\text{cal}}$	Phase type Mesophase parameters
<b>Type C (<math>n = 4</math>) (40°C)</b>						
4.024	21.94	VS	10	4.030	21.91	$\text{Col}_{\text{hex}}$
6.99	12.63	S	11	6.982	12.65	$a = 25.30 \text{ \AA}$
8.08	10.93	S	20	8.064	10.95	$A = 554 \text{ \AA}^2$
10.69	8.27	M	21	10.674	8.28	$(Z = 1)$
7.6	11.6	M [3]	$h_{\text{sil}}$			
20.55	4.32	VS [1.0]	$h_{\text{ch}}+h_{\text{mes}}$			
<b>Type C (<math>n = 4</math>) (64°C)</b>						
3.95	22.35	S [4]	$D_{\text{col}}$			N
8.09	10.9	S [2]	$h_{\text{sil}}$			
20.3	4.38	VS [0.8]	$h_{\text{ch}}+h_{\text{mes}}$			
<b>Type C (<math>n = 4</math>) (80°C)</b>						
3.94	22.4	S [3]	$D_{\text{col}}$			Iso
8.01	11.0	S [2]	$h_{\text{sil}}$			
20.0	4.43	VS [0.7]	$h_{\text{ch}}+h_{\text{mes}}$			
<b>Type C (<math>n = 11</math>) (23°C)</b>						
2.84	31.1	M [8]	$D_{\text{mol}}$			N
6.29	14.0	S [3]	$D_{\text{sil}}$			
19.7	4.51	VS [0.9]	$h_{\text{ch}}+h_{\text{mes}}$			
<b>Type C (<math>n = 11</math>) (60°C)</b>						
6.42	13.8	S [3]	$D_{\text{sil}}$			Iso
19.2	4.62	VS [0.9]	$h_{\text{ch}}+h_{\text{mes}}$			

$2\theta_{\text{exp}}$  (°),  $d_{\text{exp}}$  (Å),  $2\theta_{\text{cal}}$  (°),  $d_{\text{cal}}$  (Å): experimental and calculated angles and d-spacings from peak position of maximum;  $\xi$ (nm): correlation length from peak width using Scherrer equation with shape factor  $K = 0.9$  (no indication: long-range periodicity from sharp reflection); I: intensity of reflection, signal intensity code: VS = very strong, S = strong, M = medium, W = weak, VW = very weak; ( $hk$ ) are the Miller indices of the reflections from the columnar lattice;  $D_{\text{col}}$  (Å): average spacing of silsesquioxane columns;  $h_{\text{sil}}$  (Å): average piling distance along silsesquioxane columns;  $h_{\text{ch}}$  (Å),  $h_{\text{mes}}$  (Å): average lateral distances between molten chains and between mesogens;  $D_{\text{mol}}$  (Å): molecular layer thickness;  $D_{\text{sil}}$  (Å): average lateral spacing of silsesquioxane units;  $\text{Col}_{\text{hex}}$ , N, Iso: hexagonal columnar mesophase, nematic mesophase, isotropic liquid phase;  $a$ ,  $b$ ,  $A$ ,  $Z$ : columnar lattice parameters, lattice area and number of columns per lattice.

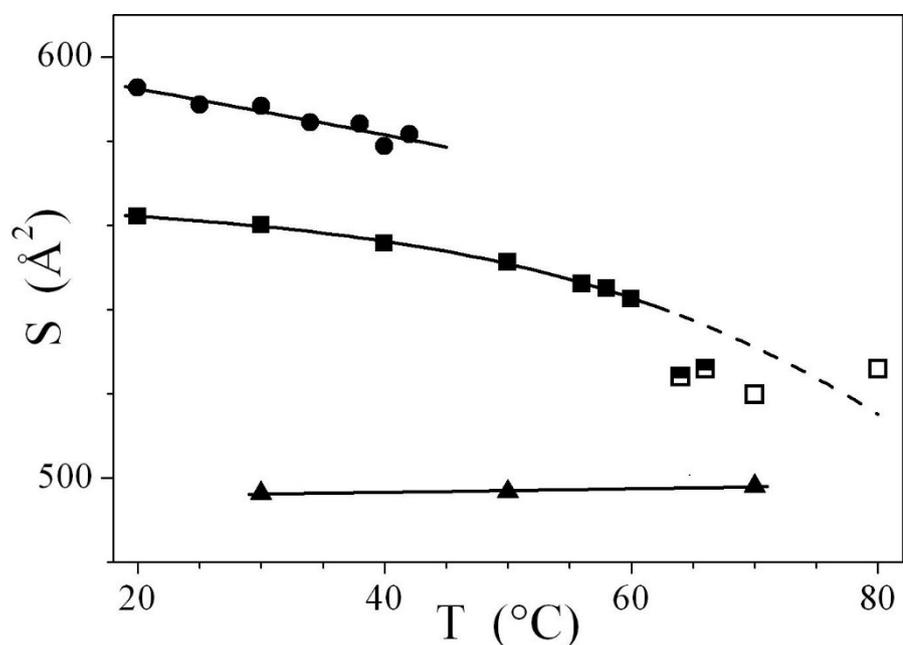


Figure S11 Variation as a function of temperature of the columnar area  $S$  in the columnar phase of Type C ( $n = 4$ ) (squares), Type C ( $n = 6$ ) (discs), and Type B ( $n = 4$ ) (triangles), deduced from the first order reflection of the hexagonal lattice  $d_{10}$  by using  $S = (2/\sqrt{3})d_{10}^2$ . Equivalent string areas  $S$  for Type C ( $n = 4$ ) in the nematic phase (half solid symbols) and isotropic phase (open symbols) were evaluated from the scattering maximum  $D_{\text{sil}}$  by using the relation  $S = (D_{\text{sil}}/0.9763)^2$  developed in reference: M. Marcos, R. Giménez, J. L. Serrano, B. Donnio, B. Heinrich and D. Guillon, *Chem. Eur. J.*, 2001, **7**, 1006.

## 6. References

- [1] K. Kaneko and N. Nakamura, *Liq. Cryst.*, 2007, **34**, 229.
- [2] Y. Kanaoka, K. Tanizawa, E. Sato, O. Yonemitsu and Y. Ban, *Chem. Pharm. Bull.*, 1967, **15**, 593.
- [3] K. Kaneko and N. Nakamura, *Liq. Cryst.*, 2007, **34**, 229. K. Kaneko, A. Mandai, B. Heinrich, B. Donnio and T. Hanasaki, *ChemPhysChem*, 2010, **11**, 3596.