Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Columnar liquid crystals derived from crown ethers with two lateral ester-substituted *ortho*-terphenyl units: unexpected destabilisation of the mesophase by potassium iodide

Nelli Steinke[a]; Martin Kaller[a]; Manfred Nimtz[b]; Angelika Baro[a]; Sabine Laschat[a]
[a] Institut für Organische Chemie, Universität Stuttgart, Stuttgart, Germany [b] Helmholtz-Zentrum für Infektionsforschung, Braunschweig, Germany

Online publication date: 09 September 2010

To cite this Article Steinke, Nelli , Kaller, Martin , Nimtz, Manfred , Baro, Angelika and Laschat, Sabine(2010) 'Columnar liquid crystals derived from crown ethers with two lateral ester-substituted *ortho*-terphenyl units: unexpected destabilisation of the mesophase by potassium iodide', Liquid Crystals, 37: 9, 1139 — 1149
To link to this Article: DOI: 10.1080/02678292.2010.489159
URL: http://dx.doi.org/10.1080/02678292.2010.489159

Liquid Crystals,
Vol. 37, No. 9, September 2010, 1139–1149

Taylor & Francis
Taylor & Francis Group

Columnar liquid crystals derived from crown ethers with two lateral ester-substituted *ortho*-terphenyl units: unexpected destabilisation of the mesophase by potassium iodide

Nelli Steinke[a], Martin Kaller[a], Manfred Nimtz[b], Angelika Baro[a] and Sabine Laschat[a]*

[a]*Institut für Organische Chemie, Universität Stuttgart, Stuttgart, Germany;* [b]*Helmholtz-Zentrum für Infektionsforschung, Braunschweig, Germany*

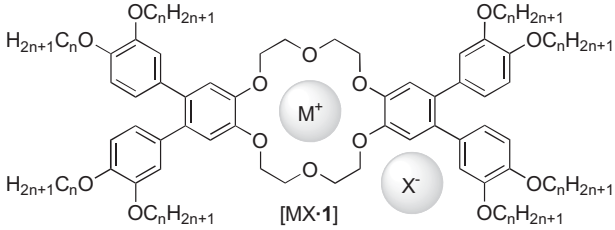
(*Received 18 February 2010; final version received 23 April 2010*)

Gallic acid substituted *ortho*-terphenyl dimers linked by a central [18]crown-6 ether and their KI complexes were synthesised and characterised by differential scanning calorimetry, polarising optical microscopy and X-ray diffraction. With one exception, all salt free derivatives were liquid crystalline. They formed hexagonal columnar mesophases, whose columnar order is retained even upon cooling to room temperature. An odd–even effect of the clearing temperatures was observed with higher clearing points for compounds bearing even-numbered side chains as compared to odd-numbered ones. The calculation of molecules per unit cell resulted in $Z \sim 2$, thus a disc with a dimeric subunit of two molecules oriented perpendicular to each other is assumed. In contrast, all KI complexes were non-mesomorphic.

Keywords: crown ether; cation complexation; columnar liquid crystals; *o*-terphenyl; gallic acid

1. Introduction

As a result of their orientation in the columnar mesophase, discotic liquid crystals are promising candidates for applications in optoelectronics [1–3]. A variety of molecular structures has been successfully utilised for the design of columnar mesogens. Among them are conventional types with flat core units and flexible side chains and many other structural motifs such as cone-shaped, wedge-shaped or even calamitic compounds which self-assemble into columnar aggregates [4–7]. Liquid crystalline building blocks combined with crown ethers or aza crowns are very attractive because the crown ether unit enables by uptake of metal ions a modification of mesophases, the induction of novel mesophases or gel formation. Furthermore, solubility and conductivity can be improved [2, 7, 8–13]. However, it is rather difficult to predict the influence of the metal ion on the type and stability of the mesophase. For example, the calamitic 4,4′-didecyloxy-*p*-terphenyl derivatives with lateral crown ethers formed nematic and smectic A phases [14]. Upon complexation with alkali metal salts the thermotropic system was converted into a lyotropic system which displayed rectangular columnar mesophases. Cation complexation not only induced novel mesophases or stabilised existing mesophases as observed for azacrowns with lateral ester groups [12], for oligophenylene vinylene benzocrown ether conjugates [15], or for taper-shaped crown ethers with gallic esters forming supramolecular channels [16–21], but even tuned the helicity of fibres made from chiral crown ether-substituted phthalocyanines as was published by Nolte and co-workers [22, 23]. NaI complexes of unsymmetrical benzo[15]crown-5 ethers with one peripheral propeller-shaped *ortho*-terphenyl unit and four alkoxy side chains yielded columnar mesophases with a higher stability as compared to the corresponding salt-free systems [24]. On the other hand, a mesophase destabilisation by cation complexation was reported by He *et al.* for calamitic liquid crystals bearing terminal crown ethers [25]. Previously symmetrical dibenzo[18]crown-6 ethers **1** with two peripheral *ortho*-terphenyl units and eight alkoxy side chains were described which displayed hexagonal and rectangular columnar mesophases depending on the anion (Scheme 1) [26, 27]. It was found that complexation with potassium salts possessing soft anions, e.g. KI or KPF_6, improved the mesophase stability considerably [26, 27].



n = 6-12; MX = KF, KCl, KBr, KI, KSCN, KBF_4, KPF_6, NH_4PF_6

Scheme 1. Complexes of alkoxy-substituted *O*-terphenyl dimers linked by [18] crown–6 ether.

*Corresponding author. Email: sabine.laschat@oc.uni-stuttgart.de

ISSN 0267-8292 print/ISSN 1366-5855 online

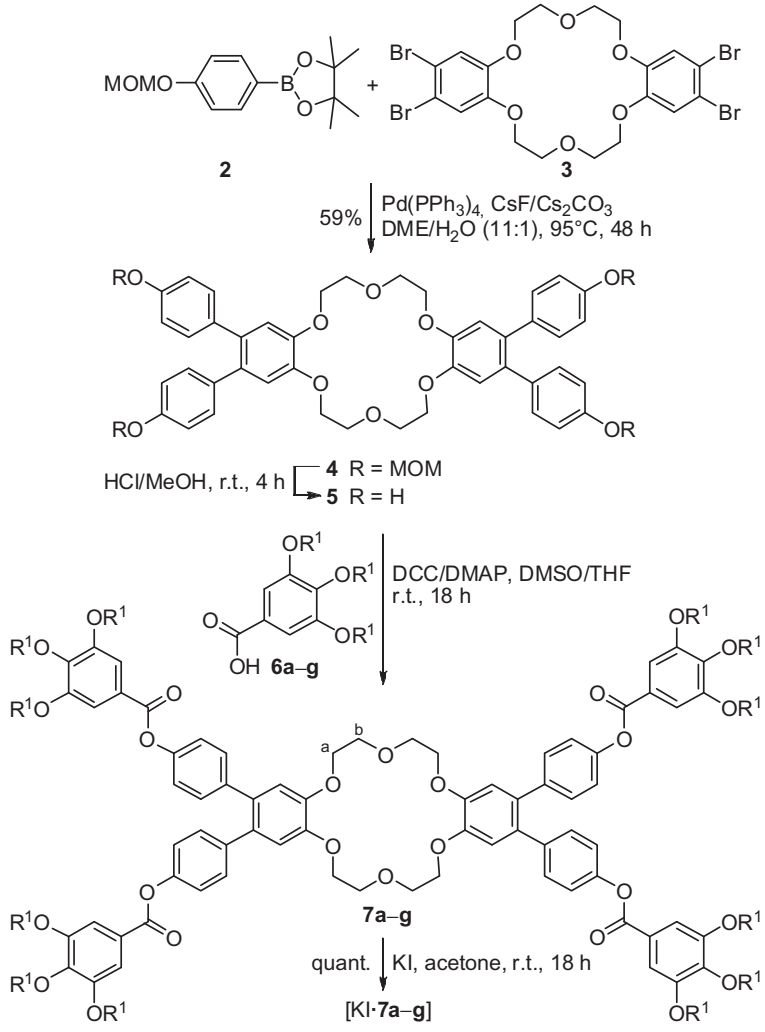
DOI: 10.1080/02678292.2010.489159
http://www.informaworld.com

Besides complexation the polarity difference between the polar core unit and non-polar side chains may effect mesophase formation. In the symmetrical *o*-terphenyl-substituted dibenzo[18]crown-6 ethers **7** (Scheme 2) the core unit was extended and the weak polarity enhanced by the ester-linked gallic acid units together with the increased number of non-polar side chains. In order to gain a deeper understanding of the structure–property relationships of crown ether bearing thermotropic liquid crystals it was thus of interest to study both the influence of the gallic ester substituents and the metal ion complexation on the mesomorphic properties of derivatives **7**. The results are described below.

2. Experimental

2.1 Synthesis

2-(4′-Methoxymethoxyphenyl)-4,4,5,5-tetramethyl[1,3,2]-dioxaborolane (**2**) [28–32] and 4,4′,5,5′-tetrabromodibenzo[18]crown-6 (**3**) [33] were prepared according to procedures described in the literature. Compounds **4**, **5** and **7** presented were prepared following the synthesis shown in Scheme 2. Melting points were measured on a Mettler Toledo DSC822 and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vektor22 spectrometer with a MKII Golden Gate Single Reflection Diamant ATR system. Mass spectra



7	a	b	c	d	e	f	g
R^1	C_6H_{13}	C_7H_{15}	C_8H_{18}	C_9H_{19}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{14}H_{29}$
Yield	83%	73%	93%	55%	41%	74%	72%

Scheme 2. Synthesis of crown ether derivatives **7** and their potassium complexes KI·**7**.

were recorded on a Varian MAT 711 spectrometer. MALDI-TOF spectra were recorded on a Bruker Reflex IV spectrometer.

2.1.1 4,4′,5,5′-Tetrakis(4″-methoxymethoxyphenyl)-dibenzo[18]crown-6 (**4**)

To a solution of **3** (1.63 g, 2.42 mmol) in degassed dimethoxyethane/H_2O (80 mL : 7 mL) were added borolane **2** (2.82 g, 10.7 mmol), Cs_2CO_3 (9.65 g, 29.6 mmol), CsF (6.63 g, 43.6 mmol) and $Pd(PPh_3)_4$ (0.33 g, 0.29 mmol) and the mixture was stirred at 95°C for 48 h. After cooling to room temperature, the residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 50 mL), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on SiO_2 (hexanes/EtOAc = 1 : 2) and recrystallisation from CH_2Cl_2/EtOH to yield **4** (1.43 g, 65 %) as colourless crystals. Melting point (m.p.) 162°C.

FTIR (ATR): 1605, 1500 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz), δ: 3.09 (s, 12H, CH_3), 3.77–3.78 (m, 8H, ArOCH$_2$CH_2O), 3.93–3.95 (m, 8H, ArOCH_2CH$_2$O), 4.79 (s, 8H, OCH_2OCH$_3$), 6.91 (s, 4H, 3-H, 6-H), 6.99–7.00 (m, 8H, 3′-H, 5′-H), 7.19–7.22 (m, 8H, 2′-H, 6′-H) ppm; ^{13}C NMR (C_6D_6, 125 MHz), δ: 55.6 (*C*H$_3$), 69.3, 70.1 (ArO*C*H$_2$*C*H$_2$O), 94.5 (O*C*H$_2$OCH$_3$), 116.2, 116.4 (C-3, C-6, C-3′, C-5′), 131.5 (C-2′, C-6″), 133.3, 136.0 (C-1′, C-4, C-5), 148.8 (C-1, C-2), 156.6 (C-4′) ppm; EIMS (*m*/*z* (%)): 906 (10), 905 (32), 904 (59) [M^+], 75 (5), 45 (100) [CH_2OCH_3]. Elemental analysis calculated for $C_{52}H_{56}O_{14}$: C 69.01, H 6.24; found: C 68.83, H 6.21.

2.1.2 4,4′,5,5′-Tetrakis(4″-hydroxyphenyl)-dibenzo[18]crown-6 (**5**)

To a solution of **4** (1.84 g, 2.03 mmol) in MeOH/CH_2Cl_2 (15 mL each) was added concentrated HCl (10 mL) and the reaction mixture was stirred at room temperature for 4 h. After evaporation of the solvent, **5** (1.49 g, quant.) was isolated as a colourless solid, which was used without further purification. M.p. 352°C.

FTIR (ATR): 3411, 1606, 1496 cm^{-1}; ^1H NMR (d_6-DMSO, 500 MHz), δ: 3.37 (bs, 8H, ArOCH$_2$CH_2O), 3.87 (bs, 8H, ArOCH_2CH$_2$O), 6.61–6.62 (m, 8H, 3′-H, 5′-H), 6.85 (s, 4H, 3-H, 6-H), 6.89–6.91 (m, 8H, 2′-H, 6′-H), 9.30 (bs, 4H, O*H*) ppm; ^{13}C NMR (d_6-DMSO, 125 MHz), δ: 67.8, 68.9 (ArO*C*H$_2$*C*H$_2$O), 114.5 (C-3, C-6), 114.7 (C-3′, C-5′), 130.6 (C-2′, C-6′), 131.97, 132.00 (C-4, C-5, C-1′), 146.7 (C-1, C-2), 155.7 (C-4′) ppm; EIMS (*m*/*z* (%)): 730 (12), 729 (47), 728 (100) [M^+], 364 (20), 320 (50), 294 (21), 247 (12), 84 (12). High resolution mass spectrometry (HRMS) (EI, *m*/*z*): calculated for $C_{44}H_{40}O_{10}$ 728.2621; found: 728.2642.

2.1.3 Synthesis of the crown ethers **7**

A solution of **5** (0.07 g, 0.10 mmol) in tetrahydrofuran/dimethylsulfoxide (THF/DMSO) (5 mL : 0.5 mL) was added to a solution of the respective gallic acid **6** (0.80 mmol), N, N′- dicyclohexyl carbodiimide (DCC) (0.21 g, 1.00 mmol) and 4-N, N-dimethylaminopyridine (0.18 g, 0.15 mmol) in CH_2Cl_2 (2 mL) at 0°C. The reaction mixture was warmed to room temperature and then stirred for 18 h. The precipitate was filtered off, and the filtrate concentrated and taken up in dichloromethane (40 mL). The solution was washed with HCl (1 M, 1 × 10 mL) and water (2 × 10 mL), dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with hexanes/EtOAc (3:1) to give products **7** as colourless solids.

2.1.3.1 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trihexyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7a**)

Yield: 260 mg, 83%; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.89–0.91 (m, 36H, CH_3), 1.33–1.34 (m, 48H, CH_2), 1.47–1.50 (m, 24H, CH_2), 1.74–1.84 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.08–4.10 (m, 8H, ArOCH$_2$CH_2O), 4.25–4.30 (m, 8H, ArOCH_2CH$_2$O), 6.96 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3'-H, 5'-H), 7.18–7.20 (m, 8H, 2'-H, 6'-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.0, 14.1 (CH_3), 22.6, 22.7, 25.7, 25.8, 29.3, 30.3, 31.7 (CH_2), 69.0 (ArOCH$_2$CH$_2$O), 69.3, 73.6 (OCH_2), 69.9 (ArOCH$_2$CH$_2$O), 108.5 (C-2″, C-6″), 115.7 (C-3, C-6), 121.3 (C-3′, C-5′), 123.9 (C-1″), 131.0 (C-2′, C-6′), 132.5 (C-4, C-5), 138.9 (C-1′), 143.0 (C-4″), 148.1, 149.6 (C-1, C-2, C-4′), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm; MS (MALDI-TOF): *m*/*z* 2368.302 $[M + Na]^+$. Elemental analysis calculated for $C_{144}H_{200}O_{26}$: C 73.69, H 8.59; found: C 73.62, H 8.66.

2.1.3.2 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-triheptyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7b**)

Yield: 230 mg, 73%; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.87–0.91 (m, 36H, CH_3), 1.26–1.39 (m, 72H, CH_2), 1.45–1.51 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.08–4.10 (m, 8H, ArOCH$_2$CH_2O), 4.28–4.29 (m, 8H, ArOCH_2CH$_2$O), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.09, 14.12 (*C*H$_3$), 22.6, 22.7, 26.00, 26.04, 29.1, 29.2, 29.3, 30.4, 31.8, 31.9 (*C*H$_2$), 69.0 (ArO*C*H$_2$CH$_2$O), 69.2, 73.6 (O*C*H$_2$), 69.9 (ArOCH$_2$*C*H$_2$O), 108.5 (C-2″, C-6″),

115.8 (C-3, C-6), 121.3 (C-3′, C-5′), 123.9 (C-1″), 131.0 (C-2′, C-6′), 132.5 (C-4, C-5), 138.9 (C-1′), 143.0 (C-4″), 148.1, 149.6 (C-1, C-2, C-4′), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm; MS (MALDI-TOF): *m/z* 2536.474 $[M + Na]^+$. Elemental analysis calculated for $C_{156}H_{224}O_{26}$: C 74.49, H 8.98; found: C 74.27, H 8.94.

2.1.3.3 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trioctyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7c**). Yield: 350 mg, 93%; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), *δ*: 0.86–0.91 (m, 36H, CH_3), 1.28–1.35 (m, 96H, CH_2), 1.45–1.50 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.07 (m, 24H, OCH_2), 4.09–4.10 (m, 8H, $ArOCH_2CH_2O$), 4.28–4.29 (m, 8H, $ArOCH_2CH_2O$), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR (C_6D_6, 125 MHz), *δ*: 14.3 (CH_3), 23.06, 23.08, 26.4, 25.6, 29.67, 29.71, 29.8, 29.9, 31.0, 32.2, 32.3 (CH_2), 69.1 ($ArOCH_2CH_2O$), 69.2, 73.6 (OCH_2), 70.0 ($ArOCH_2CH_2O$), 109.2 (C-2″, C-6″), 115.7 (C-3, C-6), 122.0 (C-3′, C-5′), 124.8 (C-1″), 131.5 (C-2′, C-6′), 132.7 (C-4, C-5), 139.6 (C-1′), 143.9 (C-4″), 149.0, 150.4 (C-1, C-2, C-4′), 153.8 (C-3″, C-5″), 165.1 (C=O) ppm; MS (MALDI-TOF): *m/z* 2704.798 $[M + Na]^+$. Elemental analysis calculated for $C_{168}H_{248}O_{26}$: C 75.19, H 9.31; found: C 75.01, H 9.23.

2.1.3.4 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trinonyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7d**). Yield: 220 mg, 55%; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), *δ*: 0.86–0.90 (m, 36H, CH_3), 1.27–1.37 (m, 120H, CH_2), 1.45–1.50 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.06 (m, 24H, OCH_2), 4.08–4.10 (m, 8H, $ArOCH_2CH_2O$), 4.27–4.29 (m, 8H, $ArOCH_2CH_2O$), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), *δ*: 14.1 (CH_3), 22.69, 22.71, 26.06, 26.09, 29.3, 29.38, 29.40, 29.6, 29.7, 30.4, 31.9, 32.0 (CH_2), 69.0 ($ArOCH_2CH_2O$), 69.2, 73.6 (OCH_2), 69.9 ($ArOCH_2CH_2O$), 108.5 (C-2″, C-6″), 115.7 (C-3, C-6), 121.3 (C-3′, C-5′), 123.9 (C-1″), 131.0 (C-2′, C-6′), 132.5 (C-4, C-5), 138.9 (C-1′), 143.0 (C-4″), 148.1, 149.6 (C-1, C-2, C-4′), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 2872.807 $[M + Na]^+$. Elemental analysis calculated for $C_{180}H_{272}O_{26}$: C 75.80, H 9.61; found: C 75.52, H 9.62.

2.1.3.5 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tridecyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7e**). Yield: 100 mg, 41 %; FTIR (ATR): 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), *δ*: 0.86–0.90 (m, 36H, CH_3), 1.27–1.37 (m, 144H, CH_2), 1.45–1.50 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.06 (m, 24H, OCH_2), 4.08–4.10 (m, 8H, $ArOCH_2CH_2O$), 4.27–4.29 (m, 8H, $ArOCH_2CH_2O$), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR (C_6D_6, 125 MHz), *δ*: 14.3 (CH_3), 23.1, 26.5, 26.6, 29.75, 29.79, 29.83, 30.01, 30.03, 30.05, 30.1, 30.2, 31.0, 32.3 (CH_2), 69.2 ($ArOCH_2CH_2O$, OCH_2), 70.0 ($ArOCH_2CH_2O$), 73.6 (OCH_2), 109.2 (C-2″, C-6″), 115.8 (C-3, C-6), 122.0 (C-3′, C-5′), 124.8 (C-1″), 131.5 (C-2′, C-6′), 132.7 (C-4, C-5), 139.6 (C-1′), 143.9 (C-4″), 149.0, 150.4 (C-1, C-2, C-4′), 153.8 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF) *m/z* 3041.126 $[M + Na]^+$. Elemental analysis calculated for $C_{192}H_{296}O_{26}$: C 76.35, H 9.88; C 76.29, H 9.73.

2.1.3.6 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tridodecyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7f**). Yield: 180 mg, 74 %; FTIR (ATR): 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), *δ*: 0.86–0.89 (m, 36H, CH_3), 1.26–1.37 (m, 192H, CH_2), 1.44–1.52 (m, 24H, CH_2), 1.74–1.85 (m, 24H, CH_2), 4.02–4.06 (m, 24H, OCH_2), 4.08–4.11 (m, 8H, $ArOCH_2CH_2O$), 4.28–4.29 (m, 8H, $ArOCH_2CH_2O$), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), *δ*: 14.1 (CH_3), 22.7, 26.07, 26.11, 29.3, 29.37, 29.41, 29.6, 29.65, 29.67, 29.71, 29.75, 29.77, 30.4, 31.9, 32.0 (CH_2), 69.0 ($ArOCH_2CH_2O$), 69.2, 73.6 (OCH_2), 69.8 ($ArOCH_2CH_2O$), 108.5 (C-2″, C-6″), 115.7 (C-3, C-6), 121.3 (C-3′, C-5′), 123.9 (C-1″), 131.0 (C-2′, C-6′), 132.5 (C-4, C-5), 138.9 (C-1′), 143.0 (C-4″), 148.1, 149.6 (C-1, C-2, C-4′), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 3377.572 $[M + Na]^+$. Elemental analysis calculated for $C_{216}H_{344}O_{26}$: C 77.28, H 10.33; found: C 77.20, H 10.30.

2.1.3.7 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tritetradecyloxybenzoyl)phenyl]dibenzo[18]crown-6 (**7g**). Yield: 210 mg, 72%; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), *δ*: 0.86–0.89 (m, 36H, CH_3), 1.25–1.35 (m, 240H, CH_2), 1.45–1.49 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.06 (m, 24H, OCH_2), 4.08–4.10 (m, 8H, $ArOCH_2CH_2O$), 4.26–4.29 (m, 8H, $ArOCH_2CH_2O$), 6.97 (s, 4H, 3-H, 6-H), 7.06–7.07 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), *δ*: 14.1 (CH_3), 22.7, 26.08, 26.11, 29.3, 29.38, 29.40, 29.42, 29.6, 29.65, 29.68, 29.72, 29.8, 30.4, 31.9 (CH_2), 69.0 ($ArOCH_2CH_2O$), 69.3, 73.6 (OCH_2), 69.9 ($ArOCH_2CH_2O$), 108.5 (C-2″, C-6″), 115.9 (C-3, C-6), 121.3 (C-3′, C-5′), 123.9 (C-1″), 131.0 (C-2′, C-6′), 132.5 (C-4, C-5), 138.9 (C-1′), 143.0 (C-4″), 148.1, 149.6 (C-1,

C-2, C-4′), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 3715.078 $[M + Na]^+$. Elemental analysis calculated for $C_{240}H_{392}O_{26}$: C 78.04, H 10.70; found: C 77.78, H 10.70.

2.1.4 Synthesis of the potassium complexes

A solution of KI (0.01 mmol) in MeOH (1 mL) was added to a solution of the respective **7** (0.01 mmol) in CH_2Cl_2 (1 mL) and the reaction mixture stirred overnight. After evaporation of the solvent, the residue was taken up in CH_2Cl_2 (2 mL) and filtered to remove any excess KI. Evaporation of the solvent and drying under high vacuum yielded the complexes KI·**7** as brown solids.

2.1.4.1 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trihexyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7a**). Yield: 21.5 mg, quant.; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.89–0.92 (m, 36H, CH_3), 1.30–1.38 (m, 48H, CH_2), 1.46–1.50 (m, 24H, CH_2), 1.73–1.86 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.23–4.38 (m, 16H, $ArOCH_2CH_2O$), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.0, 14.1 (CH_3), 22.6, 22.7, 25.70, 25.74, 25.9, 29.2, 29.7, 30.3, 31.0, 31.5, 31.7 (CH_2), 67.6, 69.1 ($ArOCH_2CH_2O$), 69.2, 73.6 (OCH_2), 108.5 (C-2″, C-6″), 113.6 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.5 (C-1, C-2, C-1′, C-2′), 149.7 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 2368.3 $[M + Na]^+$, 2384.3 $[M + K]^+$, calculated for $C_{144}H_{200}O_{26}K^+$: 2384.4.

2.1.4.2 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-triheptyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7b**). Yield: 26.8 mg, quant.; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.87–0.91 (m, 36H, CH_3), 1.29–1.39 (m, 72H, CH_2), 1.45–1.51 (m, 24H, CH_2), 1.73–1.86 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.21–4.42 (m, 16H, $ArOCH_2CH_2O$), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3'-H, 5'-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.09, 14.12 (CH_3), 22.6, 22.7, 25.70, 26.00, 26.04, 29.1, 29.2, 29.3, 30.3, 31.8, 31.9 (CH_2), 67.4, 68.9 ($ArOCH_2CH_2O$), 69.3, 73.6 (OCH_2), 108.5 (C-2″, C-6″), 113.5 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.3 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF) *m/z* 2536.6 $[M + Na]^+$, 2552.5 $[M + K]^+$, calculated for $C_{156}H_{224}O_{26}K^+$: 2552.6.

2.1.4.3 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trioctyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7c**). Yield: 14.3 mg, quant.; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.86–0.90 (m, 36H, CH_3), 1.26–1.38 (m, 96H, CH_2), 1.45–1.51 (m, 24H, CH_2), 1.73–1.86 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.26–4.40 (m, 16H, $ArOCH_2CH_2O$), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.1 (CH_3), 22.67, 22.70, 26.05, 26.09, 29.28, 29.34, 29.4, 29.5, 30.3, 31.8, 31.9 (CH_2), 67.4, 68.9 ($ArOCH_2CH_2O$), 69.3, 73.6 (OCH_2), 108.5 (C-2″, C-6″), 113.4 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.2 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 2704.9 $[M + Na]^+$, 2720.9 $[M + K]^+$, calculated for $C_{168}H_{248}O_{26}K^+$: 2720.8.

2.1.4.4 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-trinonyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7d**). Yield: 27.2 mg, quant.; FTIR (ATR): 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.86–0.90 (m, 36H, CH_3), 1.27–1.37 (m, 120H, CH_2), 1.45–1.51 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.24–4.42 (m, 16H, $ArOCH_2CH_2O$), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.11, 14.13 (CH_3), 22.69, 22.71, 26.06, 26.09, 29.3, 29.38, 29.40, 29.6, 29.7, 30.4, 31.8, 31.9 (CH_2), 67.4, 68.9 ($ArOCH_2CH_2O$), 69.3, 73.6 (OCH_2), 108.5 (C-2″, C-6″), 113.4 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.2 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 2873.1 $[M + Na]^+$, 2889.1 $[M + K]^+$, calculated for $C_{180}H_{272}O_{26}K^+$: 2889.0.

2.1.4.5 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tridecyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7e**). Yield: 19.5 mg, quant.; FTIR (ATR): 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ: 0.86–0.90 (m, 36H, CH_3), 1.27–1.36 (m, 144H, CH_2), 1.45–1.50 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.07 (m, 24H, OCH_2), 4.26–4.39 (m, 16H,

ArOCH_2CH_2O), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.1 (*C*H_3), 22.70, 22.72, 26.07, 26.10, 29.3, 29.36, 29.41, 29.60, 29.64, 29.69, 29.74, 30.4, 31.9, 32.0 (*C*H_2), 67.4, 68.9 (ArO*C*H_2*C*H_2O), 69.3, 73.6 (O*C*H_2), 108.5 (C-2″, C-6″), 113.5 (C-3, C-6), 121.4 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.2 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 3041.0 $[M + Na]^+$, 3057.0 $[M + K]^+$, calculated for $C_{192}H_{296}O_{26}K^+$: 3057.1.

2.1.4.6 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tridodecyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7f**). Yield: 18.3 mg, quant.; FTIR (ATR): 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.86–0.89 (m, 36H, CH_3), 1.26–1.35 (m, 192H, CH_2), 1.45–1.50 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.03–4.07 (m, 24H, OCH_2), 4.24–4.40 (m, 16H, ArOCH_2CH_2O), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.1 (*C*H_3), 22.7, 26.07, 26.10, 29.3, 29.38, 29.41, 29.6, 29.65, 29.67, 29.71, 29.8, 30.4, 31.9, 32.0 (*C*H_2), 67.4, 69.1 (ArO*C*H_2*C*H_2O), 69.3, 73.6 (O*C*H_2), 108.5 (C-2″, C-6″), 113.5 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.2 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 3377.8 $[M + Na]^+$, 3393.9 $[M + K]^+$, calculated for $C_{216}H_{344}O_{26}K^+$: 3393.5.

2.1.4.7 4,4′,5,5′-Tetrakis[4″-(3‴,4‴,5‴-tritetradecyloxybenzoyl)phenyl]dibenzo[18]crown-6 potassium iodide complex (KI·**7g**). Yield: 15.4 mg, quant.; FTIR (ATR): 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.86–0.89 (m, 36H, CH_3), 1.25–1.35 (m, 240H, CH_2), 1.45–1.49 (m, 24H, CH_2), 1.73–1.85 (m, 24H, CH_2), 4.02–4.07 (m, 24H, OCH_2), 4.25–4.43 (m, 16H, ArOCH_2CH_2O), 6.94 (s, 4H, 3-H, 6-H), 7.07–7.09 (m, 8H, 3′-H, 5′-H), 7.18–7.20 (m, 8H, 2′-H, 6′-H), 7.39 (s, 8H, 2″-H, 6″-H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 14.1 (*C*H_3), 22.7, 26.07, 26.11, 29.31, 29.38, 29.40, 29.42, 29.6, 29.65, 29.68, 29.72, 29.8, 30.4, 31.0, 31.9 (*C*H_2), 67.4, 68.8 (ArO*C*H_2*C*H_2O), 69.3, 73.6 (O*C*H_2), 108.5 (C-2″, C-6″), 113.4 (C-3, C-6), 121.5 (C-3′, C-5′), 123.8 (C-1″), 131.0 (C-2′, C-6′), 132.8 (C-4, C-5), 138.5 (C-1′), 143.0 (C-4″), 146.2 (C-1, C-2, C-1′, C-2′), 149.8 (C-4″), 153.0 (C-3″, C-5″), 165.1 (C=O) ppm. MS (MALDI-TOF): *m/z* 3714.1 $[M + Na]^+$, 3730.1 $[M + K]^+$, calculated for $C_{240}H_{392}O_{26}K^+$: 3729.9.

2.2 Mesophase characterisation

X-ray experiments were performed on a Bruker Nanostar; software: SAXS 4.1.26. The samples were kept in Hilgenberg glass capillaries of 0.7 mm outside diameter in a temperature-controlled hot stage (±1°C). A monochromatic Cu–$K_{\alpha 1}$ beam (λ = 1.5405 Å) was obtained using a ceramic tube generator (1500 W) with cross-coupled Göbel mirrors as the monochromator. The diffraction patterns were recorded on a real-time two-dimensional detector (HI-STAR, Bruker). The calibration of the patterns occurred with the powder pattern of Ag-Behenate. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822, and polarising optical microscopy using an Olympus BX50 polarising microscope combined with a Linkam LTS350 hot stage and a Linkam TP93 central processor.

3. Results and discussion

3.1 Synthesis of crown ethers and their potassium complexes

The synthesis of target crown ethers **7** commenced with fourfold Suzuki coupling [34, 35] of methoxymethyl (MOM)-protected borolane **2** [28–32, 35] with tetrabromodibenzo[18]crown-6 **3** [33, 36] under modified coupling conditions (Scheme 2). In order to circumvent the high coordination tendency of the crown ether moiety towards potassium cations, Cs_2CO_3 (five equivalents) and CsF (five equivalents) replaced the commonly used potassium salts giving coupling product tetrakis(4-methoxymethoxyphenyl)dibenzo[18]crown-6 **4** in 59% yield. Subsequent removal of the MOM groups was achieved with HCl in MeOH at room temperature. Because of poor solubility, the resulting colourless alcohol **5** was directly treated with gallic acids **6a**–**g** [37] in the presence of DCC and DMAP in DMSO/THF (10 : 1) at room temperature according to a procedure by Andreu *et al.* [38] to give the gallic esters **7a**–**g** in 41–93% yield. Treatment with KI in acetone at room temperature following the procedure by Pedersen [39] finally yielded the complexes KI·**7a**–**g** quantitatively. The presence of (1:1) crown : salt ratios was stated by Matrix–Assisted Laser Desorption/Ionisation – Time of Flight (MALDI-TOF) mass spectrometry and NMR spectroscopy, as previously discussed in detail [27]. Whereas neat crown ethers **7** do not show a $[M + K^+]$ peak in MALDI-TOF mass spectra, this peak is the most dominant one in the spectra of the complexes KI·**7** and thus can be taken as evidence for complexation [27]. For further information, NMR spectra were examined in detail. In ^{1}H NMR spectra of neat derivatives **7** the H-a and H-b proton signals (for the numbering see Scheme 2) were detected as multiplets at δ = 4.09 and δ = 4.29 ppm, respectively.

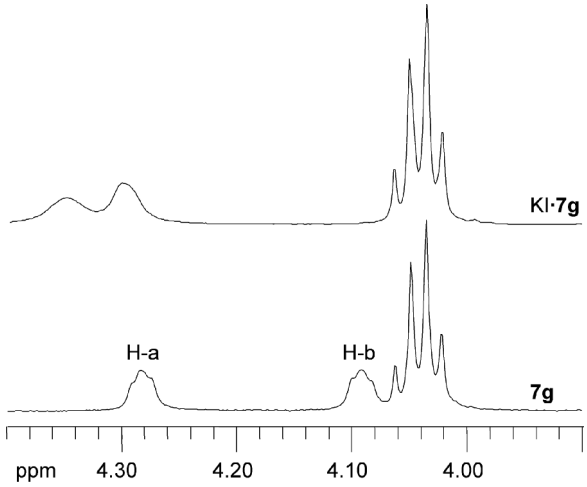


Figure 1. Section of the ^{1}H NMR spectra (500 MHz, $CDCl_3$) of derivatives **7g** and KI·**7g**.

After complexation, these signals are shifted downfield to $\delta = 4.30$ and $\delta = 4.35$ ppm, respectively, as exemplified for derivative **7g** and KI·**7g** (see Figure 1). Such a downfield shift is typical for the (1:1) complexation mode [40–42].

In the ^{13}C NMR spectra, complexation of **7** with KI led to an upfield shift of the C-a and C-b signals by $\Delta\delta = 1$–1.7 ppm from $\delta = 69.04$ and $\delta = 69.89$ ppm to $\delta = 67.37$ and $\delta = 68.84$ ppm, respectively, a value which is typical for the formation of tight ion pairs (see Figure 2) [40–42].

3.2 Mesomorphic properties

The mesomorphic properties of gallic esters **7a**–**g** and their KI complexes KI·**7a**–**g** were investigated by DSC (see Table 1) and polarising optical microscopy.

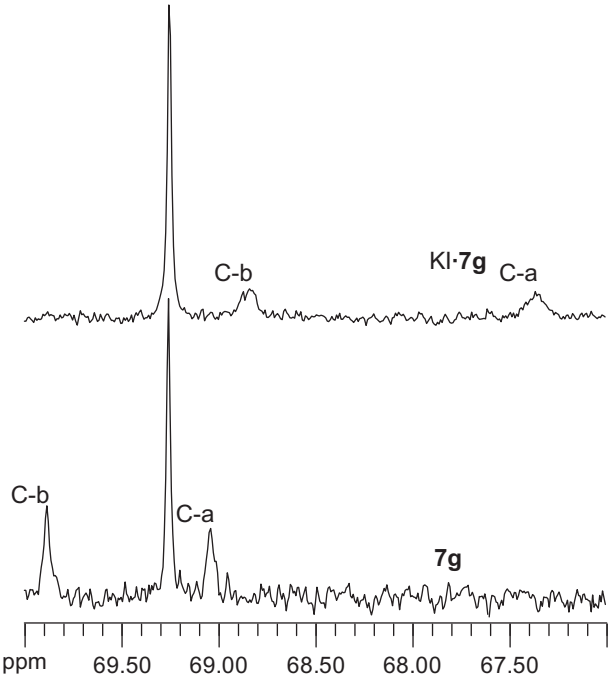


Figure 2. Section of the ^{13}C NMR spectra (125 MHz, $CDCl_3$) of derivatives **7g** and KI·**7g**.

Compounds **7** were isolated as sticky solids, which underwent a glass transition upon heating and a clearing transition at elevated temperatures. With the exception of compound **7f**, the derivatives **7** displayed enantiotropic mesophases. In contrast, crown ether **7g** was non-mesomorphic. A typical DSC trace is shown in Figure 3 for compound **7a**.

Under the microscope pseudo-focal conic textures were observed for all derivatives **7a**–**f** upon slow cooling from the isotropic liquid, as exemplified for crown ether **7e** in Figure 4(a). These textures are

Table 1. Phase transition temperatures and enthalpies ΔH of gallic esters **7a**–**f** [a].

7	R =	G	T_g [°C]	Col_h	T [°C]	ΔH [kJ mol^{-1}]	I	
a	C_6H_{13}	•	59.0	•	91.1	5.7	•	1. heating
		–		•	83.6	–5.4	•	1. cooling
b	C_7H_{15}	•	56.4	•	89.4	5.2	•	1. heating
		–		•	80.9	–5.3	•	1. cooling
c	C_8H_{17}	•	57.4	•	98.5	6.0	•	1. heating
		–		•	95.9	–5.6	•	1. cooling
d	C_9H_{19}	•	59.7	•	85.9	4.3	•	1. heating
		–		•	77.8	–4.8	•	1. cooling
e	$C_{10}H_{21}$	•	62.8	•	94.6	5.3	•	1. heating
		–		•	88.1	–5.1	•	1. cooling
f	$C_{12}H_{25}$	•	53.6	•	79.0	0.7	•	1. heating
	[b]	–		–		–	•	1. cooling

Notes: [a] • Phase was observed, – phase was not observed, G = glass; heating/cooling rate 5 K min^{-1}.
[b] The transition of the isotropic liquid in the Col_h mesophase was not observed but crystallisation occurred at –20.1°C (–10.7 kJ mol^{-1}) upon cooling.

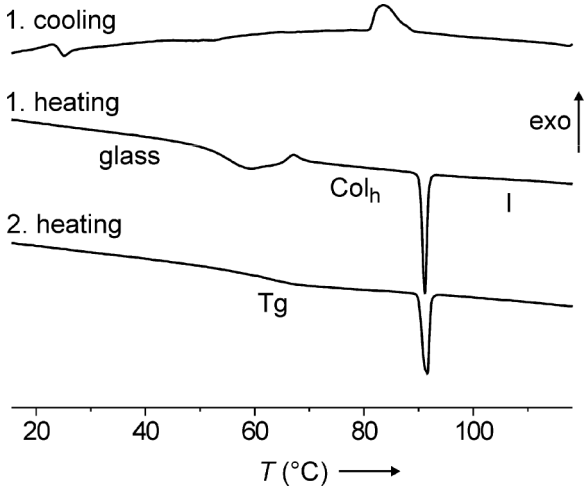


Figure 3. DSC traces of compound **7a** (heating/cooling rate 5 K min^{-1}).

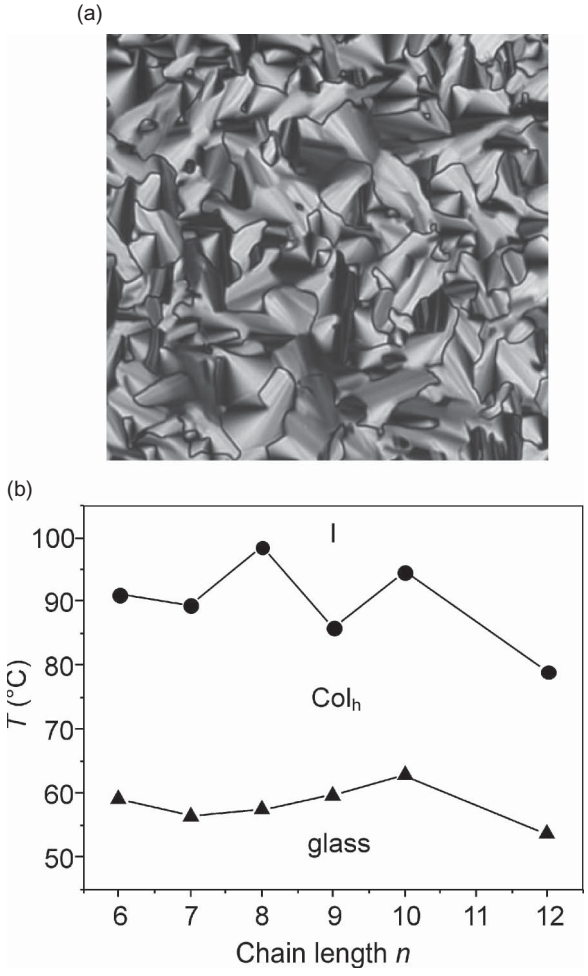


Figure 4. (a) Pseudo-focal conic texture of gallic ester **7e** at 80°C as seen between crossed polarisers upon cooling from the isotropic liquid (cooling rate 1 K min^{-1}, magnification × 200). (b) Dependence of the phase transition temperature on chain lengths of crown ether derivatives **7a**–**f**.

characteristic for columnar mesophases [43]. The phase type was assigned unambiguously by X-ray diffraction (see later). Neither derivative could be converted to the crystalline phase. A pronounced odd–even effect of the clearing temperatures of crown ethers **7** was found (Figure 4(b)). The compounds with even-numbered side chains (concerning the number of C atoms in the side chains of the gallic acid moieties) showed a higher clearing point than the homologues with odd-numbered side chains.

3.3 X-ray diffraction

Temperature-dependent X-ray diffraction experiments were carried out on samples of **7** which were aligned by extrusion of thin fibres. The results are summarised in Table 2.

In the wide-angle region ($2\theta \sim 20°$) a broad, diffuse scattering halo was observed which corresponds to a spacing of 4.6 Å. The halo originates from the overlapping intensities from diffuse scattering of the alkyl chains in a liquid-like order and the disordered intracolumnar stacking of the aromatic units [44–47]. Therefore, the exact intracolumnar distance between neighbouring molecules could not be determined. However, there is only one maximum and no splitting of the signals which would point to a regular inclination of mesogens.

X-ray diffraction patterns and small-angle scattering (SAXS) confirmed a hexagonal columnar mesophase for all derivatives **7a**–**f**. At 70°C, four (three for **7f** at room temperature) sharp reflections with reciprocal spacings in the ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$ were observed at small angles. These peaks were indexed as $(hk) = (10), (11), (20), (21)$ being characteristic of a two-dimensional hexagonal lattice. Figure 5 reveals the X-ray diffraction profile of ester **7a** which is typical for all derivatives **7**.

When samples of **7** were cooled from the hexagonal columnar mesophase to room temperature, X-ray diffraction revealed that the resulting glasses still retain their columnar order. This behaviour might be useful for applications in optoelectronics because the frozen columnar order should retain charge transport mobilities as required for xerographic applications, organic field effect transistors and light emitting diodes (see for example [48–50]). It should be noted that the lattice parameter a increases with decreasing temperature. For example, a increases for gallic ester **7f** from 46.6 Å at 50°C to 47.7 Å at room temperature (see Table 2). With decreasing temperature, the intracolumnar distance between the discs decreases. Consequently, there is less space for the aliphatic chains along the columns and they must extend in the plane of the discs leading to a higher degree of s-trans configured aliphatic chains, and thus to larger

Table 2. X-ray diffraction data of the Col_h mesophases of compounds **7a**–**f**.

7	T [°C]	Parameter	2θ [°]	d_{obs} [Å]	d_{calc} [Å]	hk	Z [a]
7a	70	$a = 41.1$ Å	2.48	35.56	35.56	10	1.7
			4.32	20.45	20.53	11	
			4.98	17.72	17.78	20	
			6.65	13.28	13.44	21	
			19.33 halo	4.59	–		
7b	70	$a = 41.9$ Å	2.44	36.25	36.25	10	1.7
			4.20	21.02	20.93	11	
			4.86	18.16	18.12	20	
			6.50	13.58	13.70	21	
7c	70	$a = 43.3$ Å	2.36	37.46	37.46	10	1.7
			4.08	21.63	21.63	11	
			4.71	18.75	18.73	20	
			6.35	13.91	14.16	21	
7d	70	$a = 43.8$ Å	2.33	37.94	37.94	10	1.6
			3.99	22.11	21.90	11	
			4.63	19.06	18.97	20	
			6.22	14.20	14.34	21	
7e	70	$a = 45.0$ Å	2.27	38.92	38.92	10	1.6
			3.87	22.79	22.47	11	
			4.51	19.59	19.46	20	
			6.01	14.68	14.71	21	
7f	50	$a = 46.6$ Å	2.19	40.35	40.35	10	1.6
			3.73	23.68	23.29	11	
			4.34	20.33	20.17	20	
			5.85	15.09	15.25	21	
	r.t.	$a = 47.7$ Å	2.14	41.34	41.34	10	1.6
			3.73	23.68	23.87	11	
			4.34	20.33	20.67	20	

Notes: [a] The number of molecules in the unit cell, Z, was calculated by using Equation (1), where N_A = Avogadro's constant, $a^2 \cdot \sin 60$ = columnar cross section, M = molecular weight, ρ = density (assumed 1 g cm^{-3} for organic substances), h = height of the columnar unit, obtained from the angular position of the halo in the wide-angle X-ray scattering (WAXS) measurements, r.t. = room temperature.

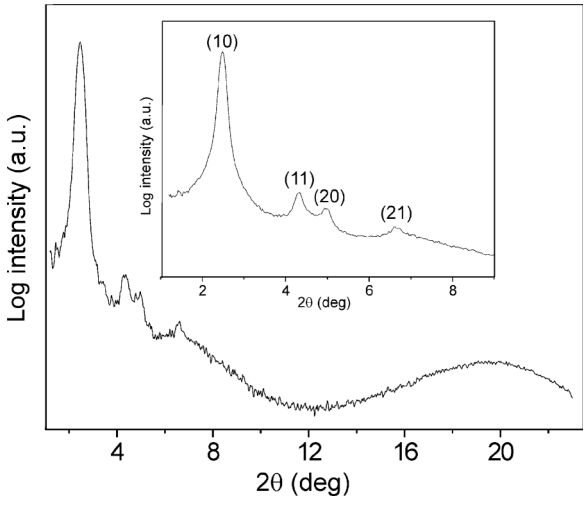


Figure 5. X-ray diffraction profile (whole section) of compound **7a** at 70°C in the hexagonal columnar mesophase; inset: SAXS profile.

parameters a. Increasing the temperature results in a larger distance of the discs, the formation of gauche configured aliphatic chains and thus a smaller disc diameter albeit with an increasing volume of the columnar unit.

3.4 Packing study

It seems surprising that the ellipsoid molecules **7** form hexagonal columnar mesophases rather than rectangular columnar mesophases. In order to explain this particular packing pattern, we assume that the polar core units are located at the centre of the column while the non-polar alkyl chains form a hydrophobic mantle [11, 51]. Following a method by Donnio *et al.* [52] the number of molecules forming a columnar unit, Z, was calculated from the X-ray data by using the following equation:

$$Z = N_A \cdot a^2 \cdot \sin 60 \cdot h \cdot \rho \cdot M^{-1}. \quad (1)$$

Although the intracolumnar distance could not be exactly determined as mentioned above, the d value of 4.6 Å from the broad halo in the wide-angle

region is in good agreement with typical core–core interactions. Applying Equation (1) to derivatives **7** resulted in $Z = 1.6$–1.7 (see Table 2). It must be mentioned that a density of $\rho \sim 1$ is a rough estimate, lowering the accuracy of the calculation. As the hexagonal lattice consists only of one column per unit cell with a circular cross section, presumably the crown ethers are oriented perpendicular on top of each other. A similar packing was studied recently by Percec *et al.* [53]. A schematic drawing of the packing pattern of **7a** is shown in Figure 6(a). The proposed structure was supported by simple molecular modelling of such a disc containing a dimeric unit by using Chem3D with energy minimisation (see Figure 6(b)).

Unexpectedly, none of the complexes KI·**7** revealed any mesomorphic properties (see Table S1 in the supplementary material which is available via the multimedia link on the online article webpage). Only a glass to crystal transition was found in each case. The complete destabilisation of the columnar mesophase by complexation with KI could arise from tight ion pairs (see Figure 2), which introduce a high degree of order preventing mesophase formation, or it seems also conceivable that the salt increased the polarity and thus induced crystallisation. Coco *et al.* recently reported the stabilisation of smectic mesophases of dibenzo[18]crown-6 derivatives with peripheral Pd complexes upon complexation with $KClO_4$. The stabilising effect was attributed to $K^+ \cdots O_2ClO_2^-$ interactions [54]. In our case, the polar gallic ester moieties might interfere with the counterion, thus destabilising the intracolumnar packing via the KI salt.

4. Summary

A novel class of liquid crystalline crown ethers **7** with ellipsoid molecular shape were accessible from MOM-protected borolane **2** in three steps involving modified Suzuki coupling, removal of the MOM group and esterification with gallic acids. Regardless of side chain lengths and despite their shape, compounds **7a**–**f** display hexagonal columnar mesophases, whose order was maintained even in the glassy state. However, upon complexation of compounds **7a**–**f** with KI, mesomorphism is completely lost, revealing that a subtle balance of polar and non-polar moieties is required for broad mesophases.

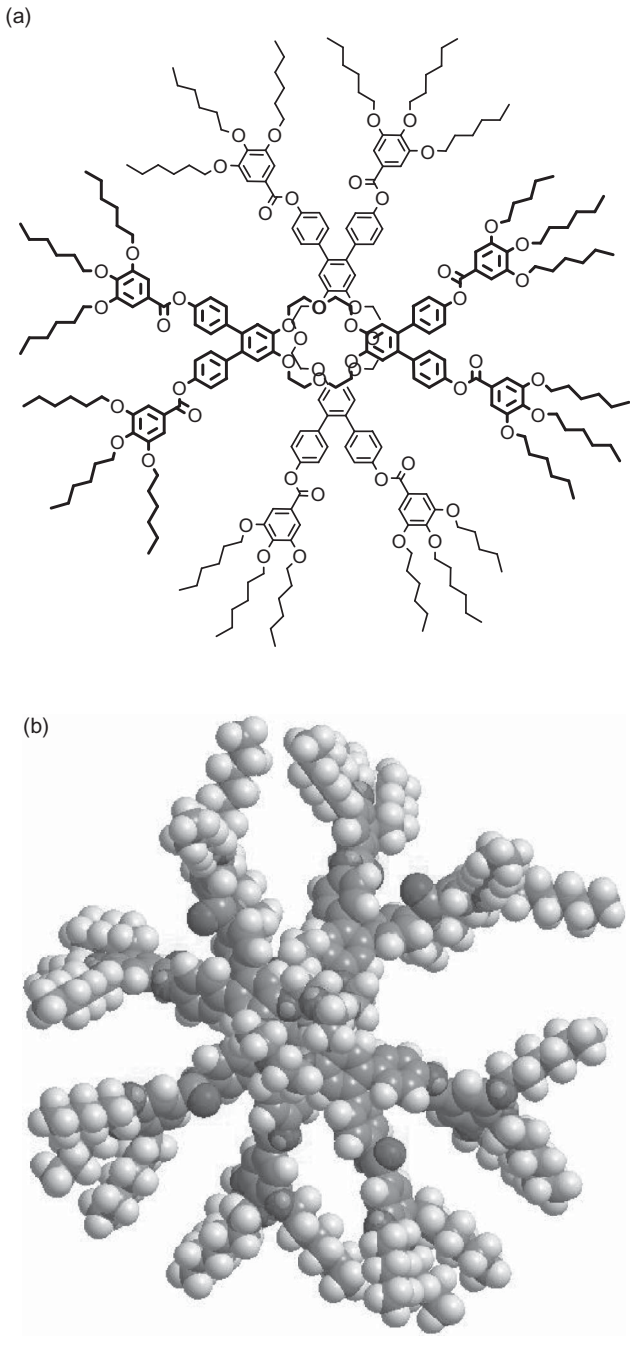


Figure 6. (a) A schematic drawing of a dimeric subunit of compound **7a** consisting of two molecules oriented perpendicular with respect to each other. (b) A model of the dimeric subunit of **7a** obtained by molecular modelling (Chem3D with energy minimisation) (colour version online).

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft, the Max-Planck-Gesellschaft (International Max Planck Research School for Advanced Materials fellowship for M. K.), the Fonds der Chemischen Industrie, the Bundesministerium für Bildung und Forschung (BMBF grant #01 RI 05177) and the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg is gratefully acknowledged. We would like to thank one of the referees for valuable suggestions.

References

[1] Sergeyev, S.; Pisula, W.; Geerts, Y.H. *Chem. Soc. Rev*. **2007**, *36*, 1902–1929.

[2] Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem*. **2007**, *119*, 4916–4973; Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem. Int. Ed*. **2007**, *46*, 4832–4887.

[3] Ohta, K.; Hatsusaka, K.; Sugibayashi, M.; Ariyoshi, M.; Ban, K.; Maeda, F.; Naito, R.; Nishizawa, K.; van de Craats, A.M.; Warman, J.M. *Mol. Cryst. Liq. Cryst*. **2003**, *397*, 325–345.

[4] Guillon, D. *Structure and Bonding*, Vol. 95; Springer: Berlin, 1999; pp 41–82.

[5] Kumar, S. *Chem. Soc. Rev*. **2006**, *35*, 83–109.

[6] Boden, N.; Bushby, R.J.; Lozman, O.R. *Mol. Cryst. Liq. Cryst*. **2003**, *400*, 105–113.

[7] Tschierske, C. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem*. **2001**, *97*, 191–267.

[8] Nolte, R.J.M. *Liq. Cryst*. **2006**, *33*, 1373–1377.

[9] Akopova, O.B. *Russ. J. Gen. Chem*. **2002**, *72*, 1531–1548.

[10] Abdallah, D.J.; Weiss, R.G. *Adv. Mater*. **2000**, *12*, 1237–1247.

[11] Tschierske, C. *J. Mater. Chem*. **1998**, *8*, 1485–1508.

[12] Goodby, J.W.; Mehl, G.H.; Saez, I.M.; Tuffin, R.P.; Mackenzie, G.; Auzély-Velty, R.; Benvegnu, T.; Plusquellec, D. *Chem. Commun*. **1998**, 2057–2070.

[13] van Nostrum, C.F. *Adv. Mater*. **1996**, *8*, 1027–1030.

[14] Schröter, J.A.; Tschierske, C.; Wittenberg, M.; Wendorff, J.H. *Angew. Chem*. **1997**, *109*, 1160–1163; Schröter, J.A.; Tschierske, C.; Wittenberg, M.; Wendorff, J.H. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1119–1121.

[15] Gutiérrez-Nava, M.; Jaeggy, M.; Nierengarten, H.; Masson, P.; Guillon, D.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett*. **2003**, *44*, 3039–3042.

[16] Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D.J.P. *Chem. Eur. J*. **2002**, *8*, 2011–2025.

[17] Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S.V. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1411–1420.

[18] Beginn, U.; Zipp, G.; Möller, M. *Chem. Eur. J*. **2000**, *6*, 2016–2023.

[19] Beginn, U.; Zipp, G.; Möller, M. *Adv. Mater*. **2000**, *12*, 510–513.

[20] Beginn, U.; Zipp, G.; Mourran, A.; Walther, P.; Möller, M. *Adv. Mater*. **2000**, *12*, 513–516.

[21] Percec, V.; Zipp, G.; Johansson, G.; Beginn, U.; Möller, M. *Macromol. Chem. Phys*. **1997**, *198*, 265–277.

[22] Samorí, P.; Engelkamp, H.; de Witte, P.; Rowan, A.E.; Nolte, R.J.M.; Rabe, J.P. *Angew. Chem*. **2001**, *113*, 2410–2412; Samorí, P.; Engelkamp, H.; de Witte, P.; Rowan, A.E.; Nolte, R.J.M.; Rabe, J.P. *Angew. Chem. Int. Ed*. **2001**, *40*, 2348–2350.

[23] Engelkamp, H.; Middelbeek, S.; Nolte, R.J.M. *Science* **1999**, *284*, 785–788.

[24] Steinke, N.; Frey, W.; Baro, A.; Laschat, S.; Drees, C.; Nimtz, M.; Hägele, C.; Giesselmann, F. *Chem. Eur. J*. **2006**, *12*, 1026–1035.

[25] He, G.-X.; Wada, F.; Kikukawa, K.; Shinkai, S.; Matsuda, T. *J. Org. Chem*. **1990**, *55*, 541–548.

[26] Schultz, A.; Laschat, S.; Saipa, A.; Gießelmann, F.; Nimtz, M.; Schulte, J.L.; Baro, A.; Miehlich, B. *Adv. Funct. Mater*. **2004**, *14*, 163–168.

[27] Kaller, M.; Tussetschläger, S.; Fischer, P.; Deck, C.; Baro, A.; Giesselmann, F.; Laschat, S. *Chem. Eur. J*. **2009**, *15*, 9530–9542.

[28] Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633–9695.

[29] Herrmann, W.A. In *Applied Homogeneous Catalysis with Organometallic Compounds*: Cornils, B., Herrmann, W.A., Eds.; Wiley-VCH: Weinheim, 2002; pp 591–598.

[30] Beller, M.; Zapf, A. In *Handbook of Organopalladium Chemistry for Organic Synthesis*: Negishi, E., Ed.; Wiley: New York, 2002; pp 1209–1222.

[31] Suzuki, A. *J. Organomet. Chem*. **1999**, *576*, 147–168.

[32] Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457–2483.

[33] Hird, M.; Toyne, K.J.; Slaney, A.J.; Goodby, J.W.; Gray, G.W. *J. Chem. Soc. Perkin Trans. 2* **1993**, 2337–2349.

[34] Krämer, C.S.; Zimmermann, V; Sailer, V; Müller, T.J.J. *Synthesis* **2002**, 1163–1170.

[35] Steinke, N.; Jahr, M.; Lehmann, M.; Baro, A.; Frey, W.; Tussetschläger, S.; Sauer, S.; Laschat, S. *J. Mater. Chem*. **2009**, *19*, 645–654.

[36] Lowe, N.D.; Garner, C.D. *J. Chem. Soc. Dalton Trans*. **1993**, 2197–2207.

[37] Sheehan, J.C.; Hess, G.P. *J. Am. Chem. Soc*. **1955**, *77*, 1067–1068.

[38] Andreu, R.; Garín, J.; Orduna, J.; Barberá, J.; Serrano, J.L.; Sierra, T.; Sallé, M.; Gorgues, A. *Tetrahedron* **1998**, *54*, 3895–3912.

[39] Pedersen, C.J. *J. Am. Chem. Soc*. **1967**, *89*, 7017–7036.

[40] Live, D.; Chan, S.I. *J. Am. Chem. Soc*. **1976**, *98*, 3769–3778.

[41] Lockhart, J.C.; Robson, A.C.; Thompson, M.E.; Tyson, P.D.; Wallace, I.H.M. *J. Chem. Soc. Dalton Trans*. **1978**, 611–617.

[42] Fedarko, M.-C. *J. Magn. Resonance* **1973**, *12*, 30–35.

[43] Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen, H.T.; Levelut, A.M.; Malthête, J. *Mol. Cryst. Liq. Cryst*. **1984**, *106*, 121–146.

[44] Prasad, S.K.; Shankar Rao, D.S.; Chandrasekhar, S.; Kumar, S. *Mol. Cryst. Liq. Cryst*. **2003**, *396*, 121–139.

[45] Levelut, A.M.; Malthête, J.; Collet, A. *J. Physique* **1986**, *47*, 351–357.

[46] Levelut, A.M. *J. Chim. Phys. Phys.-Chim. Biol*. **1983**, *80*, 149–161.

[47] Levelut, A.M. *J. Physique Lett*. **1979**, *40*, 81–84.

[48] Adam, D.; Schuhmacher, P.; Simmerer, J.; Häußling, L.; Paulus, W.; Siemensmeyer, K.; Etzbach, K.-H.; Ringsdorf, H.; Haarer, D. *Adv. Mater*. **1995**, *7*, 276–280.

[49] Werth, M.; Vallerien, S.U.; Spiess, H.W. *Liq. Cryst*. **1991**, *10*, 759–770.

[50] Vallerien, S.U.; Werth, M.; Kremer, F.; Spiess, H.W. *Liq. Cryst*. **1990**, *8*, 889–893.

[51] Tschierske, C. *J. Mater. Chem*. **2001**, *11*, 2647–2671.

[52] Donnio, B.; Heinrich, B.; Allouchi, H.; Kain, J.; Diele, S.; Guillon, D.; Bruce, D.W. *J. Am. Chem. Soc*. **2004**, *126*, 15258–15268.

[53] Percec, V.; Won, B.C.; Peterca, M.; Heiney, P.A. *J. Am. Chem. Soc*. **2007**, *129*, 11265–11278.

[54] Coco, S.; Cordovilla, C.; Espinet, P.; Gallani, J.-L.; Guillon, D.; Donnio, B. *Eur. J. Inorg. Chem*. **2008**, 1210–1218.