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Liquid Crystals

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Online publication date: 10 December 2010

To cite this Article Kovářová, Anna , Svoboda, Jiří , Novotná, Vladimíra , Glogarová, Milada , Salamonczyk, Mirosław , Pocięcha, Damian and Gorecka, Ewa(2010) '[2]Benzothiophene bent-shaped liquid crystals', *Liquid Crystals*, 37: 12, 1501 – 1513

To link to this Article: DOI: 10.1080/02678292.2010.530299

URL: <http://dx.doi.org/10.1080/02678292.2010.530299>

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[2]Benzothiophene bent-shaped liquid crystals

Anna Kovářová^a, Jiří Svoboda^{a*}, Vladimíra Novotná^b, Milada Glogarová^b, Mirosław Salamonczyk^c, Damian Pocięcha^c and Ewa Gorecka^c

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(Received 7 July 2010; final version received 5 October 2010)

New liquid crystalline (LC) compounds containing the [2]benzothiophene chromophore unit have been synthesised and their mesomorphic and fluorescent properties studied. Mesomorphic and fluorescent properties have been modified by various chemical moieties. Among others, terminal fluoroalkyl and/or chiral chains were introduced to stabilise mesophases and support the formation of polar phases. In spite of the bent shape due to the central 1,3-diphenylbenzo[*c*]thiophene unit, all compounds exhibit phases typical for the rod-like LC: nematic, smectic A and smectic C or their chiral analogues using the chiral (*S*)-C₂H₅CH(CH₃)(CH₂)₆CO or (*S*)-C₁₀H₂₁OCH(CH₃)CO chain. The orientational order in the nematic phase was studied by polarised infrared measurements. The fluorescent properties of the studied compounds have been measured and their parameters established.

Keywords: [2]benzothiophene; liquid crystals; mesomorphic properties; fluorescence; polarised infrared measurements

1. Introduction

In the past decade, bent-shaped liquid crystals have become the object of considerable interest and their general structure–property relationships have been recognised and reviewed [1–4]. However, only a few heterocyclic ring systems were incorporated as a central core in the bent materials. While the six-membered heterocycles such as 2,6-disubstituted pyridine [5], tetrahydropyran [6] and piperazine [7–9] preserve the bending angle around 120°, the introduction of five-membered heterocyclic units such as 1,3,4-oxadiazole [10–12], 1,2,4-oxadiazole [13], 1,3-oxazole [14], 1,3,4-thiadiazole [2,15] and thiophene [16] increases the bend angle, and both calamitic and banana phases were observed. The incorporation of a fluorescent moiety into the molecule leads to new functional LC materials, which can be tuned by an external stimulus [17–20]. Changes of the polarised absorption or emission intensity by the applied electric field give the possibility to control the polarisation of emitted or absorbed light by the electric field [21, 22]. This is favourable for liquid crystalline phases with a strongly dichroic character, i.e. for molecules which absorb light with an electric field only along a particular molecular direction and with strong emission in the visible range. Among such materials, anthraquinone, naphthalimide [23, 24], acenequinone [25], oligothiophenes [26, 27], benzothiadiazole [28–30], perylene [31, 32], cyanine derivatives [33], pyrene [34–36], oxadiazole [37–39] and BODIPY-dyes [40, 41] belong to those

that have been most intensively studied. As a continuation of our study of new heterocyclic liquid crystals [42–47], we herein report the synthesis and physical study of a series of liquid crystals with the fluorescent 1,3-diphenyl[2]benzothiophene central unit [48], which has not been hitherto utilised in the design of bent-shaped materials so far. From the known crystallographic data [49] of the dimethoxy derivative **1** (Figure 1), we calculate the bending angle 136° to be within the generally accepted range [3] for materials exhibiting layer polarity.

2. Experimental

2.1 Synthesis

The previously described 1,3-diphenylbenzo[*c*]thiophene **1** was prepared by the reported method [49] and the new 1,3-diarylbenzo[*c*]thiophenes **2,3** were synthesised analogously. The protecting methyl groups in **1–3** were removed by means of boron tribromide to give the central units **4–6** (Figure 1). In order to obtain non-symmetrical bent-shaped materials, one of the hydroxylic groups in **4** was protected by the *tert*-butyl(dimethyl)silyl (TBDMS) group.

To design four- to seven-ring bent-shaped materials **I** exhibiting versatile mesomorphic behaviour, a series of both non-chiral and chiral acids **8,9** were chosen as lengthening arms (Figure 2) with the aim of modifying the molecular structure of the target bent-shaped materials **I**. Their preparation employed

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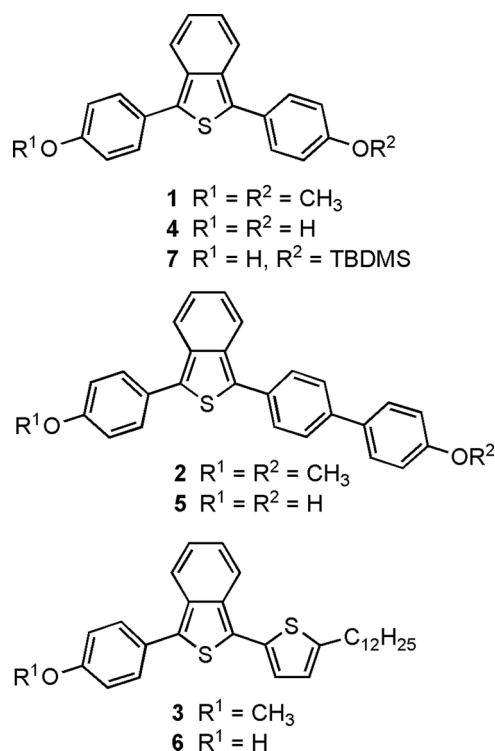


Figure 1. Structures of the central cores **4–7** and their precursors **1–3**.

known synthetic procedures [50–53]. Materials **1a,d,e** were prepared by esterification of **4** and **5** with acids **8a**, **8d**, respectively, in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-dimethylaminopyridine (DMAP) (Scheme 1).

Synthesis of non-symmetrical materials **1b,c,f–j** started with the protected derivative **7** (Scheme 2). Its acylation with acids **8a–c** was accomplished by the DCC-mediated coupling to yield esters **10a–c**. The silyl protecting group was removed by the action of tetrabutylammonium fluoride in tetrahydrofuran (THF) and the liberated hydroxy esters **11a–c** were successively acylated with acids **8c**, **8e**, **8f** and **9**

under identical conditions. Analogously, esterification of hydroxy derivative **6** with acids **8a** and **8c** gave rise to mesogens **1k** and **1l**.

2.2 Chemical characterisation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 300 HC instrument at 300 MHz. Deuteriochloroform was used as solvent and signals of the solvent served as the internal standard (chemical shifts (δ_{H}) are given in ppm, *J* values are given in hertz). Elemental analyses were carried out on a Perkin–Elmer 2400. Column chromatography was carried out using a Merck Kieselgel 60 (60–100 μm). The final compounds were crystallised from a toluene/hexane mixture and were obtained in the form of yellow-green (**1a–1j**) and yellow-orange crystals (**1k,1l**). The purity of all of the final compounds was checked by high-performance liquid chromatography analysis (Tessek C18 25x4.5 RP column) and were found to be greater than 99.8%.

2.2.1 1-(4'-Methoxy-1,1'-biphenyl-4-yl)-3-(4-methoxyphenyl)[2]benzothiophene (**2**)

A solution of 4'-methoxybiphenyl-4-ylmagnesium bromide, prepared from 4-bromo-4'-methoxybiphenyl (4.38 g; 16.6 mmol) and magnesium turnings (0.4 g; 16.0 mmol) in THF (40 ml), was added dropwise to a solution of 3-(4-methoxyphenyl)-3H-isobenzofuran-2-on (2.0 g, 8.32 mmol) in THF (30 ml) at 0°C. The reaction mixture was stirred at room temperature for 3 h, then poured onto an ice-cooled ammonium chloride solution (1.7 g in 80 ml water) and extracted with dichloromethane (3 \times 80 ml). The combined organic layers were washed with brine (50 ml) and dried with anhydrous magnesium sulphate. After evaporation of the solvent, the crude product was dissolved in dichloromethane (60 ml), Lawesson reagent (1.68 g; 4.15 mmol) was added and the reaction mixture was

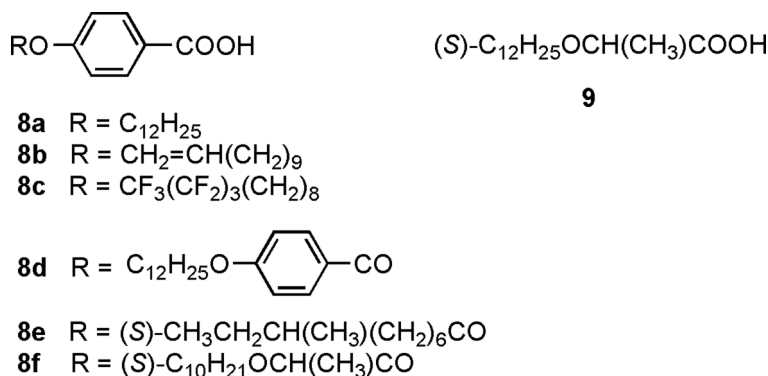
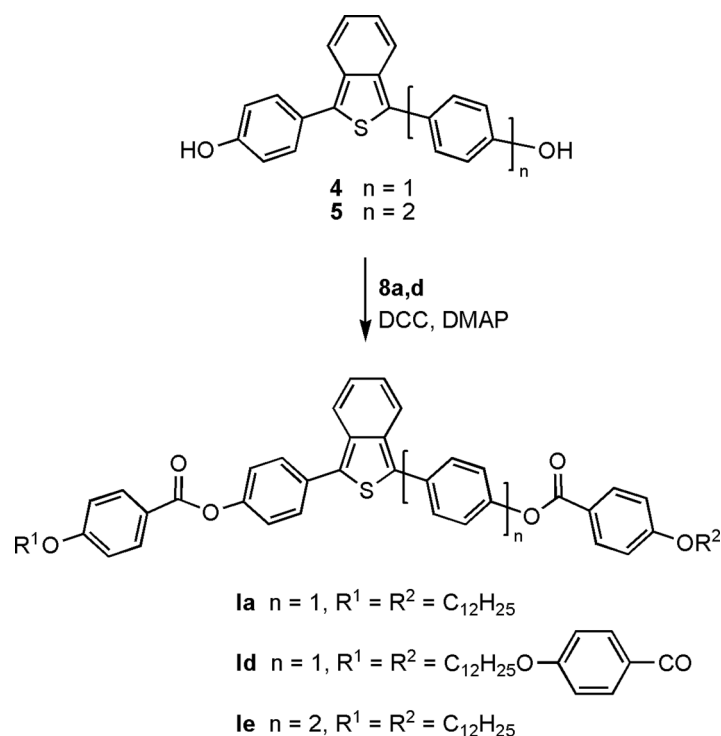


Figure 2. Structures of the lengthening arms of **8** and **9**.

Scheme 1. Synthesis of materials **Ia**, **Id**, **Ie**.

stirred at room temperature overnight. The solvent was removed and the crude product was purified by column chromatography (toluene) to yield 1.1 g (31%) of **2**, melting point (m.p.) 197–198°C.

$^1\text{H NMR}$: 3.88 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 7.03 (m, 4 H), 7.09 (m, 2 H), 7.62 (m, 4 H), 7.68 (d, $J = 8.2$, 2 H), 7.75 (d, $J = 8.5$, 2 H), 7.79 (m, 1 H), 7.88 (m, 1 H). Elemental analysis for $\text{C}_{28}\text{H}_{22}\text{O}_2\text{S}$ (422.55): calcd C 79.59, H 5.25; found C 79.44, H 5.11%.

In the same way, 1-(5-dodecylthien-2-yl)-3-(4-methoxyphenyl)benzo[*c*]thiophene (**3**) was obtained as viscous oil, with yield 65%.

$^1\text{H NMR}$: 0.88 (t, 3 H, CH_3), 1.32 (m, 18 H (CH_2)₉), 1.71 (m, 2 H, CH_2), 2.85 (t, 2 H, CH_2), 3.87 (s, 3 H, OCH_3), 6.80 (d, $J = 3.4$, 1 H), 7.02 (d, $J = 8.8$, 2 H), 7.07 (m, 2 H), 7.14 (d, $J = 3.8$, 1 H), 7.58 (d, $J = 8.8$, 2 H), 7.73 (m, 1 H), 7.94 (m, 1 H). Elemental analysis for $\text{C}_{31}\text{H}_{38}\text{OS}_2$ (490.78): calcd C 75.87, H 7.80; found C 75.69, H 7.88%.

2.2.2 4,4'-(*[2]*Benzothien-1,3-diyl)diphenol (**4**)

Boron tribromide (2.96 g; 11.8 mmol) was added dropwise to a stirred solution of **1** (1.9 g; 5.48 mmol) in dry dichloromethane (60 ml) at -78°C in argon atmosphere. The mixture was stirred at room temperature for 16 h, decomposed with water (80 ml) and

extracted with dichloromethane (3×60 ml). The combined organic layer was washed with brine (50 ml) and dried with anhydrous magnesium sulphate. The crude product after evaporation was crystallised from toluene to give 1.58 g (90%) of **2**, dark green crystals, m.p. 206–208°C.

$^1\text{H NMR}$: 4.94 (s, 2 H, $2 \times \text{OH}$), 6.96 (d, $J = 8.5$, 4 H), 7.05 (m, 2 H), 7.55 (d, $J = 8.2$, 4 H), 7.74 (m, 2 H). Elemental analysis for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$ (318.40): calcd C 75.45, H 4.43; found C 75.32, H 4.52%.

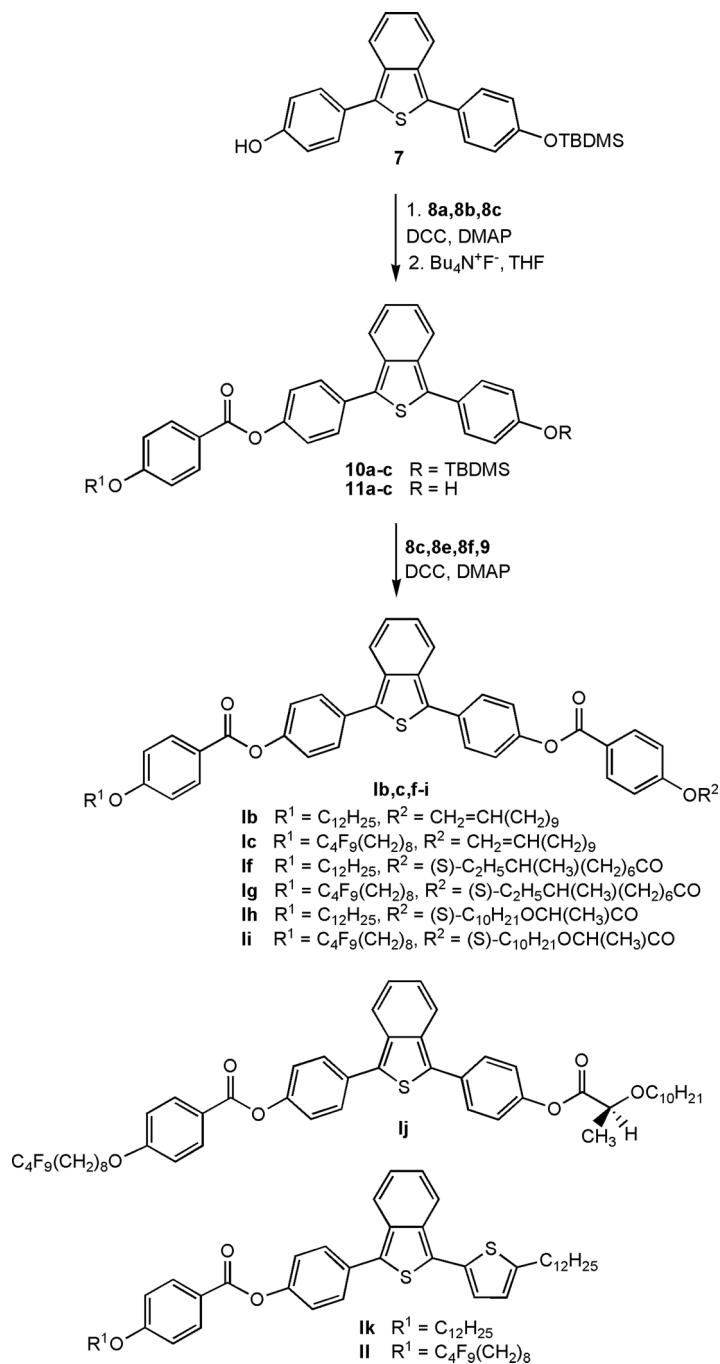
2.2.3 4-[3-(4'-Hydroxy-1,1'-biphen-4-yl)[2]benzothien-1-yl]phenol (**5**)

This compound was obtained by deprotection of **2** (0.36 g; 0.85 mmol) in the same way as for **4**, with a yield of 0.30 g (89%), m.p. 202–204°C.

$^1\text{H NMR}$: 4.88 (s, 1 H, OH), 4.95 (s, 1 H, OH), 6.96 (m, 4 H), 7.09 (m, 2 H), 7.56 (m, 4 H), 7.66 (d, $J = 8.2$, 2 H), 7.74 (d, $J = 8.2$, 2 H), 7.78 (m, 1 H), 7.86 (m, 1 H) ppm. Elemental analysis for $\text{C}_{26}\text{H}_{18}\text{O}_2\text{S}$ (394.50): calcd C 79.16, H 4.60; found C 78.95, H 4.55%.

2.2.4 4-[3-(5-Dodecylthien-2-yl)[2]benzothien-1-yl]phenol (**6**)

Deprotection of **3** (5.6 g, 11.4 mmol) with boron tribromide (3.9 g, 15.6 mmol) was achieved analogously.

Scheme 2. Synthesis of the non-symmetrical materials **Ib**, **Ic**, **If-II**.

The crude product was purified by column chromatography (dichloromethane), with a yield of 3.88 g (72%) of **6**, m.p. 66–68°C.

^1H NMR: 0.88 (t, 3 H, CH_3), 1.35 (m, 18 H, $(\text{CH}_2)_9$), 1.73 (m, 2 H, CH_2), 2.85 (t, 2 H, CH_2), 5.02 (s, 1 H, OH), 6.80 (d, $J = 3.4$, 1 H), 6.95 (d, $J = 8.6$, 2 H), 7.07 (m, 2 H), 7.14 (d, $J = 3.8$, 1 H), 7.53 (d, $J = 8.4$, 2 H), 7.72 (m, 1 H), 7.94 (m, 1 H). Elemental analysis

for $\text{C}_{30}\text{H}_{36}\text{OS}_2$ (476.75): calcd C 75.58, H 7.61; found C 75.44, H 7.41%.

2.2.5 4-[3-(4-(*tert*-Butyldimethylsilyloxy)phenyl)[2]benzothien-1-yl]phenol (**7**)

To a solution of **4** (0.62 g, 1.9 mmol) in a mixture of dry pyridine (4.6 ml) and *N,N*-dimethylformamide

(10 ml) was added dropwise a solution of *tert*-butyl(dimethyl)silyl chloride (0.32 g; 2.1 mmol) in dry *N,N*-dimethylformamide (10 ml) at 0°C. The mixture was stirred at room temperature for 2 days, diluted with water (60 ml) and extracted with ethyl acetate (3×60 ml). The combined organic solution was dried with anhydrous magnesium sulphate and evaporated, and the crude product was purified by column chromatography (hexane/ethyl acetate 4/1) to obtain 0.38 g (48%) of **7** as a yellow viscous liquid.

¹H NMR: 0.26 (s, 6 H, 2 × CH₃), 1.03 (s, 9 H, (CH₃)₃C), 5.01 (s, 1 H, OH), 6.96 (d, *J* = 8.5, 4 H), 7.05 (m, 2 H), 7.54 (m, 4 H), 7.75 (m, 2 H). Elemental analysis for C₂₆H₂₈O₂SSi (432.66): calcd C 72.18, H 6.52; found C 72.02, H 6.70%.

2.2.6 4,4'-([2]Benzothien-1,3-diyl)diphenyl bis (4-dodecyloxybenzoate) (**Ia**)

A mixture of **4** (0.12 g; 0.37 mmol), acid **8a-c** (0.27 g; 0.9 mmol), DCC (0.21 g; 1.02 mmol) and DMAP (30 mg) in dry dichloromethane (30 ml) was stirred at room temperature in an argon atmosphere for 3 h. Water (0.5 ml) was added and after 20 min the mixture was filtered, the solid was washed with dichloromethane (2×10 ml) and the combined filtrate evaporated. The residue was purified by column chromatography (toluene/*tert*-butyl methyl ether 30/1) and the product was crystallised from toluene, to give a yield of 0.25 g (74%).

¹H NMR: 0.88 (t, 6 H, 2 × CH₃), 1.35 (m, 36 H, 2 × (CH₂)₉), 1.83 (m, 4 H, 2 × CH₂), 4.06 (t, 4 H, 2 × OCH₂), 6.99 (d, *J* = 7.1, 4 H), 7.12 (m, 2 H), 7.40 (d, *J* = 6.6, 4 H), 7.74 (d, *J* = 6.6, 4 H), 7.84 (m, 2 H), 8.17 (d, *J* = 7.1, 4 H) ppm. ¹³C NMR: 14.38, 22.94, 26.22, 29.34, 29.60, 29.81, 29.84, 29.89, 29.90, 32.16, 68.59, 114.59, 121.29, 121.59, 122.74, 124.64, 130.44, 132.02, 132.60, 133.54, 135.51, 150.76, 163.88, 165.21 ppm. Elemental analysis for C₅₈H₇₀O₆S (895.26): calcd C 77.81, H 7.88; found C 77.98, H 7.71%.

Compounds **Id** and **Ie** were prepared analogously.

(4,4'-([2]Benzothien-1,3-diyl)diphenyl) bis[4-[(4-dodecyloxy)benzoyloxy]benzoate] (**Id**), yield 72%. ¹H NMR: 0.89 (t, 6 H, 2 × CH₃), 1.38 (m, 36 H, 2 × (CH₂)₉), 1.83 (m, 4 H, 2 × CH₂), 4.06 (t, 4 H, 2 × OCH₂), 6.99 (d, *J* = 8.8, 4 H), 7.14 (m, 2 H), 7.40 (m, 8 H), 7.76 (d, *J* = 8.5, 4 H), 7.85 (m, 2 H), 8.17 (d, *J* = 8.8, 4 H), 8.32 (d, *J* = 8.5, 4 H) ppm. ¹³C NMR: 14.39, 22.95, 26.23, 29.33, 29.61, 29.81, 29.84, 29.89, 29.91, 32.17, 68.63, 114.69, 121.15, 122.42, 122.66, 124.72, 126.98, 130.52, 132.13, 132.27, 132.68, 133.50, 135.57, 150.56, 155.72, 164.08, 164.59, 164.73 ppm. Elemental analysis for C₇₂H₇₈O₁₀S (1135.48): calcd C 76.16, H 6.92; found C 75.97, H 7.05%.

4-{3-[4'-(4-Dodecyloxybenzoyloxy)-1,1'-biphen-4-yl][2]benzothien-1-yl}phenyl (4-dodecyloxy)benzoate (**Ie**), yield 68%. ¹H NMR: 0.88 (t, 6 H, *J* = 7.0, 2 × CH₃), 1.40 (m, 36 H, 2 × (CH₂)₉), 1.83 (m, 4 H, 2 × CH₂), 4.06 (t, 4 H, *J* = 6.9, 2 × OCH₂), 6.99 (d, *J* = 8.5, 4 H), 7.14 (m, 2 H), 7.34 (m, 4 H), 7.75 (m, 8 H), 7.88 (m, 2 H), 8.18 (d, *J* = 8.2, 4 H). ¹³C NMR: 14.39, 22.95, 26.24, 29.35, 29.61, 29.62, 29.81, 29.85, 29.89, 29.92, 32.17, 68.59, 114.57, 114.59, 121.59, 121.68, 122.49, 122.75, 124.64, 124.67, 127.94, 128.29, 129.78, 130.45, 132.06, 132.57, 132.60, 133.58, 133.63, 134.06, 135.45, 135.65, 138.34, 139.71, 150.78, 150.93, 163.84, 163.89, 165.21, 165.26 ppm. Elemental analysis for C₆₄H₇₄O₆S (971.36): calcd C 79.14 H 7.68; found C 78.92, H 7.86.

2.2.7 General synthesis of 10a-c

A mixture of phenol **7** (1 mmol), acid **8a-c** (1.25 mmol), DCC (1.5 mmol) and a catalytic amount of DMAP in dry dichloromethane (60 ml) was stirred at room temperature in an argon atmosphere for 3 h. Water (0.5 ml) was added and after 20 min the mixture was filtered, the solid was washed with dichloromethane (2×10 ml) and the combined filtrate evaporated. The residue was purified by column chromatography (toluene/*tert*-butyl methyl ether 30/1).

4-(3-[4-(*tert*-Butyldimethylsilyloxy)phenyl][2]benzothien-1-yl)phenyl 4-(dodecyloxy)benzoate (**10a**), yield 94%, m.p. 86–87.5°C. ¹H NMR: 0.27 (s, 6 H, 2 × CH₃), 0.89 (t, 3 H, *J* = 6.6, CH₃), 1.03 (s, 9 H, 3 × CH₃), 1.40 (m, 18 H, (CH₂)₉), 1.82 (m, 2 H, CH₂), 4.06 (t, 2 H, *J* = 6.7, OCH₂), 6.98 (m, 4 H), 7.08 (m, 2 H), 7.34 (d, *J* = 8.5, 2 H), 7.55 (d, *J* = 8.8, 2 H), 7.72 (d, *J* = 8.5, 2 H), 7.80 (m, 2 H), 8.18 (d, *J* = 9.1, 2 H). Elemental analysis for C₄₅H₅₆O₄SSi (721.1): calcd C 74.96, H 7.83; found C 74.82, H 7.93%.

4-(3-[4-(*tert*-Butyldimethylsilyloxy)phenyl][2]benzothien-1-yl)phenyl 4-(undec-10-enyl-oxy)benzoate (**10b**), yield 89%, m.p. 72.5–74°C. ¹H NMR: 0.26 (s, 6 H, 2 × CH₃), 1.02 (s, 9 H, 3 × CH₃), 1.35 (m, 12 H, (CH₂)₆), 1.82 (m, 2 H, CH₂), 2.05 (m, 2 H, CH₂), 4.06 (t, 2 H, *J* = 6.7, OCH₂), 4.98 (m, 2 H, CH₂=CH), 5.82 (m, 1 H, CH₂=CH), 6.98 (m, 4 H), 7.09 (m, 2 H), 7.34 (d, *J* = 8.2, 2 H), 7.55 (d, *J* = 8.5, 2 H), 7.72 (d, *J* = 8.5, 2 H), 7.80 (m, 2 H), 8.18 (d, *J* = 8.2, 2 H). Elemental analysis for C₄₄H₅₂O₄SSi (705.05): calcd C 74.96, H 7.43; found C 75.08, H 7.33%.

4-(3-[4-(*tert*-Butyldimethylsilyloxy)phenyl][2]benzothien-1-yl)phenyl 4-(9,9,10,10,11,11,12,12,12-nonafuorododecyloxy)benzoate (**10c**), yield 98%, m.p. 70–99.5°C. ¹H NMR: 0.27 (s, 6 H, 2 × CH₃), 1.03 (s, 9 H, 3 × CH₃), 1.45 (m, 10 H, (CH₂)₅), 1.84 (m, 2 H, CH₂), 2.05 (m, 2 H, CH₂CF₂), 4.06 (t, 2 H, *J* = 6.7, OCH₂), 6.98 (m, 4 H), 7.08 (m, 2 H),

7.33 (d, $J = 8.8$, 2 H), 7.55 (d, $J = 8.5$, 2 H), 7.72 (d, $J = 8.5$, 2 H), 7.80 (m, 2 H), 8.18 (d, $J = 8.8$, 2 H). Elemental analysis for $C_{45}H_{47}F_9O_4SSi$ (883.01): calcd C 61.21, H 5.37; found C 61.12, H 5.49.

2.2.8 Deprotection of silyl derivatives 10a–c

A mixture of **10a** (0.62 mmol), tetrabutylammonium fluoride trihydrate (0.11 g, 0.35 mmol) and THF (25 ml) was stirred at room temperature for 1 h. The solution was diluted with water (50 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layer was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 6/1).

4-[3-(4-Hydroxyphenyl)[2]benzothien-1-yl]phenyl 4-(dodecyloxy)benzoate (**11a**), yield 75%, m.p. 155–157°C. 1H NMR: 0.89 (t, 3 H, $J = 6.6$, CH_3), 1.40 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, CH_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 5.02 (s, 1 H, OH), 6.98 (m, 4 H), 7.08 (m, 2 H), 7.33 (d, $J = 8.2$, 2 H), 7.56 (d, $J = 8.5$, 2 H), 7.72 (d, $J = 8.5$, 2 H), 7.80 (m, 2 H), 8.18 (d, $J = 8.2$, 2 H). Elemental analysis for $C_{39}H_{42}O_4S$ (606.83): calcd C 77.19, H 6.98; found C 77.08, H 7.08%.

4-[3-(4-Hydroxyphenyl)[2]benzothien-1-yl]phenyl 4-(undec-10-enyloxy)benzoate (**11b**), yield 73%, m.p. 154–157°C. 1H NMR: 1.40 (m, 12 H, $(CH_2)_6$), 1.83 (m, 2 H, CH_2), 2.04 (m, 2 H, CH_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 4.97 (m, 2 H, $CH_2=CH$), 5.00 (s, 1 H, OH), 5.82 (m, 1 H, $CH_2=CH$), 6.97 (m, 4 H), 7.08 (m, 2 H), 7.33 (d, $J = 7.7$, 2 H), 7.55 (d, $J = 8.5$, 2 H), 7.72 (d, $J = 8.8$, 2 H), 7.80 (m, 2 H), 8.18 (d, $J = 9.1$, 2 H). Elemental analysis for $C_{38}H_{38}O_4S$ (590.79): calcd C 77.26, H 6.48; found C 77.09, H 6.55.

4-[3-(4-Hydroxyphenyl)[2]benzothien-1-yl]phenyl 4-(9,9,10,10,11,11,12,12,12-nona-fluorododecyloxy) benzoate (**11c**), yield 62%, m.p. 127–169°C. 1H NMR: 1.43 (m, 10 H, CH_2), 1.84 (m, 2 H, CH_2), 2.05 (m, 2 H, CH_2CF_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 5.15 (s, 1 H, OH), 6.97 (m, 4 H), 7.08 (m, 2 H), 7.33 (d, $J = 8.5$, 2 H), 7.55 (d, $J = 8.5$, 2 H), 7.72 (d, $J = 8.5$, 2 H), 7.80 (m, 2 H), 8.18 (d, $J = 8.8$, 2 H). Elemental analysis for $C_{39}H_{33}F_9O_4S$ (768.75): calcd C 60.94, H 4.33; found C 60.82, H 4.45%.

2.2.9 General synthesis of Ib,c,f-l

A mixture of phenol **6,10a–c** (1 mmol), acid **8b,e,f,9** (1.25 mmol), DCC (1.5 mmol) and catalytic amount of DMAP in dry dichloromethane (60 ml) was stirred at room temperature in an argon atmosphere for 3 h. Water (0.5 ml) was added and after 20 min the mixture was filtered, the solid was washed with dichloromethane (2×10 ml) and the combined filtrate

evaporated. The residue was purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether 30/1).

4-[3-(4-(4-Dodecyloxybenzoyloxy)phenyl)[2]benzothien-1-yl]phenyl 4-(undec-10-enyl-oxy)benzoate (**1b**), yield 96%. 1H NMR spectrum: 0.89 (t, 3 H, $J = 6.7$, CH_3), 1.20–1.60 (m, 30 H), 1.83 (m, 4 H, $2 \times CH_2$), 2.05 (m, 2 H, CH_2), 4.06 (t, 4 H, $J = 6.7$, $2 \times OCH_2$), 4.97 (m, 2 H, $CH_2=CH$), 5.82 (m, 1 H, $CH_2=CH$), 7.00 (d, $J = 8.8$, 4 H), 7.12 (m, 2 H), 7.35 (d, $J = 8.8$, 4 H), 7.74 (d, $J = 8.8$, 4 H), 7.84 (m, 2 H), 8.18 (d, $J = 9.0$, 4 H). ^{13}C NMR: 14.42, 22.97, 26.25, 29.18, 29.37, 29.38, 29.64, 29.69, 29.77, 29.84, 29.87, 29.92, 29.94, 32.20, 34.07, 68.59, 114.43, 114.59, 121.31, 121.62, 122.75, 124.66, 130.43, 132.02, 132.60, 133.54, 135.53, 139.44, 150.77, 163.89, 165.18 ppm. Elemental analysis for $C_{57}H_{66}O_6S$ (879.22): calcd C 77.87, H 7.57; found C 77.79, H 7.64%.

4-[3-(4-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy)benzoyloxy)phenyl)[2]benzothien-1-yl]phenyl 4-(undec-10-enyloxy)benzoate (**1c**), yield 96%. 1H NMR: 1.35 (m, 22 H, $11 \times CH_2$), 1.83 (m, 4 H, $2 \times CH_2$), 2.05 (m, 4 H, $2 \times CH_2$), 4.06 (t, 4 H, $J = 6.7$, $2 \times OCH_2$), 4.97 (m, 2 H, $CH_2=CH$), 5.82 (m, 1 H, $CH_2=CH$), 6.99 (d, $J = 8.8$, 4 H), 7.12 (m, 2 H), 7.35 (d, $J = 8.5$, 4 H), 7.74 (d, $J = 8.5$, 4 H), 7.84 (m, 2 H), 8.18 (d, $J = 8.8$, 4 H). ^{13}C NMR: 20.31, 26.17, 26.22, 29.17, 29.26, 29.30, 29.36, 29.40, 29.59, 29.66, 29.74, 30.99, 34.06, 68.47, 68.58, 114.40, 114.58, 121.31, 121.68, 122.74, 124.65, 130.44, 132.03, 132.61, 133.53, 135.52, 139.44, 150.77, 163.82, 163.88, 165.19 ppm. Elemental analysis for $C_{57}H_{57}F_9O_6S$ (1041.14): calcd C 65.76, H 5.52; found C 65.86, H 5.48%.

(*S*)-4-[3-(4-(4-Dodecyloxybenzoyloxy)phenyl)[2]benzothien-1-yl]phenyl 4-(8-methyl-decanoyloxy)benzoate (**1f**), yield 60%. 1H NMR: 0.88 (t, 9 H, $J = 6.6$, $3 \times CH_3$), 1.02–1.55 (m, 29 H), 1.81 (m, 4 H, $2 \times CH_2$), 2.61 (t, 3 H, $J = 7.4$, $COCH_2$), 4.06 (t, 3 H, $J = 6.7$, OCH_2), 7.00 (d, $J = 9.1$, 2 H), 7.13 (m, 2 H), 7.27 (d, $J = 8.5$, 2 H), 7.36 (d, $J = 8.6$, 4 H), 7.75 (m, 4 H), 7.84 (m, 2 H), 8.19 (d, $J = 8.8$, 2 H), 8.28 (d, $J = 8.8$, 2 H). ^{13}C NMR: 11.67, 14.38, 19.46, 22.94, 25.07, 26.21, 27.14, 29.31, 29.37, 29.60, 29.72, 29.84, 29.88, 32.16, 34.61, 34.65, 36.77, 68.60, 114.62, 121.33, 121.57, 122.18, 122.61, 122.75, 124.64, 124.71, 127.03, 130.46, 130.52, 131.98, 132.13, 132.32, 132.60, 133.34, 133.67, 135.51, 135.54, 150.49, 150.78, 155.30, 163.89, 164.69, 165.22, 171.99 ppm. Elemental analysis for $C_{57}H_{66}O_7S$ (895.22): calcd C 76.48, H 7.43; found C 76.29, H 7.38%.

(*S*)-4-[3-(4-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy)benzoyloxy)phenyl)[2]-benzothien-1-yl]phenyl 4-(8-methyldecanoyloxy)benzoate (**1g**), yield 87%. 1H NMR: 0.87 (t, 6 H, $J = 6.6$, $2 \times CH_3$), 1.10–1.50 (m, 21 H), 1.84 (m, 4 H, $2 \times CH_2$), 2.05 (m,

2 H, CH_2CF_2), 2.60 (t, 2 H, $J = 7.2$, COCH_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 7.00 (d, $J = 9.1$, 2 H), 7.13 (m, 2 H), 7.26 (m, 2 H), 7.36 (d, $J = 8.8$, 4 H), 7.75 (m, 4 H), 7.84 (m, 2 H), 8.18 (d, $J = 8.8$, 2 H), 8.28 (d, $J = 8.8$, 2 H). ^{13}C NMR: 11.67, 19.46, 20.30, 25.09, 26.16, 27.15, 29.26, 29.29, 29.34, 29.38, 29.73, 29.84, 30.98, 34.61, 34.67, 36.78, 68.46, 114.57, 121.26, 121.65, 122.19, 122.61, 122.74, 124.66, 124.71, 127.03, 130.46, 130.51, 132.0, 132.11, 132.31, 132.61, 133.36, 133.66, 135.55, 135.52, 150.50, 150.77, 155.31, 163.82, 164.68, 165.19, 171.98 ppm. Elemental analysis for $\text{C}_{57}\text{H}_{57}\text{F}_9\text{O}_7\text{S}$ (1057.14): calcd C 64.76, H 5.43; found C 64.71, H 5.55%.

(*S*)-4-[3-(4-(4-Dodecyloxybenzoyloxy) phenyl)[2]benzothien-1-yl]phenyl 4-(2-decyloxypropanoyloxy) benzoate (**h**), yield 52%. ^1H NMR: 0.88 (t, 6 H, $J = 6.7$, $2 \times \text{CH}_3$), 1.20–1.60 (m, 37 H), 1.83 (m, 2 H, CH_2), 3.51 (m, 1 H), 3.70 (m, 1 H), 4.06 (t, 2 H, $J = 6.8$, OCH_2), 4.23 (m, 1 H, CH), 7.00 (d, $J = 8.8$, 2 H), 7.14 (m, 2 H), 7.36 (m, 6 H), 7.75 (d, $J = 8.5$, 4 H), 7.84 (m, 2 H), 8.18 (d, $J = 8.8$, 2 H), 8.30 (d, $J = 8.5$, 2 H). ^{13}C NMR: 14.38, 18.94, 22.94, 26.23, 26.30, 29.34, 29.57, 29.60, 29.67, 29.81, 29.83, 29.88, 30.01, 32.14, 32.17, 68.60, 71.12, 75.23, 114.60, 121.32, 121.57, 121.98, 122.59, 122.75, 124.66, 124.72, 127.33, 130.46, 130.52, 131.98, 132.18, 132.36, 132.61, 133.31, 133.69, 135.53, 135.56, 150.45, 150.78, 154.98, 163.90, 164.60, 165.25, 171.76 ppm. Elemental analysis for $\text{C}_{59}\text{H}_{70}\text{O}_8\text{S}$ (939.27): calcd C 75.45, H 7.51; found C 75.38, H 7.48%.

(*S*)-4-[3-(4-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy)benzoyloxy)phenyl)[2]-benzothien-1-yl]phenyl 4-(2-decyloxypropanoyloxy)benzoate (**i**), yield 71%. ^1H NMR: 0.88 (t, 3 H, $J = 6.7$, CH_3), 1.20–1.60 (m, 29 H), 1.84 (m, 2 H, CH_2), 2.05 (m, 2 H, CH_2CF_2), 3.51 (m, 1 H, CH), 3.71 (m, 1 H), 4.07 (t, 2 H, $J = 6.7$, OCH_2), 4.23 (m, 1 H, CH), 7.00 (d, $J = 9.0$, 2 H), 7.13 (m, 2 H), 7.32 (m, 6 H), 7.75 (d, $J = 8.6$, 4 H), 7.84 (m, 2 H), 8.19 (d, $J = 8.8$, 2 H), 8.29 (d, $J = 8.6$, 2 H). ^{13}C NMR: 14.37, 18.94, 20.31, 22.93, 26.16, 26.30, 29.26, 29.34, 29.39, 29.56, 29.67, 29.81, 30.01, 68.47, 71.12, 75.21, 114.57, 121.26, 121.65, 121.98, 122.60, 122.74, 124.66, 124.72, 127.33, 130.46, 130.51, 131.99, 132.17, 132.35, 132.61, 133.32, 133.68, 135.52, 150.45, 150.77, 154.98, 163.83, 164.58, 165.20, 171.74 ppm. Elemental analysis for $\text{C}_{59}\text{H}_{61}\text{F}_9\text{O}_8\text{S}$ (1101.19): calcd C 64.35, H 5.58; found C 64.42, H 5.48%.

(*S*)-4-[3-(4-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy) benzoyloxy)phenyl)[2]-benzothien-1-yl]phenyl 2-dodecyloxypropanoate (**j**), yield 70%. ^1H NMR: 0.87 (t, 3 H, $J = 6.7$, CH_3), 1.20–1.60 (m, 33 H), 1.84 (m, 2 H, CH_2), 2.05 (m, 2 H, CH_2CF_2), 3.52 (m, 1 H), 3.72 (m, 1 H), 4.06 (t, 2 H, $J = 6.8$, OCH_2), 4.23 (m, 1 H, CH), 7.00 (d, $J = 9.0$, 2 H), 7.12 (m, 2 H), 7.26 (m, 2 H), 7.35 (d, $J = 8.8$, 2 H), 7.72

(m, 4 H), 7.83 (m, 2 H), 8.16 (d, $J = 9.0$, 2 H). ^{13}C NMR: 14.36, 19.0, 20.29, 22.93, 26.16, 26.32, 29.26, 29.29, 29.34, 29.39, 29.60, 29.70, 29.84, 29.86, 29.89, 29.92, 30.04, 30.97, 32.16, 68.46, 71.04, 75.26, 114.57, 121.18, 121.32, 121.65, 122.28, 122.74, 124.65, 124.72, 130.46, 131.97, 132.33, 132.61, 133.22, 133.69, 135.51, 135.54, 150.092, 150.78, 163.83, 165.18, 172.34 ppm. Elemental analysis for $\text{C}_{52}\text{H}_{57}\text{F}_9\text{O}_6\text{S}$ (981.08): calcd C 63.66, H 5.86; found C 63.82, H 5.69%.

4-[3-(5-Dodecylthien-2-yl)[2]benzothien-1-yl]phenyl 4-(dodecyloxy)benzoate (**k**), yield 83%. ^1H NMR: 0.88 (t, 6 H, $J = 6.7$, $2 \times \text{CH}_3$), 1.20–1.60 (m, 18 H, $2 \times (\text{CH}_2)_9$), 1.70 (m, 4 H), 2.86 (t, 2 H, $J = 7.6$, CH_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 6.82 (d, $J = 3.8$, 1 H), 6.99 (d, $J = 8.8$, 2 H), 7.11 (m, 2 H), 7.17 (d, $J = 3.6$, 1 H), 7.33 (d, $J = 8.6$, 2 H), 7.70 (d, $J = 8.4$, 2 H), 7.80 (m, 1 H), 7.96 (m, 1 H), 8.18 (d, $J = 8.8$, 2 H). ^{13}C NMR: 14.40, 22.96, 26.24, 29.35, 29.43, 29.63, 29.83, 29.86, 29.92, 29.95, 30.51, 31.91, 32.19, 68.59, 114.57, 121.28, 121.59, 121.91, 122.72, 124.54, 124.75, 125.08, 128.10, 130.38, 131.91, 132.23, 132.60, 133.45, 135.17, 135.48, 146.74, 150.72, 163.89, 165.18 ppm. Elemental analysis for $\text{C}_{49}\text{H}_{64}\text{O}_3\text{S}_2$ (765.18): calcd C 76.92, H 8.43; found C 76.99, H 8.32%.

4-[3-(5-Dodecylthien-2-yl)[2]benzothien-1-yl]phenyl 4-(9,9,10,10,11,11,12,12,12-nona-fluorododecyloxy)benzoate (**l**), yield 72%. ^1H NMR: 0.88 (t, 3 H, $J = 6.6$, CH_3), 1.20–1.80 (m, 32 H), 2.05 (m, 2 H, CH_2CF_2), 2.86 (t, 2 H, $J = 7.6$, CH_2), 4.06 (t, 2 H, $J = 6.7$, OCH_2), 6.82 (d, $J = 3.6$, 1 H), 6.99 (d, $J = 9.0$, 2 H), 7.13 (m, 2 H), 7.17 (d, $J = 3.6$, 1 H), 7.33 (d, $J = 8.4$, 2 H), 7.71 (d, $J = 8.4$, 2 H), 7.79 (m, 1 H), 7.97 (m, 1 H), 8.18 (d, $J = 8.8$, 2 H). ^{13}C NMR: 14.38, 20.31, 22.95, 26.17, 29.26, 29.30, 29.35, 29.40, 29.42, 29.62, 29.64, 29.82, 29.91, 29.93, 30.50, 30.99, 31.90, 32.18, 68.46, 114.56, 121.27, 121.67, 121.91, 122.72, 124.54, 124.76, 125.08, 125.41, 128.11, 130.38, 131.92, 132.21, 132.60, 133.44, 135.17, 135.48, 146.75, 150.70, 163.82, 165.16 ppm. Elemental analysis for $\text{C}_{49}\text{H}_{55}\text{F}_9\text{O}_3\text{S}_2$ (927.10): calcd C 63.48, H 5.98; found C 63.28, H 6.21%.

2.3 Measurements

Phase transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) studies (Pyris Diamond Perkin–Elmer 7) under cooling and heating runs at a rate of 5 K/min. Samples of 2–5 mg were hermetically sealed in aluminium pans and placed in the calorimeter chamber inflated by nitrogen. The planar samples for texture observations and electric field studies were filled by capillarity action in the isotropic phase into cells composed of glasses with indium tin oxide (ITO) transparent electrodes ($5 \times 5 \text{ mm}^2$). The sample thickness was

defined by mylar sheets. All texture observations were performed using a polarising microscope (Nikon Eclipse) equipped with a Linkam hot stage.

X-ray studies were performed on a D8-Discover Bruker system and $\text{CuK}\alpha$ radiation was used. The signal intensities were registered by a linear Vantec detector. The steady-state fluorescence measurements were performed in dilute solutions in dichloromethane (ca. $2 \times 10^{-2} \text{ g/dm}^3$) using a FluoroLog HORIBA Jobin Yvon spectrometer. Fluorescence quantum yields were measured using fluorescence in a 0.1 M NaOH solution excited at 470 nm as reference, for which quantum yield reaches 0.79.

Infrared (IR) spectra were registered on a Nicolet 6700FT-IR spectrometer. The sample was placed on a BaF_2 plate, aligned by shearing and heated with a microscope Linkam hot stage. The IR polariser was rotated with respect to rubbing direction in the sample, to obtain variation of the IR signal intensities. The molecular structure and size were evaluated using the HyperChem application suite.

3. Results and discussion

3.1 Mesomorphic properties

The phase transition temperatures and the enthalpy changes were evaluated from DSC thermograms. All the studied materials formed enantiotropic liquid crystalline phases; for some materials, LC phases persisted even if the compound was cooled down to -20°C . However, upon heating, the samples re-crystallised, which could be observed in the DSC scans as an exothermic signal on the heating run (Figure 3). The type of phase was determined from observations of optical textures under a polarising microscope and their changes with temperature. All observed phases, i.e. nematic, smectic A (SmA) and smectic C (SmC), were typical for rod-like molecules. The mesophase type, phase transition temperatures and corresponding enthalpies in kJ/mol are summarised in Table 1.

The five-ring material **Ia**, the six-ring material **Ie** and the seven-ring material **Id** exhibited the nematic phase over a broad temperature interval. As usual for rod-like mesogens, elongation of the mesogenic core led to an increase of the clearing temperature, which systematically grew from 153°C for five-ring **Ia**, to 231°C for six-ring **Ie** and up to 304°C for seven-ring compound **Id**. The increase of the clearing temperature was ca. 75 K per each phenyl ring. **Id** with six phenyl rings in the molecular structure exhibits an extremely broad temperature range of the nematic phase (200 K). On the other hand, elongation of the mesogenic core influences the melting point of **Ia**, **Ie** and **Id** within the interval of 30 K only.

The target materials **Ib** and **Ic** (see Scheme 2) possessing a double bond in the terminal alkyl chain serve as model monomers for polymeric liquid crystals. To support the formation of lamellar phases [28, 53], a nonafluorododecyl terminal chain R^1 was introduced to give materials **Ic**, **Ig**, **Ii**, **Ij** (Table 1). Replacing the alkyl chains by perfluorinated chains led to the modification of the mesomorphic properties. Comparing compounds **Ib** and **Ic** differing in chain R^1 , the SmC phase below the nematic phase appeared in **Ic** compound with a nonafluorododecyl chain. For **Ib** with $\text{R}^1 = \text{C}_{12}\text{H}_{25}$, only the nematic phase was observed.

Formation of the chiral phases was induced by the attachment of chiral terminal chains: $(S)\text{-C}_2\text{H}_5\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CO}$ in compounds **If** and **Ig**, and $(S)\text{-C}_{10}\text{H}_{21}\text{OCH}(\text{CH}_3)\text{CO}$ in compounds **Ih**, **Ii** and **Ij**. Introduction of nonafluorododecyl as the non-chiral chain R^1 for material **Ig** lead to an appearance of the chiral SmC (SmC^*) phase below the chiral nematic phase in comparison with **If** with $\text{R}^1 = \text{C}_{12}\text{H}_{25}$ forming only the chiral nematic phase. For compounds with the second type of chiral chain $(S)\text{-C}_{10}\text{H}_{21}\text{OCH}(\text{CH}_3)\text{CO}$, replacing the opposite non-chiral chain $\text{R}^1 = \text{C}_{12}\text{H}_{25}$ by nonafluorododecyl leads to a larger variety of smectic phases; the SmA and SmC^* phases have been found in material **Ii**. For both types of chiral chains, introduction of nonafluorododecyl into the opposite non-chiral chain caused stabilisation of the LC phases (increase of the phase transition temperatures from the isotropic to nematic phase and decrease of melting points, see Table 1) and introduction of lamellar mesophases.

To modify the fluorescence properties, one of the benzene rings was replaced by an additional thiophene unit (materials **Ik**, **Ij**). For **Ij**, the SmA phase appeared instead of the nematic phase observed for **Ik**. For non-chiral materials, only non-polar phases were observed regardless of the mesogenic branch length and molecular symmetry, and no banana mesophases were observed. Apparently, the bending angle (ca. 136°) introduced by the central unit is too large to impose steric constraints on the molecular rotation around the long molecular axis, and subsequently a long-range correlation of molecular dipole moments.

For compounds **Ig** and **Ii**, polar properties appear in the tilted smectic phase due to the symmetry breaking caused by the presence of the chiral carbon atom placed at the terminal chain. However, the measured spontaneous polarisation, P_s , is weak (ca. 20 nC/cm^2 for **Ii**, Figure 4(a)). Moving the chiral centre farther from the mesogenic core in compound **Ig** results in a substantial decrease of P_s values ($< 0.1 \text{ nC/cm}^2$), although electrooptic switching is still evident (Figures 4(b) and 4(c)).

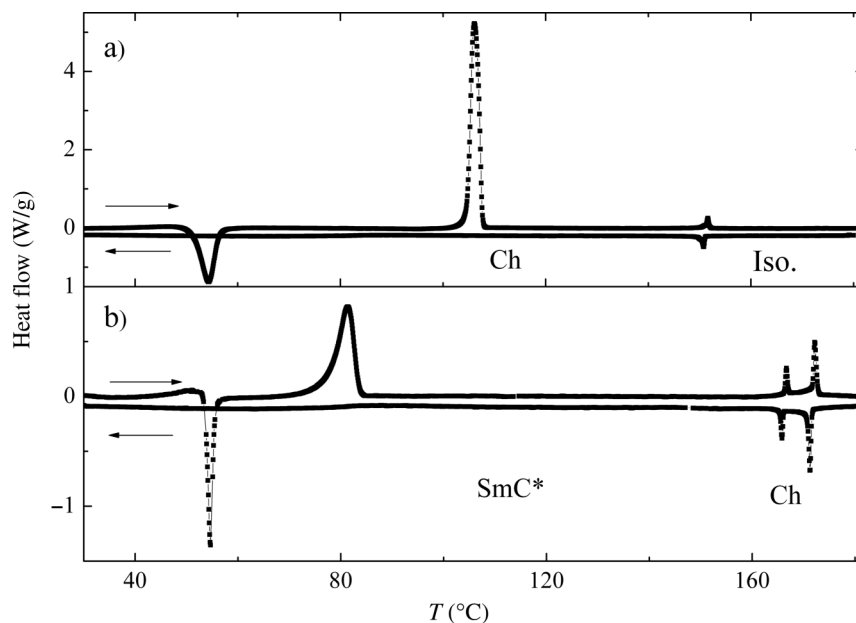


Figure 3. DSC thermographs for compounds (a) **If** and (b) **Ig** taken at a rate of 5 K/min. Arrows indicate second heating and subsequent cooling runs from the isotropic phase.

Table 1. Phase transitions for compounds **Ia** – **Ii**.

Compound.	m.p. ΔH	M_3	T_{tr} ΔH	M_2	T_{tr} ΔH	M_1	T_{tr} ΔH	Iso
Ia	133 +49.1	–	–	–	–	N	153 –0.56	•
Ib	131 +51.4	–	–	–	–	N	157 –0.78	•
Ic	124 +41.0	SmC	135 –0.19	–	–	N	163 –0.90	•
Id	104 +24.8	–	–	–	–	N	304 –0.88	•
Ie	130 +60.1	–	–	–	–	N	231 –0.69	•
If	104 +38.4	–	–	–	–	N*	151 –0.65	•
Ig	81 +11.5	SmC*	166 –0.44	–	–	N*	172 –1.31	•
Ih	93 +44.0	–	–	–	–	N*	104 –0.24	•
Ii	85 +33.6	SmC*	124 –0.08	SmA	135 –0.23	N*	137 –2.91	•
Ij	42.7 +38.1	–	–	SmA	74.1 –1.28	–	–	•
Ik	67 +43.3	–	–	–	–	N	74 –0.69	•
Il	76 +32.7	–	–	SmA	104 –4.45	–	–	•

Notes: Melting point, m.p., was measured on second heating. The phase transition temperatures, T_{tr} , taken on second cooling are presented in °C and the corresponding enthalpies, ΔH , are in kJ/mol. All temperature changes were performed at a rate of 5 K/min.

3.2 Structural studies

The phase sequence for the studied materials was confirmed by X-ray studies. In the nematic phase,

only diffused signals were observed, showing mean intermolecular distance along and perpendicular to the long molecular axis, while in smectic phases

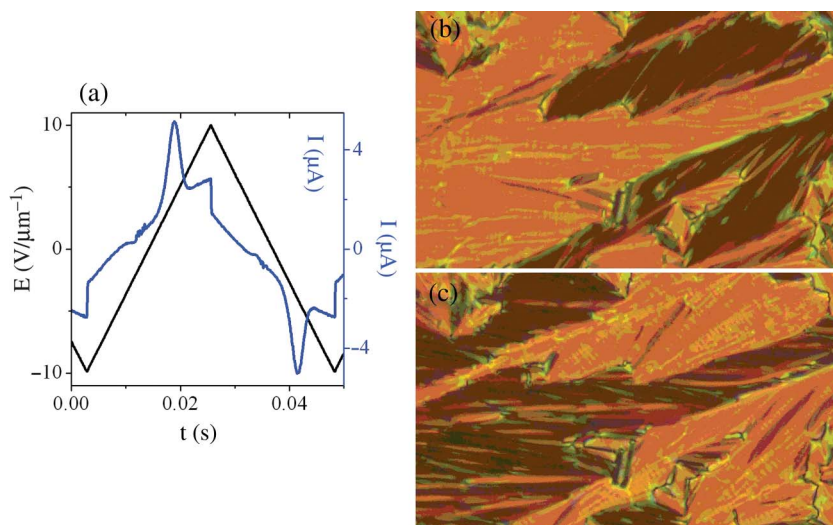


Figure 4. (a) Current peak recorded during switching of electric polarisation in the SmC* phase ($T = 90^\circ\text{C}$) of compound **II**. Calculated $P_s = 18 \text{ nC/cm}$. (b), (c) Texture of the SmC* phase of compound **IIg** under application of a dc voltage of opposite polarity, note the change of extinction direction (colour version online).

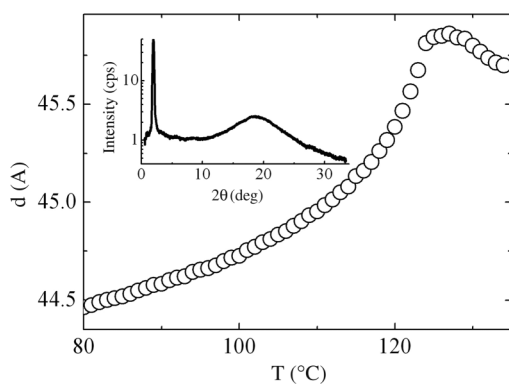


Figure 5. Temperature dependence of layer spacing for material **II**; the inset shows the intensity of X-ray signals vs. scattering angle in the SmC* phase. The diffuse signal centred at $2\theta = 18$ degrees points to liquid-like molecular ordering within smectic layers.

the signal corresponding to molecular length became sharp, reflecting a long-range ordering (Figure 5). All of the observed smectic phases were liquid-type with only short-range intermolecular correlations within layers. The small negative thermal expansion of the layer thickness (-0.03 \AA/K) in the SmA phase is caused by the increase of the orientational order parameter and changes in molecular conformation on cooling (Figure 5). For compound **II**, the layer spacing starts to decrease at the onset of the SmA–SmC* phase transition, and the tilt angle calculated from the layer thickness far from the phase transition temperature (ca. 15°) agrees well with values obtained by optical measurements.

To study the degree of the orientational order in the nematic phase, polarised IR measurements were

performed. Absorption bands related to symmetric stretching of the phenyl ring (ca. 1605 cm^{-1}), the C=O (1735 cm^{-1}) group and the CH₂ group (ca. 2925 cm^{-1}) were analysed for material **IIk** (Figure 6). The phenyl stretching signal exhibits strong anisotropy, and the intensity of the band is strongest when the polariser axis is oriented along the *director*, showing that the transition moment is located close to the long molecular axis. For the C=O and CH₂ signals the anisotropy is much smaller and reversed: the strongest signal for these bands is obtained if the polariser axis is oriented perpendicular to the *director*. Based on the molecular modelling, the phenyl ring stretching transition moment is tilted by about 10° from the long molecular axis (its position was determined by averaging several most probable conformations), while the dipole transition moments of the C=O and CH₂ groups are inclined at angles of 60° and 90° to the molecular axis, respectively. The intensity of the absorption for molecules rotating freely around the long molecular axis, and averaged over possible internal molecular rotations is

$$I(\omega) = \frac{1}{3} - \frac{1}{2}S \cos^2(\beta) + \frac{3}{2}S \cos^2(\beta) \cos^2(\omega) - \frac{1}{2}S \cos^2(\omega) + \frac{1}{6}S,$$

where β is the inclination of the transition dipole moment from the long molecular axis, ω is the angle between the polariser and director and S is the orientational order parameter. Knowing the dichroism of the band, defined as the ratio of the absorption for

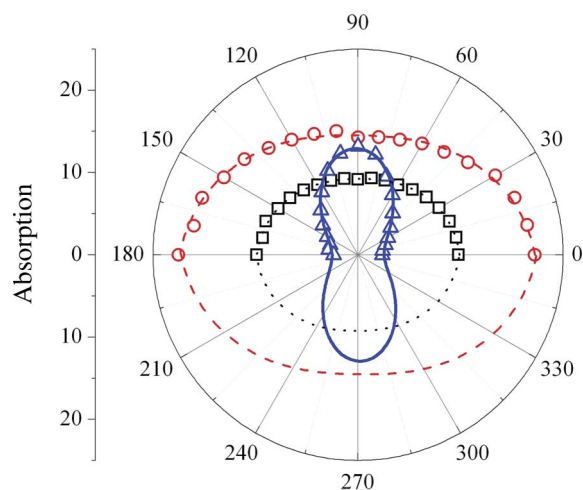


Figure 6. Intensity of the IR absorption bands for phenyl (1605 cm^{-1}), represented by circles, C=O (1735 cm^{-1}), represented by triangles and CH_2 (2925 cm^{-1}), represented by squares, stretching for compound **IIk** at 60°C (nematic phase) vs. angle between the polariser and *director* in the sample (colour version online).

the polariser axis at 0 and 90 degrees to the director, $D=I(0)/I(\pi/2)$), both the ‘phenyl’ and ‘C=O’ bands provide similar order parameter of $S \sim 0.6$. On the other hand, a much smaller order parameter is deduced from the dichroism of the CH_2 symmetric stretching, showing that the ordering of alkyl chains is much lower than that of the mesogenic cores. It is usually assumed that the alkyl chains are in a molten state in the liquid crystalline phase.

3.3 Fluorescent properties

The 1,3-diphenylbenzo[*c*]thiophene derivatives show two strong absorption maxima at ca. 290 and ca. 400 nm and strong fluorescence of green light (Figure 7) in the solution. The emission is apparently stronger if the molecules are excited by longer wavelength light. The position of the emission band (and longer wavelength absorption band) is affected by the surroundings of the central unit; if one of the phenyl rings attached to the 1,3-diphenylbenzo[*c*]thiophene unit is replaced by a thiophene ring, the emission maximum shifts from ca. 450 nm to ca. 520 nm, and the bathochromic effect is due to the electron-donating ability of thiophene. The quantum yield for most materials is rather high ($\Phi = 0.5\text{--}0.6$).

The strong fluorescence persists also in the liquid crystalline and crystal phases [54]. The wavelength of absorption/emission is not affected by the liquid crystalline order, the dipolar order of neighbouring molecules is weak (no H- or J-type aggregates are formed [55]), and the molecules rotate quite freely along the long molecular axis. Orientational order

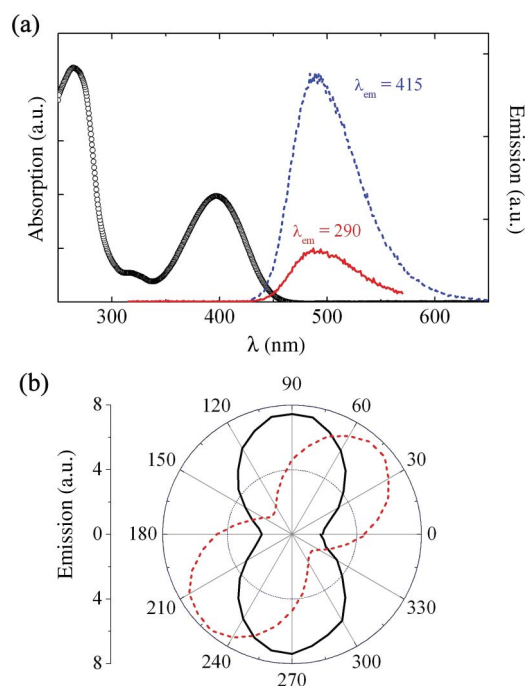


Figure 7. (a) Absorption and emission spectra for compound **II** in dichloromethane. The intensity of the fluorescence is strongly dependent on the excitation wavelength. (b) The intensity of the fluorescence (excitation at 415 nm) upon rotation of the director with respect to the polariser, recorded in the SmC^* phase of **II**. Applying a dc electric field with opposite polarity to the sample caused rotation of the transition momentum with respect to the polariser; solid and dashed lines represent $+10\text{ V}/\mu\text{m}$ and $-10\text{ V}/\mu\text{m}$, respectively (colour version online).

of long molecular axes in mesophases results in a preferable orientation of absorption/emission transition momentum that is nearly perpendicular to the molecular long axis (perpendicular for symmetric molecules). Thus, it is possible to observe linearly polarised absorption and fluorescence for these materials in the liquid crystalline state. Moreover, in the case of compounds **Ig** and **II** forming the SmC^* phase, one can control the orientation of the fluorescence polarisation plane by the application of electric field due to the coupling between the molecular tilt direction and the electric field (Figure 7(b)). The order parameter in the nematic phase deduced from the emission/absorption dichroism is comparable to that obtained for mesogenic cores from IR measurements.

4. Conclusions

New materials based on 1,3-diphenyl[2]benzothiophene were synthesised as possible fluorescent mesogens. The bending angle introduced by the central unit turns out to be too large to restrict the molecular rotation around the long molecular axis. The experimental data

show there is no close packing typical of bent-shaped mesophases, as all observed mesophases exhibit typical calamitic behaviour. It is probable that molecules rotate freely around their long axes and that neither long-range dipole order nor short-range polar aggregates are formed in the liquid crystalline phases. In order to obtain polar mesophases the chiral derivatives were synthesised. In the liquid crystalline phases the orientational order of the mesogenic cores gives rise to polarised fluorescence. In the case of the polar smectic C* phase, the intensity of the fluorescent light transmitted by the polariser can easily be controlled by the application of an electric field.

Acknowledgements

This work was supported by grant No. 202/09/0047 (Czech Science Foundation), project IAA100100911 (Grant Agency of AS of the Czech Republic) and project OC 176 (Ministry of Education, Youth and Sports of the Czech Republic). The research for this paper was in part supported by the EU through the European Social Fund, contract number UDA-POKL.04.01.01-00-072/09-00.

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