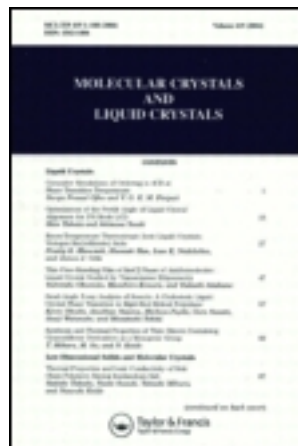


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W. M. Zoghaib^a, C. Carboni^b, A. K. George^b, S. AL-Manthari^a, A. Al-Hussaini^a & F. Al-Futaisi^a

^a Chemistry Department, Sultan Qaboos University, Al-Khod, Oman

^b Physics Department, Sultan Qaboos University, Al-Khod, Oman

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Novel Fluorinated Ferroelectric Organosiloxane Liquid Crystals

W. M. ZOGHAIB,¹ C. CARBONI,² A. K. GEORGE,²
S. AL-MANTHARI,¹ A. AL-HUSSAINI,¹ AND
F. AL-FUTAISI¹

¹Chemistry Department, Sultan Qaboos University, Al-Khod, Oman

²Physics Department, Sultan Qaboos University, Al-Khod, Oman

A progress report on the synthesis and characterisation of a series of fluorinated chiral bi-mesogen low molar mass organosiloxane materials is presented. The mesogenic moiety is identical to that in the TSiKN65F mono-mesogen material reported by Naciri et al., which displays a de Vries-type SmA phase. The parameter varied across the series is the length of the alkyl chain linking the mesogen moiety to the siloxane. The material with 10 carbon atoms in the chains displays a stable smectic phase with ferroelectric response at room temperature, whereas the materials with 6, 7 and 8 carbon atoms tend to crystallize.*

Keywords bi-mesogen; de-Vries phase; ferroelectric; organosiloxane; smectic; synthesis; trimer

1. Introduction

Low molar mass organosiloxane liquid crystal materials are good candidates for the search of materials displaying de-Vries type phases [1–6]. The mono-mesogenic materials TSiKN65 described in references [1–3] displays a transition between de-Vries SmA* phase to SmC* phase. The fluorinated homologue TSiKN65F material remains in the de-Vries SmA* phase over the entire temperature range of the smectic phase [4] indicating that the fluorine stabilizes the de-Vries phase. In the present work bi-mesogen homologues of TSiKN65F are investigated. Bi mesogens present additional interesting properties, According to the molecular conformation the material can respond to an electric fields as a ferroelectric or an anti-ferroelectric material [7]. To our knowledge there have been no reports of de-Vries phases with bi-mesogens. This paper is a progress report on this ongoing work as presented at the 23rd International Liquid Crystal Conference (ILCC) in Krakow 2010.

Address correspondence to W. M. Zoghaib, Chemistry Department, Sultan Qaboos University, PO Box 36, Al-Khod 123, Oman. Tel.: +968-24142472; Fax: +968-24141469; E-mail: zoghaibw@squ.edu.om

2. Experimental

The general synthetic scheme is summarized in Figure 1.

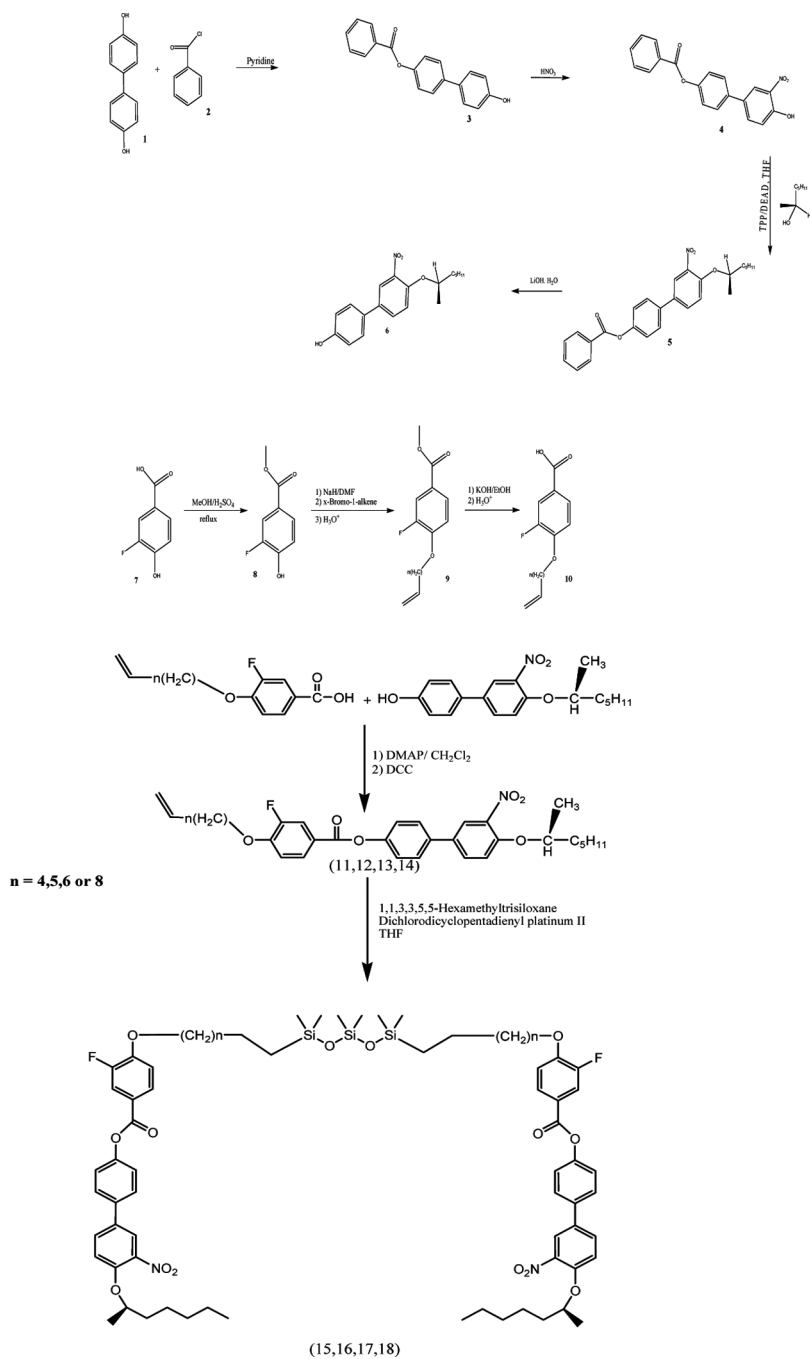


Figure 1. The general synthetic scheme.

2.1. Materials

Reagents were purchased from Aldrich and used as received. Diethyl azo dicarboxylate (DEAD) was purchased from ChemHere (Hong Kong) as a 40% solution in Toluene. The catalyst dichloro dicyclopentadienyl platinum II was purchased from STREM Chemicals (Massachusetts, USA).

2.2. Methods

Proton Magnetic Resonance (^1H -NMR) spectra were acquired and recorded using a 400 MHz AVANCE Bruker NMR spectrometer in CDCl_3 or CD_3OD . Carbon Magnetic Resonance (^{13}C -NMR) spectra were recorded at 100 MHz using the same NMR spectrometer. Chemical shifts (δ_{ppm}) were recorded in parts per million (ppm) downfield from TMS (assigned as zero ppm).

Thin layer chromatography (TLC) and preparative TLC were performed on glass plates pre-coated with Merck silica gel, whereas flash column chromatography was performed using Merck 60 silica gel purchased from Aldrich.

Rotary evaporator (BUCHI) was used to evaporate solvents at low pressure. Anhydrous reaction conditions were carried out under an inert atmosphere of dry Argon. THF was dried by distillation over potassium metal under Argon.

Liquid crystals transition temperatures were identified by polarized light microscopy in conjunction with a heating stage and a temperature control unit (Linkam TMS 94).

3. Synthesis

4-Hydroxy-4-biphenylbenzoate (3). Prepared according to known procedure [6] (70.2% yield).

4'-Hydroxy-3'-nitro-4-biphenylbenzoate (4). Prepared according to known procedure [6] (55.4% yield).

4'-((R)-1-Methylhexyloxy)-3'-nitro-4-biphenylbenzoate (5). Prepared according to known procedure [6] (87.4% yield).

4'-((R)-1-Methylhexyloxy)-3-nitro-4-hydroxybiphenyl (6). Prepared according to known procedure [6] (70.2% yield).

Methyl-3-Fluoro-4-hydroxybenzoate (8). Prepared according to known procedure [6] (50.4% yield).

4-(X-Alkenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid Methyl Esters (9). Prepared according to known procedure [6].

4-(5-Hexenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid Methyl Ester. 94% yield.

^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm): 1.48–1.55 (m, 2H, $\text{CH}_2(11)$); 1.78 (m, 2H, $\text{CH}_2(10)$); 2.06 (m, 2H, $\text{CH}_2(12)$); 3.81 (s, 1H, $\text{CH}_3(1)$); 4.01 (t, 2H, $\text{CH}_2(9)$, $J_1 = 6.5$, $J_2 = 6.5$); 4.89–4.94 (m, 1H, $\text{CH}_2(14)$); 4.94–4.99 (m, 1H, $\text{CH}_2(15)$), 5.75 (m, 1H, $\text{CH}(14)$); 6.88 (t, 1H, $\text{ArH}(6)$, $J_1 = 8.3$, $J_2 = 8.4$); 7.64–7.68 (dd, 1H, $\text{ArH}(4)$, $J_1 = 2.0$, $J_2 = 11.7$); 7.70–7.73 (m, 1H, $\text{ArH}(5)$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 25.52 $\text{CH}_2(11)$, 28.82 $\text{CH}_2(10)$, 33.73 $\text{CH}_2(12)$, 69.51 $\text{CH}_3(1)$, 77.23 $\text{CH}_2(9)$, 113.75 $\text{ArC}(4)$, 115.35 $\text{CH}_2(14)$, 117.70 $\text{ArC}(6)$, 123.04 $\text{ArC}(3)$, 126.99 $\text{CH}(6)$, 138.67 $\text{CH}(13)$, 151.60 $\text{ArC}(8)$, 153.42 $\text{ArC}(7)$, 166.43 $\text{C}=\text{O}(2)$. EI MS $m/z = \text{M}^+$: 252.5 (3%).

4-(6-Heptenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid Methyl Ester. 33.6% yield.

^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm): 1.18–1.23 (m, 2H, $\text{CH}_2(11)$); 1.39–1.41 (m, 2H, $\text{CH}_2(12)$); 1.44–2.04 (m, 2H, $\text{CH}_2(10)$); 2.00–2.04 (m, 2H, $\text{CH}_2(13)$); 3.82 (s, 1H, $\text{CH}_3(1)$); 4.01 (t, 2H, $\text{CH}_2(9)$, $J_1 = 6.6$, $J_2 = 6.5$); 4.86–4.89 (m, 1H, $\text{CH}_2(15)$); 4.91–4.96 (m, 1H, $\text{CH}_2(15)$), 5.69–5.79 (m, 1H, $\text{CH}(14)$); 6.88 (t, 1H, $\text{ArH}(6)$, $J_1 = 8.3$, $J_2 = 8.4$); 7.64–7.68 (dd, 1H, $\text{ArH}(5)$, $J_1 = 2.0$, $J_2 = 11.7$); 7.70–7.74 (m, 1H, $\text{ArH}(4)$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 25.75 $\text{CH}_2(11)$, 28.94 $\text{CH}_2(12)$, 29.27 $\text{CH}_2(10)$, 32.99 $\text{CH}_2(13)$, 52.48 $\text{CH}_3(1)$, 69.66 $\text{CH}_2(9)$, 113.75 $\text{ArC}(4)$, 114.95 $\text{CH}(15,7)$, 117.58 $\text{ArC}(3)$, 117.78 $\text{ArC}(5)$, 139.05 $\text{CH}(14)$, 151.63 $\text{ArC}(8)$, 151.74 $\text{ArC}(6)$, 166.43 $\text{C}=\text{O}(2)$. EI MS $m/z = \text{M}^+$: 266.5 (3%).

4-(7-Octenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid Methyl Ester. 98% yield.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.31–1.45 (m, 6H, $\text{CH}_2(11,12,13)$), 1.77 (m, 2H, $\text{CH}_2(10)$), 1.99 (m, 2H, $\text{CH}_2(14)$), 3.81 (s, 3H, $\text{CH}_3(1)$, 4.01 (t, 2H, $\text{CH}_2\text{O}(9)$, $J_1 = 6.5$, $J_2 = 6.5$), 4.85–5.96 (m, 2H, $\text{CH}_2=\text{CH}(16)$), 5.74 (m, 1H, $\text{CH}(15)$), 6.88 (t, 1H, $\text{ArH}(6)$, $J_1 = 8.3$, $J_2 = 8.3$), 7.64–7.70 (m, 1H, $\text{ArH}(4)$), 7.70–7.75 (m, 1H, $\text{ArH}(5)$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 26.11 $\text{CH}_2(11)$, 29.14 $\text{CH}_2(12)$, 29.36 $\text{CH}_2(10)$, 30.09 $\text{CH}_2(13)$, 34.05 $\text{CH}_2(14)$, 69.71 $\text{CH}_2(9)$, 113.78 $\text{CH}_2(16)$, 113.75 $\text{ArC}(6)$, 114.74 $\text{CH}_2(4)$, 123.11 $\text{ArC}(3)$, 126.97 $\text{ArC}(5)$, 139.32 $\text{CH}(15)$, 151.76 $\text{ArC}(8)$, 1153.47 $\text{ArC}(7)$, 166.44 $\text{C}=\text{O}(2)$.

4-(9-Decenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid Methyl Ester. 79%.

^1H NMR (CDCl_3 , TMS) δ (ppm): 1.2–2.08 (m, 14H, (CH_2)), 3.98 (t, 2H, CH_2O), 4.21 (s, 3H, OCH_3), 4.83, 4.92 (m, 2H, $\text{CH}=\text{CH}_2$), 5.70 (m, 1H, $\text{CH}=\text{CH}_2$), 6.95–8.1 (m, 8H, ArH).

4-(X-Alkenyloxy) Biphenyl-3-fluoro-4-carboxylic Acids (10). Prepared according to known procedure [6].

4-(5-Hexenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid. 53.8% yield.

^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm): 1.19–1.33 (m, 2H, $\text{CH}_2(11)$), 1.72–1.78 (m, 2H, $\text{CH}_2(10)$), 2.05–2.10 (m, 2H, $\text{CH}_2(12)$), 4.04 (t, 2H, $\text{CH}_2(9)$, $J_1 = 8.64$, $J_2 = 6.4$); 4.70–4.99 (m, 2H, $\text{CH}_2(14)$); 5.77 (m, 1H, $\text{CH}(13)$), 7.03 (t, 1H, $\text{ArH}(6)$, $J_1 = 8.4$, $J_2 = 8.4$), 7.61 (d, 1H, $\text{ArH}(5)$, $J = 11.9$), 7.71 (d, 1H, $\text{ArH}(4)$, $J = 8.4$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 22.68 $\text{CH}_2(11)$, 29.73 $\text{CH}_2(10)$, 31.73 $\text{CH}_2(12)$, 69.20 $\text{CH}_2(9)$, 113.65 $\text{ArC}(4)$, 114.20 $\text{CH}(14)$, 116.84 $\text{ArC}(6)$, 122.71 $\text{ArC}(3)$, 126.62 $\text{ArC}(5)$, 138.64 $\text{CH}(13)$, 150.88 $\text{ArC}(7)$, 153.42 $\text{ArC}(8)$, 168.34 $\text{C}=\text{O}(2)$.

4-(6-Heptenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid. 93.8% yield.

^1H NMR (400 MHz, CD_3OD , TMS) δ (ppm): 1.15–1.27 (m, 2H, $\text{CH}_2(11)$), 1.41–1.43 (m, 2H, $\text{CH}_2(12)$), 1.76–1.82 (m, 2H, $\text{CH}_2(10)$), 1.98–2.05 (m, 2H, $\text{CH}_2(13)$), 4.03 (t, 2H, $\text{CH}_2(9)$, $J_1 = 6.5$, $J_2 = 6.6$); 4.88–4.97 (m, 2H, $\text{CH}_2(15)$);

5.70–5.80 (m, 1H, CH(14)), 6.91 (t, 1H, ArH(6), $J_1 = 8.3$, $J_2 = 8.3$), 7.71–7.74 (dd, 1H, ArH(5), $J_1 = 1.7$, $J_2 = 11.5$), 7.79 (d, 1H, ArH(4), $J = 8.6$).

^{13}C NMR (100 MHz, CD_3OD , TMS) δ (ppm): 25.75 $\text{CH}_2(11)$, 28.95 $\text{CH}_2(12)$, 29.25 $\text{CH}_2(10)$, 34.00 $\text{CH}_2(13)$, 69.71 $\text{CH}_2(9)$, 113.72 $\text{CH}(4,6,15)$, 114.97 $\text{ArC}(3,5)$, 127.86 $\text{CH}(14)$, 151.01 $\text{ArC}(8)$, 1153.47 $\text{ArC}(7)$, 171.66 $\text{C}=\text{O}(2)$.

4-(7-Octenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid. 91% yield.

^1H NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 1.30–1.45 (m, 6H, $\text{CH}_2(11,12,13)$), 1.78 (m, 2H, $\text{CH}_2(10)$), 1.99 (m, 2H, $\text{CH}_2(14)$), 4.02 (t, 2H, $\text{CH}_2\text{O}(9)$, $J_1 = 6.6$, $J_2 = 6.5$), 4.85–5.95 (m, 2H, $\text{CH}_2=\text{CH}(16)$), 5.75 (m, 1H, CH(15)), 6.90 (t, 1H, ArH(6), $J_1 = 8.3$, $J_2 = 8.4$), 7.73 (d, 1H, ArH(4), $J = 1.9$), 7.80 (d, 1H, ArH(5), $J = 1.1$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 25.82 $\text{CH}_2(11)$, 28.84 $\text{CH}_2(10)$, 28.98 $\text{CH}_2(13)$, 29.13 $\text{CH}_2(12)$, 33.74 $\text{CH}_2(14)$, 69.38 $\text{CH}_2(9)$, 113.74 $\text{ArC}(4,6)$, 113.78 $\text{CH}_2(16)$, 139.01 $\text{CH}(15)$, 126.71 $\text{ArC}(5)$, 150.91 $\text{ArC}(8)$, 151.02 $\text{ArC}(7)$, 153.35 $\text{C}=\text{O}(2)$.

4-(9-Decenyloxy) Biphenyl-3-fluoro-4-carboxylic Acid. 82% yield.

^1H NMR (CDCl_3 , TMS) δ (ppm) 1.18–2.1 (m, 14H, (CH_2)), 4.02 (t, 2H, CH_2O), 4.90 (m, 2H, CHCH_2), 5.75 (m, 1H, $\text{CH}=\text{CH}_2$), 6.92 to 7.88 (m, 8H, Ar-H).

4-((R)-2-heptyloxy)-3-nitro-4-biphenyl-4-(9-hexenyloxy)-3-fluorobenzoate (11). Prepared according to modified known procedure [6].

24% yield.

^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm): 0.83 (t, 3H, $\text{CH}_3(1)$, $J_1 = 6.9$ Hz, $J_2 = 7.2$ Hz), 1.14–1.26 (m, 10H, $\text{CH}_2(2,3,4,28,29)$), 1.31 (d, 3H, $\text{CH}_3(7)$, $J = 6.1$), 1.51–1.61 (m, 2H, $\text{CH}_2(5)$), 2.06–2.15 (m, 2H, $\text{CH}_2(30)$), 4.07 (t, 2H, $\text{CH}_2(27)$, $J_1 = 6.5$, $J_2 = 6.5$), 4.45 (m, 1H, CH(6)), 4.92–4.97 (dd, 1H, $\text{CH}=\text{CH}_2(33)$, $J_1 = 1.7$ Hz, $J_2 = 9.9$ Hz), 5.01 (d, 1H, $\text{CH}=\text{CH}_2(32)$, $J = 1.7$), 5.73–5.80 (m, 2H, $\text{CH}=\text{CH}_2(31)$), 6.97 (t, 1H, ArH(25), $J_1 = 8.3$, $J_2 = 8.4$), 7.06 (d, 1H, ArH(9), $J = 8.9$), 7.22 (d, 2H, ArH(17,18), $J = 8.6$), 7.51 (d, 2H, ArH(15,16), $J = 8.6$), 7.62 (dd, ArH(11), $J_1 = 2.3$, $J_2 = 8.7$), 7.84 (dd, 1H, ArH(23), $J_1 = 2.0$, $J_2 = 11.5$), 7.90 (d, 1H, ArH(22), $J = 9.3$), 7.92 (d, 1H, ArH(12), $J = 2.3$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 14.36 $\text{CH}_3(1)$, 19.97 $\text{CH}_3(7)$, 22.93 $\text{CH}_2(2)$, 25.54 $\text{CH}_2(29)$, 25.35 $\text{CH}_2(4)$, 33.70 $\text{CH}_2(30)$, 32.08 $\text{CH}_2(3)$, 141.62 $\text{CH}_2(31)$, 36.61 $\text{CH}_2(5)$, 69.70 $\text{CH}_2(27)$, 77.60 $\text{CH}(6)$, 115.38 $\text{ArC}(9)$, 115.38 $\text{ArC}(22)$, 117.59 $\text{ArC}(25)$, 122.69 $\text{ArC}(17,18)$, 124.17 $\text{ArC}(12,21)$, 127.82 $\text{ArC}(23)$, 128.20 $\text{ArC}(15,16)$, 132.27 $\text{ArC}(13)$, 132.95 $\text{ArC}(14)$, 138.64 $\text{ArC}(10)$, 138.64 $\text{ArC}(11)$, 113.95 $\text{CH}(32)$, 151.06 $\text{ArC}(19)$, 151.30 $\text{ArC}(24)$, 152.13 $\text{ArC}(26)$, 152.36 $\text{ArC}(8)$, 164.43 $\text{C}=\text{O}(20)$.

4-((R)-2-heptyloxy)-3-nitro-4-biphenyl-4-(9-heptenyloxy)-3-fluorobenzoate (12). Prepared according to modified known procedure [6].

88% yield.

^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm): 0.76–0.88 (m, 3H, $\text{CH}_3(1)$), 1.14–1.30 (m, 10H, $\text{CH}_2(2,3,4,29,30)$), 1.31 (d, 3H, $\text{CH}_3(7)$, $J = 6.1$), 1.53–1.62 (m, 2H, $\text{CH}_2(5)$), 1.71–1.85 (m, 2H, $\text{CH}_2(28)$), 2.01–2.07 (m, 2H, $\text{CH}_2(31)$), 4.06 (t, 2H, $\text{CH}_2(27)$, $J_1 = 6.6$, $J_2 = 6.6$), 4.48 (m, 1H, CH(6)), 4.88 (d, 1H, $\text{CH}=\text{CH}_2(33)$, $J = 15.4$), 4.94 (dd, 1H, $\text{CH}=\text{CH}_2(33)$, $J_1 = 10.1$, $J_2 = 12.0$), 5.76 (m, 1H, $\text{CH}=\text{CH}_2(32)$), 6.97 (t, 1H, ArH(25), $J_1 = 8.3$, $J_2 = 8.4$), 7.06 (d, 1H, ArH(9),

$J = 8.9$), 7.20 (d, 2H, ArH(17,18), $J = 7.3$), 7.52 (d, 2H, ArH(15,16), $J = 8.7$), 7.62 (dd, ArH(11), $J_1 = 2.4$, $J_2 = 8.7$), 7.84 (dd, 1H, ArH(23), $J_1 = 2.0$, $J_2 = 11.5$), 7.90 (d, 1H, ArH(22), $J = 8.7$), 7.93 (d, 1H, ArH(12), $J = 2.3$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 14.47 CH_3 (1), 19.96 CH_3 (7), 23.36 CH_2 (2), 26.80 CH_2 (29), 29.26 CH_2 (4), 29.74 CH_2 (30), 30.08 CH_2 (28), 30.55 CH_2 (3), 32.08 CH_2 (31), 36.61 CH_2 (5), 69.82 CH_2 (27), 77.08 CH(6), 113.96 CH_2 (33), 114.98 ArC(9), 116.60 ArC(22), 122.20 ArC(17,18), 122.68 ArC(21), 124.16 ArC(12), 127.981 ArC(23), 128.20 ArC(15,16), 132.23 ArC(13), 132.26 ArC(14), 136.77 ArC(10), 139.00 ArC(11), 142.63 CH(32), 151.07 ArC(19), 151.14 ArC(24), 152.38 ArC(26), 153.60 ArC(8), 164.42 C=O(20).

4-((R)-2-heptyloxy)-3-nitro-4-biphenyl-4-(9-octenyloxy)-3-fluorobenzoate (13).

Prepared according to modified known procedure [6].

78.9% yield.

^1H NMR (CDCl_3 , TMS) δ (ppm): 0.83 (t, 3H, CH_3 (1), $J_1 = 6.9$, $J_2 = 6.9$), 1.19–2.28 (m, 12H, CH_2 (2,3,4,29,30,31)), 1.31 (d, 3H, CH_3 (7), $J = 6.1$), 1.43 (m, 2H, CH_2 (5)), 1.51 (m, 2H, CH_2 (28)), 2.01 (m, 2H, CH_2 (32)), 4.05 (t, 2H, CH_2O (27), $J_1 = 6.5$, $J_2 = 6.5$), 4.48 (m, 1H, CH(6)), 4.88 (d, 1H, $\text{CH}=\text{CH}_2$ (34), $J = 10.2$), 4.94 (d, 1H, $\text{CH}=\text{CH}_2$ (35), $J = 17.1$), 5.75 (m, 1H, $\text{CH}=\text{CH}_2$ (33)), 6.97 (t, 1H, ArH(25), $J_1 = 8.3$, $J_2 = 8.4$), 7.07 (d, 1H, ArH(9), $J = 8.8$), 7.21 (d, 2H, ArH(17,18), $J = 8.7$), 7.51 (d, 2H, ArH(15,16), $J = 8.6$), 7.62 (dd, ArH(11), $J_1 = 2.3$, $J_2 = 8.7$), 7.84 (dd, 1H, ArH(23), $J_1 = 1.9$, $J_2 = 11.5$), 7.90 (d, 1H, ArH(22), 8.7), 7.95 (d, 1H, ArH(12), $J = 2.3$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 14.38 CH_3 (1), 19.97 CH_3 (7), 22.95 CH_2 (2), 25.36 CH_2 (4), 26.13 CH_2 (29), 29.16 CH_2 (28,31), 29.35 CH_2 (30), 30.10 CH_2 (3), 32.09 CH_2 (32), 34.06 CH_2 (5), 69.83 CH_2 (27), 77.02 CH(6), 114.78 $\text{CH}_2=\text{CH}$ (34), 116.57 ArC(9,23), 118.13 ArC(25), 122.70 ArC(17,18), 124.16 ArC(21), 128.20 ArC(12), 129.97 ArC(22), 129.97 ArC(13), 132.29 ArC(15,16), 132.91 ArC(14), 136.75 ArC(10,11), 139.30 $\text{CH}_2=\text{CH}$ (33), 151.05 ArC(19), 151.31 ArC(26), 152.41 ArC(8), 152.51 ArC(24), 164.44 C=O(20).

4-((R)-2-heptyloxy)-3-nitro-4-biphenyl-4-(9-decenyloxy)-3-fluorobenzoate (14).

Prepared according to modified known procedure [6].

80% yield.

^1H NMR (CDCl_3 , TMS) δ (ppm): 0.83 (t, 3H, CH_3 (1), $J_1 = 6.9$, $J_2 = 6.9$), 1.19–2.28 (m, 16H, CH_2 (2,3,4,29,30,31,32,33)), 1.31 (d, 3H, CH_3 (7), $J = 6.1$), 1.43 (m, 2H, CH_2 (5)), 1.51 (m, 2H, CH_2 (28)), 2.01 (m, 2H, CH_2 (32)), 4.05 (t, 2H, CH_2O (27), $J_1 = 6.5$, $J_2 = 6.5$), 4.48 (m, 1H, CH(6)), 4.88 (d, 1H, $\text{CH}=\text{CH}_2$ (34), $J = 10.2$), 4.94 (d, 1H, $\text{CH}=\text{CH}_2$ (35), $J = 17.1$), 5.75 (m, 1H, $\text{CH}=\text{CH}_2$ (33)), 6.97 (t, 1H, ArH(25), $J_1 = 8.3$, $J_2 = 8.4$), 7.07 (d, 1H, ArH(9), $J = 8.8$), 7.21 (d, 2H, ArH(17,18), $J = 8.7$), 7.51 (d, 2H, ArH(15,16), $J = 8.6$), 7.62 (dd, ArH(11), $J_1 = 2.3$, $J_2 = 8.7$), 7.84 (dd, 1H, ArH(23), $J_1 = 1.9$, $J_2 = 11.5$), 7.90 (d, 1H, ArH(22), 8.7), 7.95 (d, 1H, ArH(12), $J = 2.3$).

^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm): 14.38 CH_3 (1), 19.97 CH_3 (7), 22.95 CH_2 (2), 25.36 CH_2 (4), 26.13 CH_2 (29), 29.16 CH_2 (28,31), 29.35 CH_2 (30), 29.70 CH_2 (33), 30.10 CH_2 (3), 32.09 CH_2 (32), 33.9 CH_2 (34), 34.06 CH_2 (5), 69.83 CH_2 (27), 77.02 CH(6), 115.78 $\text{CH}_2=\text{CH}$ (36), 116.57 ArC(9,23), 118.13 ArC(25), 122.70 ArC(17,18), 124.16 ArC(21), 128.20 ArC(12), 129.97 ArC(22), 129.97 ArC(13), 132.29 ArC(15,16), 132.91 ArC(14), 136.75 ArC(10,11), 137.70

CH₂=CH(35), 151.05 ArC(19), 151.31 ArC(26), 152.41 ArC(8), 152.51 ArC(24), 164.44 C=O(20).

Bis 1-[3'-Nitro-4'-(R)-(1-methylhexyloxy) Phenyl] Phenyl-4-(1,1,3,3,5,5-hexamethyltrisiloxyhexyloxy)-3-fluorobenzoate (15). Prepared according to modified known procedure [6].

29.1% yield.

¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 0.02–0.08 (m, 18H, CH₃(33,33',34,34',35,35')), 0.67–0.87 (m, 6H, CH₃(1,1')), 1.14–1.30 (m, 28H, CH₂(2,2',3,3',4,4',29,29',30,30',31,31',32',32')), 1.32 (d, 6H, CH₃(7,7')), J = 6.0 Hz), 1.55–1.61 (m, 4H, CH₂(5,5')), 1.77–1.84 (m, 4H, CH₂(28,28')), 4.06 (t, 4H, CH₂(27,27')), J₁ = 6.6, J₂ = 6.8), 4.47 (m, 2H, CH(6,6')), 6.97 (t, 2H, ArH(25,25')), J₁ = 8.4 Hz, J₂ = 8.3 Hz), 7.62 (dd, 2H, ArH(11,11')), J₁ = 2.4 Hz, J₂ = 8.4 Hz), 7.21 (d, 4H, ArH(17,17',18,18')), J = 8.6 Hz), 7.51 (d, 4H, ArH(15,15',16,16')), J = 8.6 Hz), 7.83 (dd, 2H, ArH(22,22')), J₁ = 2.0 Hz, J₂ = 11.5 Hz), 7.62 (dd, 2H, ArH(11,11')), J₁ = 2.4 Hz, J₂ = 8.4 Hz), 7.90 (d, 2H, ArH(23,23')), J = 8.5 Hz), 7.92 (d, 2H, ArH(12,12')), J = 2.3 Hz).

¹³C NMR (100 MHz, CDCl₃, TMS) δ (ppm): 1.37 CH₃(33,33',34,34'), 1.42 CH₃(35,35'), 14.49 CH₃(1,1'), 19.14 CH₂(32,32'), 19.95 CH₂(31,31'), 22.94 CH₂(7,7'), 23.04 CH₃(4,4'), 23.08 CH₂(2,2'), 25.35 CH₂(29,29'), 29.37 CH₂(28,28'), 31.98 CH₂(3,3'), 32.32 CH₂(30,30'), 36.61 CH₂(5,5'), 69.90 CH₂(27,27'), 77.02 CH(6,6'), 113.88 ArCH(19,19',22,22'), 116.56 ArCH(25,25'), 122.70 ArCH(17,17',18,18'), 123.84 ArCH(12,12'), 124.17 C(21,21'), 127.82 ArCH(23,23'), 128.20 ArCH(15,15',16,16'), 132.28 ArC(13,13'), 132.93 ArC(14,14'), 136.76 ArC(10,10',11,11'), 151.06 ArC(19,19'), 151.30 ArC(26,26'), 151.43 ArC(24,24'), 153.58 ArCH(8,8'), 164.42 C=O(20,20').

Bis 1-[3'-Nitro-4'-(R)-(1-methylhexyloxy) Phenyl] Phenyl-4-(1,1,3,3,5,5-Hexamethyltrisiloxyheptyloxy)-3-fluorobenzoate (16). Prepared according to modified known procedure [6].

40.1% yield.

¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 0.02–0.08 (m, 18H, CH₃(34,34',35,35',36,36')), 0.79–0.84 (m, 6H, CH₃(1,1')), 1.15–1.27 (m, 16H, CH₂(2,2',3,3',4,4',29,29',30,30',31,31',32,32',33,33')), 1.32 (d, 6H, CH₃(7,7')), J = 6.1), 1.56–1.62 (m, 4H, CH₂(5,5')), 1.72–1.82 (m, 4H, CH₂(28,28')), 4.06 (t, 4H, CH₂(27,27')), J₁ = 6.5, J₂ = 6.5), 4.48 (m, 2H, CH(6,6')), 6.97 (t, 2H, ArH(25,25')), J₁ = 8.3 Hz, J₂ = 8.3 Hz), 7.06 (d, 2H, ArH(9,9')), J = 8.9 Hz), 7.22 (d, 4H, ArH(17,17',18,18')), J = 8.5), 7.52 (d, 4H, ArH(15,15',16,16')), J = 8.5), 7.63 (dd, 2H, ArH(22,22')), J₁ = 2.2 Hz, J₂ = 8.7 Hz), 7.83 (d, 2H, ArH(11,11')), J = 11.5), 7.91 (m, 2H, ArH(23,23')), 7.92 (d, 2H, ArH(12,12')), J = 2.2).

¹³C NMR (100 MHz, CDCl₃, TMS) δ (ppm): 0.69 CH₃(34,34',35,35'), 1.42 CH₃(36,36'), 14.35 CH₃(1,1'), 14.47 CH₂(33,33'), 19.96 CH₂(32,32'), 22.93 CH₂(7,7'), 22.97 CH₃(2,2'), 25.34 CH₂(4,4'), 26.23 CH₂(29,29'), 29.41 CH₂(30,30'), 30.09 CH₂(28,28'), 32.08 CH₂(3,3'), 32.11 CH₂(31,31'), 36.62 CH₂(5,5'), 69.93 CH₂(27,27'), 113.96 ArC(22,22'), 116.60 ArC(9,9'), 118.33 ArC(25,25'), 122.69 ArC(17,17',18,18'), 124.15 ArC(21,21'), 127.82 C(23,23'), 128.18 ArC(15,15',16,16'), 132.25 ArC(13,13'), 132.95 ArC(14,14'), 136.77 ArC(10,10'), 141.63 ArCH(11,11'), 151.08 ArC(19,19'), 151.30 ArC(24,24'), 152.54 ArC(26,26'), 153.60 ArCH(8,8'), 164.43 C=O(20,20').

Bis 1-[3'-Nitro-4'-(R)-(1-methylhexyloxy) Phenyl] Phenyl-4-(1,1,3,3,5,5-hexamethyltrisiloxyoctyloxy)-3-fluorobenzoate (17). Prepared according to modified known procedure [6].

57.4% yield.

¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 0.004–0.08 (m, 18H, CH₃(35,35',36,36',37,37')), 0.85 (t, 6H, CH₃(1,1')' J₁ = 7.3 Hz, J₂ = 5.7 Hz), 1.17–1.26 (m, 18H, CH₂(2,2',3,3',4,4',29,29',30,30',31,31',32,32')), 1.32 (d, 6H, CH₃(7,7'), J = 6.1 Hz), 1.36–1.46 (m, 8H, CH₂(33,33',34,34'), 1.59–1.61 (m, 4H, CH₂(5,5')), 1.77–1.82 (m, 4H, CH₂(28,28')), 4.06 (t, 4H, CH₂(27,27'), J₁ = 6.5, J₂ = 6.6), 4.48 (m, 2H, CH(6,6')), 6.97 (t, 2H, ArH(25,25'), J₁ = 8.3 Hz, J₂ = 8.3 Hz), 7.06 (d, 2H, ArH(9,9'), J = 8.9 Hz), 7.21 (t, 4H, ArH(17,17',18,18'), J₁ = 8.6 Hz, J₂ = 6.7 Hz), 7.52 (d, 4H, ArH(15,15',16,16'), J = 8.6 Hz), 7.63 (dd, 2H, ArH(22,22') J₁ = 2.3 Hz, J₂ = 8.7 Hz), 7.83 (dd, 2H, ArH(11,11'), J₁ = 2.0 Hz, J₂ = 11.5 Hz), 7.91 (d, 2H, ArH(23,23'), J = 8.8 Hz), 7.93 (d, 2H, ArH(12,12'), J = 2.3 Hz).

¹³C NMR (100 MHz, CDCl₃, TMS) δ (ppm): 0.69 CH₃(35,35',36,36'), 1.25 CH₃(37,37'), 14.37 CH₃(1,1'), 14.47 CH₂(34,34'), 19.97 CH₂(33,33'), 22.94 CH₂(4,4'), 23.03 CH₃(7,7'), 25.35 CH₂(2,2'), 26.27 CH₂(29,29'), 29.40 CH₂(31,31'), 29.58 CH₂(28,28'), 29.68 CH₂(30,30'), 32.09 CH₂(3,3'), 32.18 CH₂(32,32'), 36.61 CH₂(5,5'), 69.91 CH₂(27,27'), 77.03 CH(6,6'), 113.90 ArCH(22,22'), 116.56 ArCH(9,9'), 118.13 ArCH(25,25'), 122.70 ArCH(17,17',18,18'), 124.18 ArCH(12,12'), 127.80 C(21,21'), 127.83 ArCH(23,23'), 128.21 ArCH(15,15',16,16'), 132.29 ArC(13,13'), 132.93 ArC(14,14'), 136.77 ArC(10,10'), 141.58 ArCH(11,11'), 151.05 ArC(19,19'), 151.11 ArC(26,26'), 151.30 ArC(24,24'), 152.43 ArCH(8,8'), 164.46 C=O(20,20').

Bis 1-[3'-Nitro-4'-(R)-(1-methylhexyloxy) Phenyl] Phenyl-4-(1,1,3,3,5,5-hexamethyltrisiloxydecyloxy)-3-fluorobenzoate (18). Prepared according to modified known procedure [6].

75% yield.

¹H NMR (CDCl₃, TMS) δ (ppm) 0.95 (t, 3H, CH₂CH₃); 1.33 (m, 2H, CH₃CH₂); 1.29 (m, 4H, CH₂CH₂); 1.66 (m, 2H, CHCH₂); 3.86 (m, 1H, OCH); 1.43 (d, 3H,

Table 1. The observed transition temperatures between stable phases

No. of carbon	Heating	Cooling
6	$K \xrightarrow{81} 1$	$K \xleftarrow{68} 1$
7	$K \xrightarrow{86} 1$	$K \xleftarrow{66} 1$
8	$K \xrightarrow{77} 1$	$K \xleftarrow{64} 1$
10	$SmC^* \xleftrightarrow{64} 1$	$SmC^* \xleftrightarrow{64} 1$

Table 2. Transition from the quenched metastable smectic to isotropic

No. of carbon	Heating
7	$SmC^* \xrightarrow{41} 1$
8	$SmC^* \xrightarrow{52} 1$

CHCH₃); 7.08 (dd, 1H, ArH); 7.76 (dd, 1H, ArH); 8.30 (s, 1H, ArH); 7.31 (dd, 2H, ArH); 6.79 (dd, 2H, ArH); 1.18–2.1 (m, 14H, (CH₂)), 3.58 (t, 2H, CH₂O), 6.92 to 7.88 (m, 8H, Ar-H); 0.9–1.5 (m, 18H, SiCH₃).

4. Polarised Light Microscopy Observations

The preliminary characterization of the first materials in the series was performed using polarized light microscopy. The transition temperatures observed are summarized in Table 1.

The material with 6 carbon atoms in the alkyl chain does not display any mesophases. On slow cooling the materials with 7 and 8 carbon atoms from the isotropic phase crystallization is observed; on rapid cooling a metastable smectic phase is observed. The response of this metastable smectic phase to an electric field is that of a ferroelectric SmC* phase. After a few minutes, the crystalline phase grows from the smectic phase. The transition temperatures from the metastable smectic to isotropic phase are given in Table 2.

The material with 10 carbon atoms in the chain displays a stable smectic phase at room temperature. The preliminary observations of the electro-optic response would indicate that the smectic phase is a de-Vries type SmA* however more work is required to confirm the nature of the observed phase.

5. Conclusion

It would appear that linking two mesogenic moieties to the siloxane reduces the ability to form a smectic phase and increases the tendency to crystallize. The mono-mesogen with 6 carbon atoms in the chain reported in reference [4] displays a stable smectic de-Vries phase at room temperature. The homologue with 11 carbon atom in the chains is currently under preparation. A complete characterization of all the materials in the series after thorough verification of the purity will be given in a forthcoming publication.

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