

Article

Influence of Mesogenic Properties of Cruciform-Shaped Liquid Crystals by Incorporating Side-Arms with a Laterally-Substituted-Fluorine

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Abstract: Fluoro substitution in thermotropic liquid crystals provides a general way of modifying the properties of a parent system. Transition temperatures, mesophase types and other physical properties can be affected by fluoro substitution, so that frequently the behaviors of the parent compound can be manipulated and improved in a predictable manner. This paper discusses the effects of a fluoro substitution in each side-arm of 1,2,4,5-tetrakis((4-(alkoxy)phenyl)ethynyl)benzenes on the resulting mesomorphic properties characterized by optical polarizing microscopy and differential scanning calorimetry. Without any fluoro-substituted side-arms, longer chain-length leads to a wider nematic temperature range on cooling. Incorporation of a fluoro substitution in each side-arm induces the formation of a lamellar suprastructure, lowers transition temperatures and results in a wider mesophase temperature range on cooling.

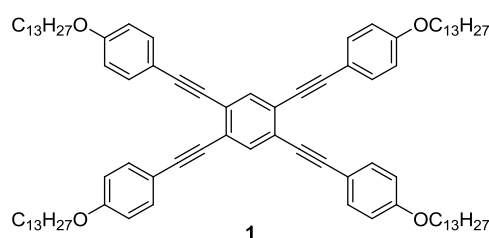
Keywords: 1,2,4,5-tetraalkoxyphenylethynylbenzene (TPEB); cruciform-shaped; mesophase; smectic phase; nematic phase

1. Introduction

Liquid crystals have many fascinating and useful properties that make them ideally suited for use in a wide range of technical devices. In a crystal, molecules occupy specific sites in a lattice and point their molecular axes in specific directions. Molecular shape concludes to a large extent the type of mesophase observed for thermotropic liquid crystals. Generally, rod-like molecules give rise to smectic and/or nematic mesophases, while disc-like molecules self-organize to furnish columnar mesophases. A wide range of molecular geometries, board-like (sanidic) molecules [1–3], polycatenar compounds resulting from calamitic compounds modified with several terminal chains [4,5], disc-like molecules where the number of substituents was reduced [3], rod-disc dimers [6], disc-disc dimers [7], different arrangements of disc-rod-disc and rod-half-disc dimers [8] were prepared and investigated. Among them, cruciform-shaped molecules exhibit spatial separation of their frontier molecular orbitals, building 1,2,4,5-tetraalkoxyphenylethynylbenzene (TPEB), and are excellent candidates for a variety of advanced materials applications, such as organic light-emitting diodes, solar cells and optical storage devices [9–16]. Carbon-rich cruciforms already possess demonstrated potential as nonlinear optical/two-photon absorption [17,18] and fluorescent sensing materials [19–21]. Changes in the substituents, substitution pattern, electronic structure and conjugation can provide highly variable photo physical properties for such materials. Therefore, it is expected that detailed study on the structure-property relationships for these materials will provide valuable information for molecular design with high performance. The cross-like TPEB (**A**), shown in Figure 1, was originally designed for achieving biaxial nematic behavior; however, nematic textures were only observed monotropically upon cooling at 74 °C on small regions, following clearing at 96 °C [22]. The mesophase stability, as well as the small nematic temperature range hampered further biaxial investigations. Recently, based on the structure shown in Figure 1, enantiotropic nematic behaviors were reported by replacing the peripheral phenyls with biphenyls to stabilize the nematic phase [23]. Nevertheless, compound **1**'s low clearing temperature can be of advantage in practical applications.

Fluorine's value as a lateral substituent in liquid crystalline materials lies in the fact that it is of small size and high electronegativity, and these two characteristics lead to a subtle modification of physical properties, often reducing melting points without totally eliminating liquid crystal phases [22]. Moreover, the great strength of the C–F bond confers chemical stability on fluoro-substituted compounds. However, a terminal fluoro substitution in calamitic mesogens tends to induce the formation of smectic phases [24].

Figure 1. The alkoxy substituted cruciform-shaped tetrakis(phenylethynyl)benzene (**1**) reported by Goodby *et al.* [25].



Current work explores the influence of attaching lateral fluorine groups on incorporating a lateral fluoro substituent ortho to the alkoxy chain onto each peripheral phenyls of the cruciform shaped compound **1**. Though still monotropic, the fluoro-substituted compounds exhibit lower transition temperatures advantageous in practical applications. Moreover, the fluoro groups induce and promote the formation lamellar mesophase for the cruciform-shaped mesogens.

2. Results and Discussion

In this study, two novel cruciform-shaped liquid crystals, one with lateral-fluoro side-arms and the other with non-fluoro side-arms, are disclosed. The liquid crystalline properties of the synthesized compounds were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

2.1. Synthesis

The synthetic procedure is illustrated in Figure 2. Compounds **5a,b** as the side-arms were obtained starting from **2** by alkylation, Sonogashira coupling with 2-methyl-3-butyn-2-ol and, then subsequent deprotection in excellent yields. Electrophilic iodination was performed at benzene in four positions to yield 1,2,4,5-tetraiodobenzene (**6**). Compound **7** without any fluorine atoms was prepared by coupling of **5a** with **6**. Furthermore, coupling of compound **6** with one equivalent of **5a** afforded 1-((4-alkoxyphenyl)ethynyl)-2,4,5-triiodobenzene (**8**). With the appropriate intermediate **8** in hand, the palladium catalyzed coupling reaction was applied for the synthesis of trifluoro-monoalkoxy TPEB (**9**). The tetrafluoro analogue **10** was obtained using the same procedure for compound **7**, except the side-arm **5b**, was employed.

2.2. Liquid Crystalline Properties

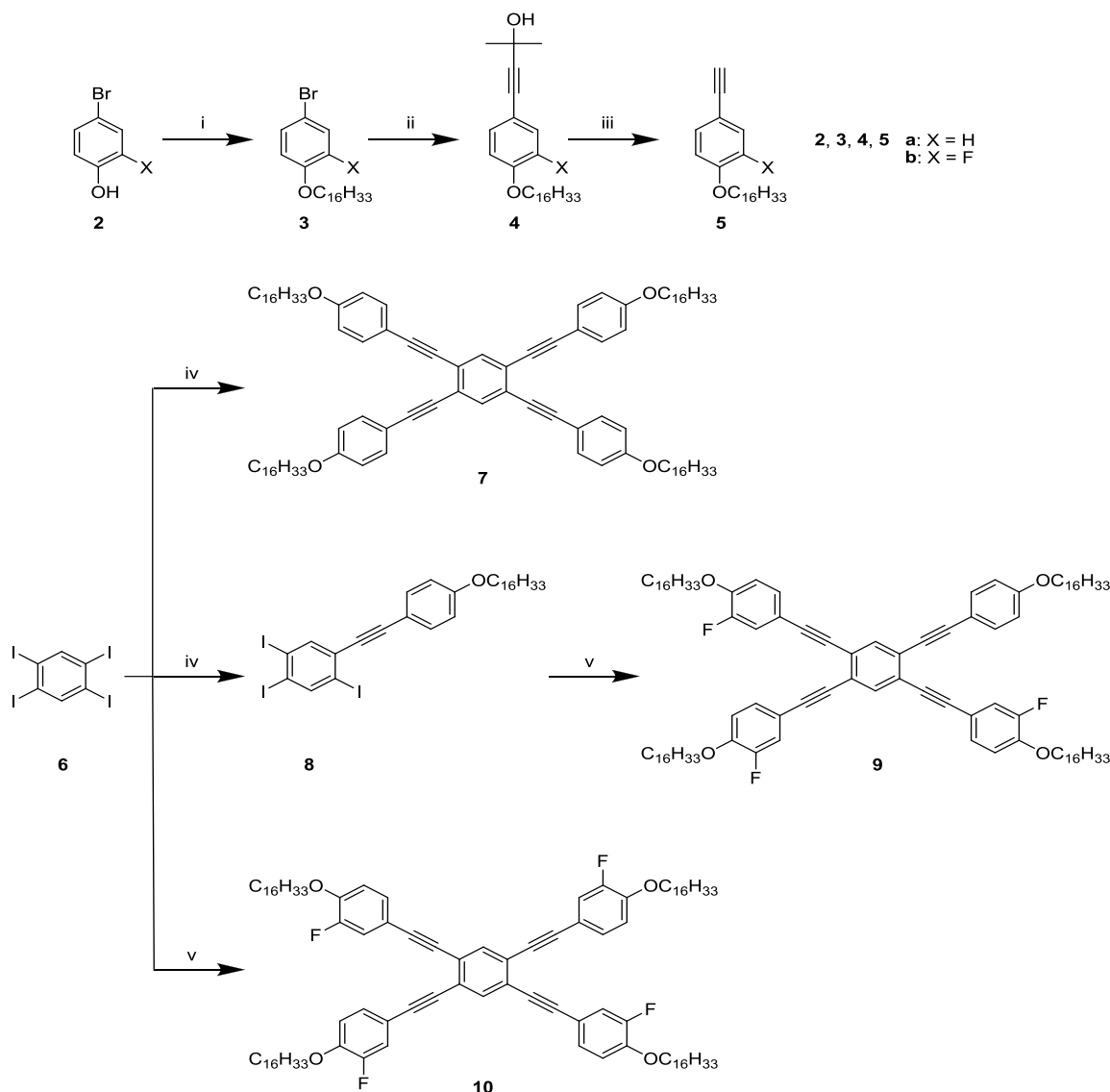
The mesophase behaviors of all the new compounds were initially examined by polarizing optical microscopy (POM). The enthalpy change of different transitions was determined by differential scanning calorimetry (DSC) scans. Phase transition temperatures and enthalpies of compounds **7**, **9** and **10** are summarized in Table 1.

Table 1. Phase behaviors of compounds **7**, **9** and **10**.

Compound	Thermal treatments ^b	Phase behavior	T [°C] (ΔH [kJ mol ⁻¹])
7	heating	Cryst-iso	84.1 (30.58)
	cooling	iso-N-Cryst	74.0 (−0.69), 60.7 (−78.75)
9	heating	Cryst-iso	81.3 (93.72)
	cooling	iso-N-SmC-Cryst ^a	66.1 (−1.05), 64.9 (−3.43), 41.7 (−67.32)
10	heating	Cryst-iso	78.3 (38.00)
	cooling	iso-SmC-Cryst	62.1 (−4.85), 40.5 (−25.92)

^a Cryst, N, SmC and iso denote crystalline, nematic, smectic C and isotropic phases; ^b Thermal treatments were recorded for the second heating and cooling runs at 10 °C/min.

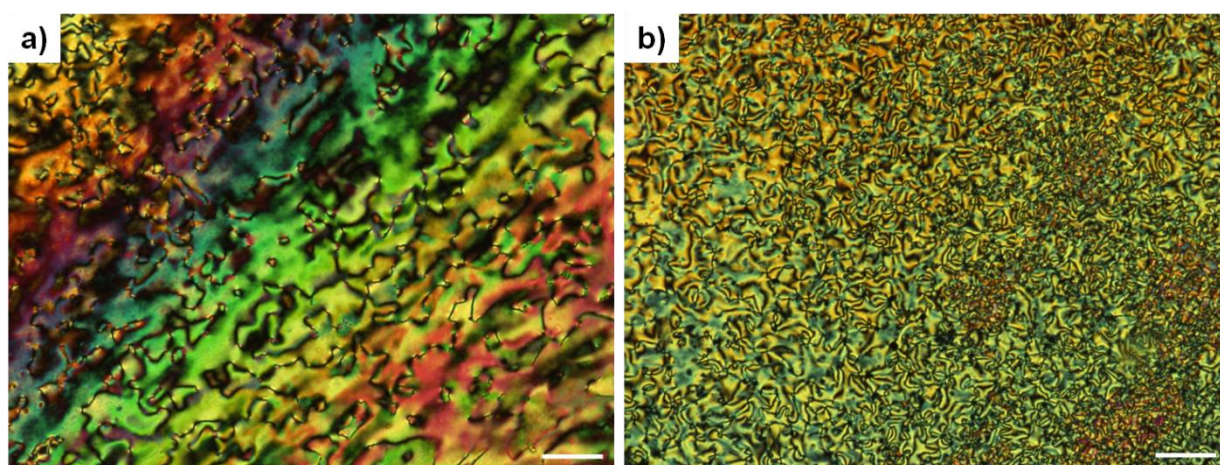
Figure 2. Synthesis of the non-fluoro OC₁₆ 1,2,4,5-tetraalkoxyphenylethynylbenzene (TPEB) (**7**), the trifluoro substituted TPEB (**9**) and the tetrafluoro substituted TPEB (**10**). Conditions: (i) RBr, K₂CO₃, KI, acetone, reflux, 24 h; (ii) Pd(PPh₃)₂Cl₂, CuI, 2-methyl-3-butyn-2-ol, (*i*-Pr)₂NH, 80 °C, 4 h; (iii) KOH, toluene, EtOH, reflux, 2 h; (iv) **5a**, Pd(PPh₃)₂Cl₂, CuI, triethylamine, room temperature (r.t.), 12 h; (v) **5b**, Pd(PPh₃)₂Cl₂, CuI, TEA, r.t., 12 h.



Compound **7** was synthesized for the realization of the influence of chain length on the transition temperatures of the nematic phase. Similar to compound **1**, compound **7** exhibited a monotropic nematic phase with the characteristic two- and four-brush Schlieren texture (Figure 3a). However, for compound **7**, the clearing temperature is significantly lower, and the nematic texture can be detected throughout the sample region within a reasonable temperature range on cooling. Herein, the balance of chain-length and conjugated core is crucial for obtaining wider mesophase ranges of cruciform-shaped TPEB. To evaluate the role of fluorine atoms on the properties of the TPEB system, additionally, two compounds with lateral fluoro substituents have been synthesized. Based on the superior mesogenic properties of compound **7**, incorporating a lateral-F group onto three side arms as in compound **9** leads

to the formation of a smectic phase in addition to a nematic phase, both on cooling, indicating that the introduction of a fluorine atom onto each of three peripheral phenyls induces the lamellar mesophase in addition to the original nematic phase. When all four side-arms are lateral-F-containing, as in compound **10**, the nematic phase disappeared, and a monotropic lamellar phase, SmC, as indicated by the blurred Schlieren texture shown in Figure 3b, emerged as the sole mesophase. The incorporation of a lateral fluorine group on each side-arm results in enhanced intermolecular lateral interactions to promote the lamellar suprastructure and to result in a wider mesophase temperature range on cooling.

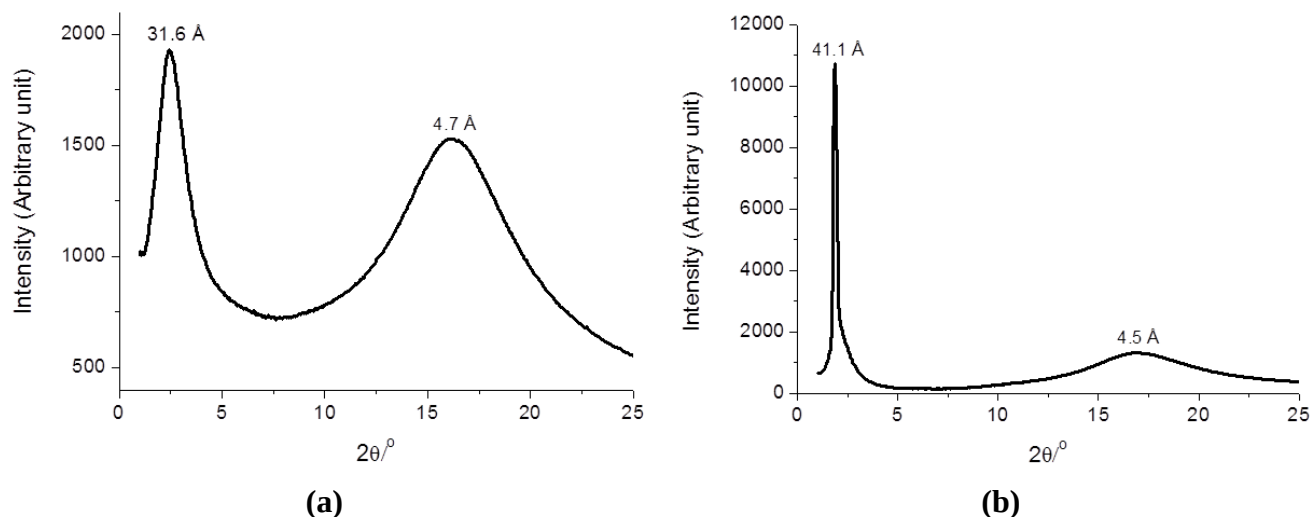
Figure 3. Polarizing optical micrographs: (a) compound **7** exhibiting a typical nematic Schlieren texture at 71 °C; (b) compound **10** showing a blurred Schlieren texture at 50 °C, indicating a smectic C phase. Samples were sandwiched between glass slides and viewed through crossed polarizers. (Scale bar: 50 µm).



3. X-ray Diffraction Studies

The two mesophases exhibited by the TPEB derivative of compound **9** were probed by X-ray diffraction (XRD) studies, and the results are shown in Figure 4. The XRD pattern of compound **9** at 130 °C upon cooling showed two diffuse halos at $d = 31.6$ and 4.7 Å. Upon further cooling, the XRD pattern at 55 °C exhibited a sharp signal at 41.1 Å and a diffuse halo at 4.5 Å. At both temperatures, the diffuse halo in the wide angle regime is ascribed to the liquid-like alkyl chains, indicating mesophase formation. The diffraction pattern of two diffuse halos at higher temperature is typical for a nematic phase. At 55 °C, the sharp small angle peak indicates the formation of a lamellar supra-structure, and the d spacing does not change significantly upon further cooling, which is typical for SmC mesophases. The XRD data are in accordance with the mesophase assignments by POM observations.

Figure 4. XRD patterns of trifluoro compound **9**: (a) the N phase at 130 °C and (b) the smectic C (SmC) phase at 55 °C.



In conclusion, the incorporation of fluorine atoms laterally onto side-arms of TPEB induced and promoted the formation of a SmC phase. Though the obtained nematic and smectic phases are only kinetically stable, the wider mesophase temperature ranges on cooling do provide a better window for mesophase characterization. A new smectic phase was achieved for the cruciform mesogens.

4. Experimental Section

General Procedure: Compounds **3a**, **4a** and **5a** were prepared according to the literature procedure [23,26]. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300 at 300 MHz or a Bruker Avance 600 spectrometer at 600 MHz and a Bruker AC-300 at 75 MHz or a Bruker Avance 600 at 150 MHz, respectively. Chemical shifts were referenced to the residual solvent protons in CDCl_3 ($\delta = 7.26$ ppm), dimethyl sulphoxide (DMSO)- d_6 ($\delta = 2.49$ ppm), THF-d_8 (δ ($-\text{CH}_2$) = 1.85 ppm) or CD_2Cl_2 ($\delta = 5.32$ ppm) in ^1H NMR spectra as the internal standards and in CDCl_3 ($\delta = 77.23$ ppm), THF-d_8 (δ ($-\text{CH}_2$) = 25.62 ppm) or CD_2Cl_2 ($\delta = 53.84$ ppm) in ^{13}C NMR spectra as the internal standards. Coupling constants (J) were reported in Hertz (Hz). Resonance multiplicities are described as s (singlet); d (doublet); dd (double of doublet); dt (double of triplet); t (triplet); td (triple of doublet); tt (triple of triplet); q (quartet); and m (multiplet). Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris1 instrument with heating and cooling rates of 10 and 20 °C min^{-1} , respectively. Polarizing optical microscopy (POM) was carried out on a Nikon with a Mettler FP90/FP82HT hot stage system. Elemental analyses were performed with a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Central University, Chungli (Taiwan), and at National Cheng Kung University, Tainan (Taiwan).

4.1. 4-Bromo-2-fluoro-1-(hexadecyloxy)benzene (**3b**)

To a solution of **2b** (4.60 g, 24.1 mmol) in acetone was added K_2CO_3 (9.98 g, 72.2 mmol), KI (1.20 g, 7.22 mmol) and 1-bromotetradecane/1-bromohexadecane/1-bromohexadecane (36.05 mmol), and then, this was stirred at 85 °C overnight. The reaction mixture was poured into water and extracted

with dichloromethane. The combined organic layer was washed with brine and dried over MgSO_4 and concentrated *in vacuo* to yield crude compound and purified by silica gel column chromatography eluted using hexane to yield **3b**: ^1H NMR (CDCl_3 , 300 MHz): δ 7.22 (dd, $J = 10.4$ Hz, 2.2 Hz, 1H), 7.16 (d, $J = 8.8$ Hz, 1H), 6.82 (t, $J = 8.7$ Hz, 1H), 3.98 (t, $J = 6.6$ Hz, 2H), 1.84–1.75 (m, 2H), 1.48–1.21 (m, 26H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 152.7, 146.6, 134.5, 127.1, 119.6, 116.1, 111.8, 69.7, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 25.9, 22.7, 14.1.

4.2. 4-(3-Fluoro-4-(hexadecyloxy)phenyl)-2-methylbut-3-yn-2-ol (**4b**)

To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.173 g, 0.24 mmol), copper(I) iodide (0.46 g, 0.24 mmol) and compound **3b** (10.01 g, 24.10 mmol) dissolved in 30 mL triethylamine (TEA), 2-methyl-3-butyn-2-ol (3.5 mL, 35.66 mmol) in 30 mL TEA was added dropwise under nitrogen atmosphere at 60 °C. The reaction mixture was then refluxed for 14 h. After cooling to room temperature, 200 mL dichloromethane was added. The mixture was washed twice with saturated $\text{NH}_4\text{Cl(aq)}$ (150 mL), twice with H_2O (100 mL) and dried with anhydrous MgSO_4 . The organic layer was collected, and the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/dichloromethane 5/1 to yield compound **4b** (9.97 g, 23.82 mmol, 99%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.12–7.08 (m, 2H), 6.82 (t, $J = 8.4$ Hz, 1H), 3.99 (t, $J = 6.5$ Hz, 2H), 1.80 (m, 2H), 1.47–1.20 (m, 33H), 0.88 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 152.2, 147.6, 128.1, 119.3, 115.1, 114.3, 93.0, 81.0, 80.9, 69.4, 65.5, 31.9, 31.4, 29.7, 29.5, 29.4, 29.3, 29.1, 25.8, 22.7, 14.1.

4.3. 4-Ethynyl-2-fluoro-1-(hexadecyloxy)benzene (**5b**)

To a solution of potassium hydroxide (2.00 g, 35.70 mmol) in 50 mL toluene/ethanol (v/v = 4:1), **4b** (10.0 g, 23.9 mmol) was added to give a suspension. It was allowed to stir under reflux for 12 h, and the solvent was removed under reduced pressure. The crude residue was washed with 2 N HCl(aq) and extracted with dichloromethane. The organic layer was dried with anhydrous MgSO_4 , and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography (silica gel, *n*-hexane). Compound **5b**: Yield (6.54 g, 18.14 mmol, 76%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.21–7.16 (m, 2H), 6.86 (t, $J = 8.3$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 2H), 2.99 (s, 1H), 1.82–1.80 (m, 2H), 1.49–1.28 (m, 26H), 0.90 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 152.3, 148.1, 128.6, 119.6, 114.3, 82.5, 76.4, 67.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 25.9, 22.7, 14.1.

4.4. 1,2,4,5-Tetrakis((4-(hexadecyloxy)phenyl)ethynyl)benzene (**7**)

To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (3 mg, 0.001 mmol), copper(I) iodide (4 mg, 0.05 mmol) and 1,2,4,5-tetraiodobenzene (0.030 g, 0.052 mmol) dissolved in 9 mL TEA and 3 mL DMSO, compound **5a** (0.088 g, 0.26 mmol) in 5 mL TEA was added dropwise under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 10 h. After completion of the reaction, the mixture was recrystallized using MeOH, and the residue was purified by column chromatography (silica gel, *n*-hexane/dichloromethane 10/1) to yield compound **7**: Yield (0.058 g, 0.041 mmol, 78%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.67 (s, 2H), 7.48 (d, $J = 8.7$ Hz, 8H), 6.87

(d, $J = 7.8$ Hz, 8H), 3.97 (t, $J = 6.3$ Hz, 8H), 1.81–1.74 (m, 8H), 1.46–1.26 (m, 104H), 0.90–0.86 (m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.6, 134.4, 133.2, 125.1, 115.0, 114.7, 95.4, 86.6, 68.2, 31.9, 29.7, 29.7, 29.6, 29.4, 29.4, 29.2, 26.0, 22.7, 14.1. Anal. calcd. for $\text{C}_{102}\text{H}_{150}\text{O}_4$: C 85.06, H 10.50; found: C 85.43, H 10.83.

4.5. 1-(4-Hexadecyloxyphenylethynyl)-2,4,5-triiodobenzene (8)

To a mixture of *trans*-dichlorobis(triphenylphosphine) palladium(II) (7 mg, 0.01 mmol), copper(I) iodide (34 mg, 0.13 mmol) and 1,2,4,5-tetraiodobenzene (0.300 g, 0.51 mmol) dissolved in 5 mL TEA and 2 mL DMSO, compound **5a** (0.208 g, 0.61 mmol) in 5 mL TEA was added dropwise under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 14 h. After completion of the reaction, the mixture was recrystallized using MeOH, and the residue was purified by column chromatography (silica gel, *n*-hexane/dichloromethane 20/1) to yield compound **8**: Yield (0.067 g, 0.084 mmol, 12%). ^1H NMR (d_8 -THF, 300 MHz): δ 8.28 (s, 2H), 7.91 (s, 1H), 7.49 (d, $J = 9.3$ Hz, 1H), 6.87 (d, $J = 9.2$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 1.83–1.74 (m, 2H), 1.47–1.20 (m, 26H), 0.89 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR (d_8 -THF, 75 MHz): δ 159.9, 147.3, 141.2, 133.2, 131.5, 114.7, 114.0, 107.6, 106.9, 100.5, 95.8, 88.5, 68.1, 31.9, 29.69, 29.65, 29.58, 29.55, 29.3, 29.1, 26.0, 22.7, 14.1.

4.6. 1,2,4-Tris(3-fluoro-4-hexadecyloxyphenylethynyl)-5-(4-hexadecyloxy-phenylethynyl)benzene (9)

A similar Sonogashira coupling reaction was utilized to prepare **9**. Yield (0.055 g, 0.04 mmol, 74%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.67 (s, 2H), 7.49 (d, $J = 8.8$ Hz, 4H), 7.31–7.27 (m, 3H), 7.09 (t, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 4H), 4.07 (t, $J = 6.5$ Hz, 4H), 3.99 (t, $J = 6.5$ Hz, 4H), 1.83–1.72 (m, 8H), 1.49–1.29 (m, 104H), 0.88 (t, $J = 6.6$ Hz, 12H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 160.9, 152.9, 149.4, 135.4, 135.3, 133.9, 129.3, 126.6, 125.9, 125.9, 125.6, 119.7, 116.0, 115.9, 115.5, 115.5, 115.4, 96.9, 95.3, 95.2, 87.6, 86.5, 86.9, 69.9, 68.8, 32.9, 30.7, 30.6, 30.6, 30.4, 30.3, 30.1, 26.9, 26.9, 25.3, 23.6, 14.5.

4.7. 1,2,4,5-Tetrakis((3-fluoro-4-(hexadecyloxy)phenyl)ethynyl)benzene (10)

To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (3 mg, 0.001 mmol), copper(I) iodide (4 mg, 0.05 mmol) and 1,2,4,5-tetraiodobenzene (0.030 g, 0.052 mmol) dissolved in 9 mL TEA and 3 mL DMSO, compound **5b** (0.092 g, 0.26 mmol) in 5 mL TEA was added dropwise under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 10 h. After completion of the reaction, the mixture was recrystallized using MeOH, and the residue was purified by column chromatography (silica gel, *n*-hexane/dichloromethane 10/1) to yield compound **10**: Yield (0.021 g, 0.014 mmol, 27%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.64 (s, 2H), 7.26–7.22 (m, 8H), 6.90 (d, $J = 8.6$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 8H), 1.85–1.80 (m, 8H), 1.49–1.26 (m, 104H), 0.90–0.86 (m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 152.0, 148.2, 134.6, 128.3, 125.1, 119.2, 115.2, 114.4, 94.5, 86.9, 69.4, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.1, 25.9, 22.7, 14.1. Anal. Calcd for $\text{C}_{102}\text{H}_{146}\text{F}_4\text{O}_4$: C 81.01, H 9.73; found: C 81.92, H 9.61.

5. Conclusions

A systematic study of the influence of fluorine substituents on the liquid crystalline properties of cruciform shaped compounds based on 1,2,4,5-tetra(alkoxyphenylethynyl)benzene has been carried out. The incorporation of lateral-F-containing side-arms widens the mesophase temperature range and, at the same time, results in enhanced lateral interactions to induce and promote a smectic *C* phase.

Acknowledgments

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