



**HAL**  
open science

## Synthesis and mesomorphic properties of liquid crystals containing a perfluorinated segment via different linkers

Samir Marzouk, Ali Khalfallah, Benoît Heinrich, Jamel Eddine E Khiari,  
Abdelkader Kriaa, Stéphane Mery

### ► To cite this version:

Samir Marzouk, Ali Khalfallah, Benoît Heinrich, Jamel Eddine E Khiari, Abdelkader Kriaa, et al.. Synthesis and mesomorphic properties of liquid crystals containing a perfluorinated segment via different linkers. *Journal of Fluorine Chemistry*, 2017, 197, pp.15-23. 10.1016/j.jfluchem.2017.02.006 . hal-02372137

**HAL Id: hal-02372137**

**<https://hal.science/hal-02372137v1>**

Submitted on 20 Nov 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Synthesis and mesomorphic properties of liquid crystals containing a perfluorinated segment via different linkers

S. Marzouk<sup>1,2,3</sup>, A. Khalfallah<sup>2</sup>, B. Heinrich<sup>1</sup>, J.E. Khiari<sup>3</sup>, A. Kriaa<sup>2</sup>, S. Méry<sup>1\*</sup>

<sup>1</sup>Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, 23 Rue de Loess, BP43, 67034 Strasbourg cedex.

<sup>2</sup>Laboratoire de Chimie Organique Moléculaire, 5 avenue Taha Hussien, 1008, ENSIT, Tunis, Tunisia.

<sup>3</sup>Laboratoire de Chimie organique et Analytique, Institut Supérieur de Formation Continue, 2000 Bardo, Tunis, Tunisia.

## Abstract

*This study presents the synthesis and mesomorphic properties of a series of biphenyl benzoate liquid crystals carrying a perfluorinated segment, via three uncommon flexible linkers. In particular, a (E)-2-propenyloxy linker was used which was issued from an elegant regioselective dehydrohalogenation reaction. The remarkable microsegregation effect of the perfluorinated segment, led to the formation of highly stable untilted lamellar mesophases, including a specific SmE pseudo-B mesophase. For all mesophases, the molecular packing corresponds to a monolayer arrangement of the mesogenic parts and a partial intercalation of the perfluorinated chains.*

## 1. Introduction

Fluorinated liquid crystals have been intensively studied as early as in the 60's, because of their interest in liquid crystal displays, in particular.[1-4] Indeed, the presence of fluorine substituent in mesogenic structures has considerable influence on many properties such as phase transitions temperatures, phase structures, dipole moment, dielectric anisotropy, optical anisotropy, elastic constant and viscosity.[2-9] Fluorination can be located in various ways in the rigid aromatic moiety, the lateral chains or else, in the linking groups.[6,9] When present as perfluorinated or semiperfluorinated alkyl chains, specific organization properties take place that essentially arise from a combination of microphase separation and steric effects.[8-9] Actually, perfluorinated alkane segments are strongly not miscible with both aromatic and aliphatics, and easily tend to microsegregate from them.[10] Also, perfluorinated segments have larger molecular volume and reduced flexibility as compared to linear alkyl chains, that impact on molecular organization. For these reasons, fascinating liquid crystal organizations could be obtained on various and unusual types of molecular structures by simple insertion/substitution of perfluorinated segment(s).[9-15]

A number of liquid crystals carrying a perfluoroalkane segment have already been investigated and some general trends could be drawn and reviewed.[8,9] With rod-like mesogens for instance, F. Guittard evidenced the importance to decouple the perfluorinated segment to the rigid core by a short flexible spacer to allow molecular organization.[8] Pushing the limits of segregation on sterically hindered swallow-tailed calamitic systems, Lose and al. observed frustrated smectic phase ultimately leading to the formation of columnar mesophase.[16] Tschierske et al. also reported the stabilization of columnar phases on ("bolaamphiphilic") rod-shaped mesogens with laterally attached perfluorinated chain.[13] Finally, playing with block sequence of aromatic moieties, aliphatic chains and perfluorinated segments, Tournilhac et al. could obtain ferroelectric liquid crystals from achiral molecules.[17]

In this work, we aim at finely studying the mesomorphic properties of a series of rod-shaped biphenyl benzoate liquid crystals carrying a perfluorinated segment. This series was chosen for it allows a comparison with its fully hydrogenated counterparts, which are poorly mesogenic and only exhibit a nematic phase on a very narrow temperature range.[18] More specifically, the perfluorinated segments were of two different lengths ( $C_6F_{13}$ - and  $C_8F_{17}$ -) were connected to the rigid core via three uncommon types of flexible spacer, namely 2-iodopropoxy, (*E*)-2-propenyloxy and ethyl-3-thiopropoxy. Note that the spacer (*E*)-2-

propenyloxy was prepared essentially in its *E* isomer from a highly regioselective dehalogenation reaction.

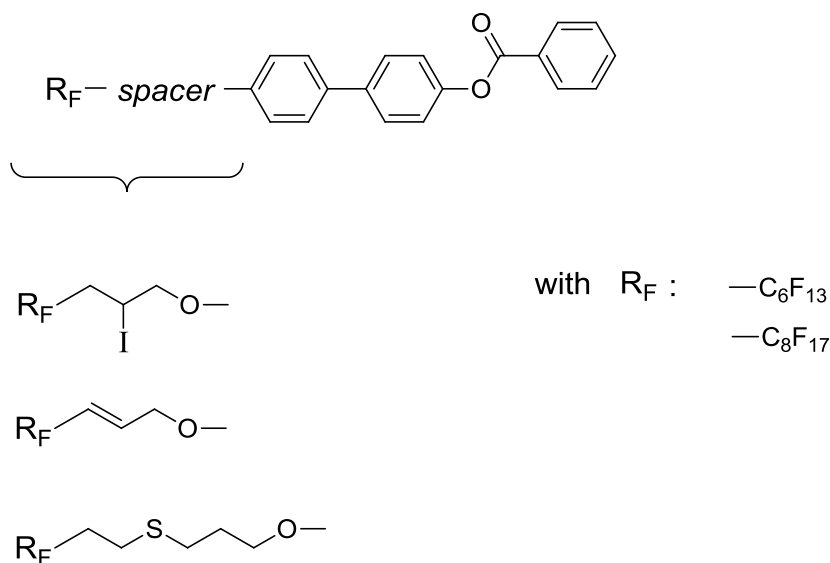


Figure 1. Molecular structure of the biphenyl benzoate liquid crystal series carrying a semiperfluorinated chain investigated herein.

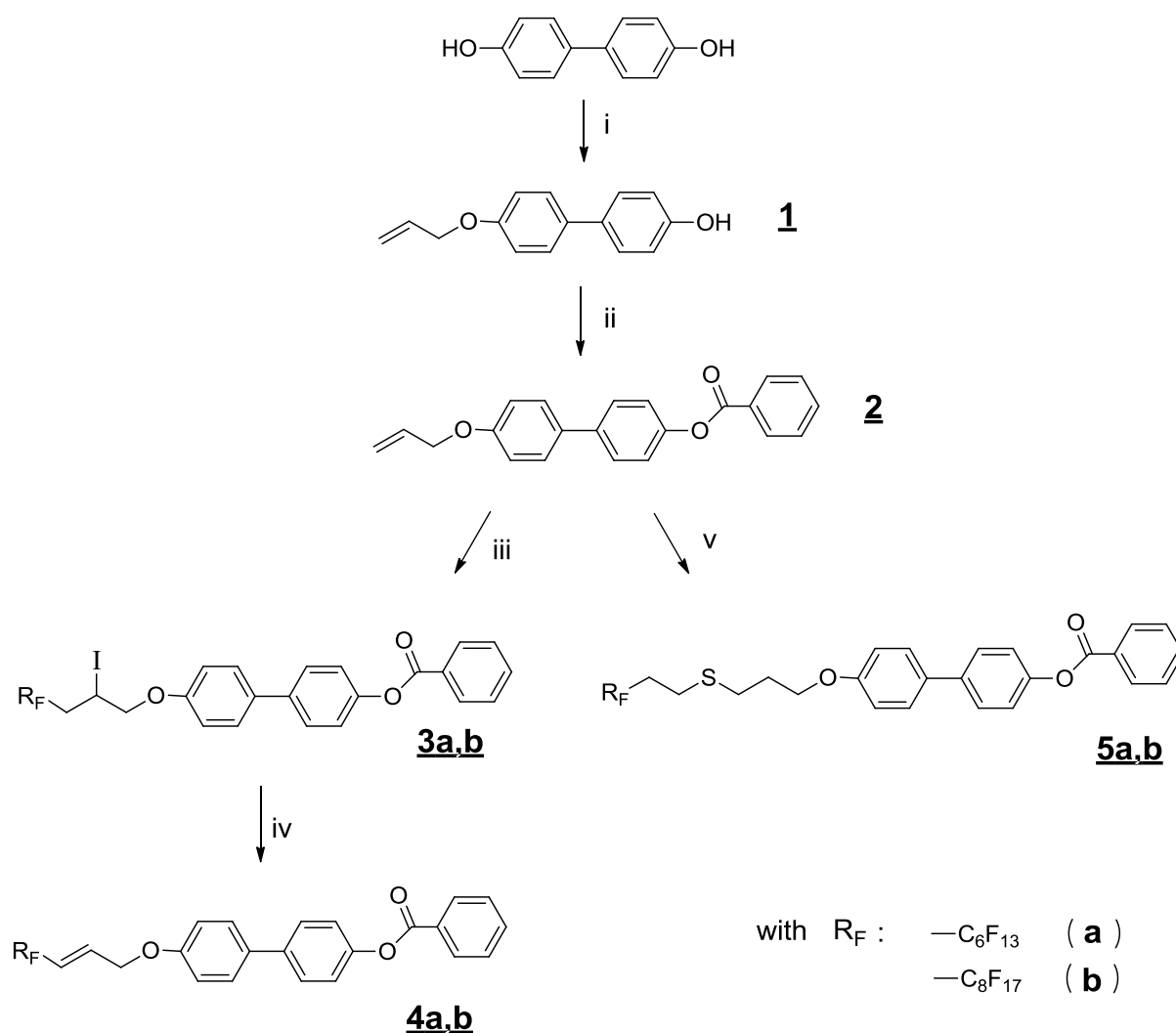
## 1. Results and discussions

### 1.1.Synthesis

The synthetic procedure for the preparation of biphenyl benzoate series carrying a perfluorinated chain (**3a,b**, **4a,b** and **5a,b**) are depicted in scheme 1. The starting compound, *i.e.* 4-allyloxy-4'-hydroxybiphenyl **1** was prepared from the reaction of biphenyl 4,4'-diol with allylbromide in presence of  $\text{K}_2\text{CO}_3$ . This compound was reacted with benzoyl chloride in triethylamine to afford the key compound 4'-allyloxybiphenyl-4-yl benzoate **2**. The latter was then used for the preparation of the three series of liquid crystals. The first series having a perfluorinated chain connected to the 2-iodopropoxy spacer (**3a,b**) was prepared by radical addition (AIBN) of perfluoro 1-iodohexane and perfluoro 1-iodooctane in 1,2-dichloroethane, giving respectively the compounds **3a** and **3b**.<sup>[19-21]</sup> Subsequent dehydroiodination of compounds **3a,b** with sterically hindered DBU base furnished the olefins **4a,b** as the second series, essentially as the *E* isomer.<sup>[20-22]</sup> Regioisomers *E* and *Z* were expected from this dehydroiodination reaction of compound **3a,b**,<sup>[23-25]</sup> however, only the *E* isomer was obtained, as confirmed by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{19}\text{F}$ -NMR (see supporting information). This

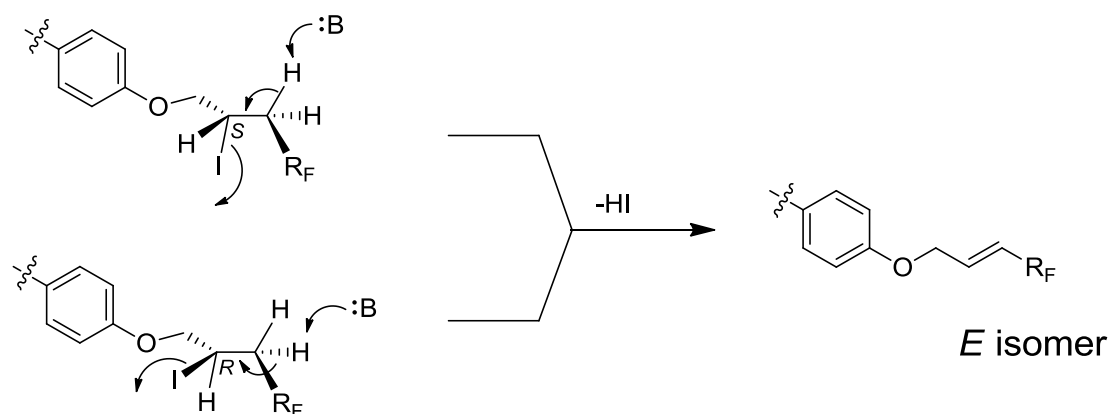
selectivity can be interpreted by the *anti* process of this elimination (the proton and halogens should be in anti-conformation) and by the fact that this reaction preferably takes place when compounds **3a,b** adopt the most stable conformation, *i.e.* where the perfluoroalkyl chain and the biphenyl moiety are *anti* to each other, to minimize the repulsive interactions and steric hindrance when B base attacks (see scheme 2).

Finally, the last series of liquid crystalline compounds was prepared by radical addition reaction of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorodecane thiol and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorononane thiol on compounds **2** in presence of AIBN in 1,2-dichloroethane,[26-28] to afford compounds **5a** and **5b**, respectively. All compounds were obtained in good purity as deduced  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FTIR, mass spectra and elemental analyses.



Scheme 1. Synthetic route for the preparation of the fluorinated biphenyl benzoate-based liquid crystals. i) Allylbromide, KOH/MeOH reflux ; ii) Benzoyl chloride, Et<sub>3</sub>N ; iii) C<sub>6</sub>F<sub>13</sub>I or

$C_8F_{17}I$ , AIBN, 1,2-dichloroethane,  $75^\circ C$  ; iv) DBU,  $CH_2Cl_2$ , RT ; v)  $C_6F_{13}CH_2CH_2SH$  or  $C_8F_{17}CH_2CH_2SH$ , AIBN, 1,2-dichloroethane,  $75^\circ C$ .

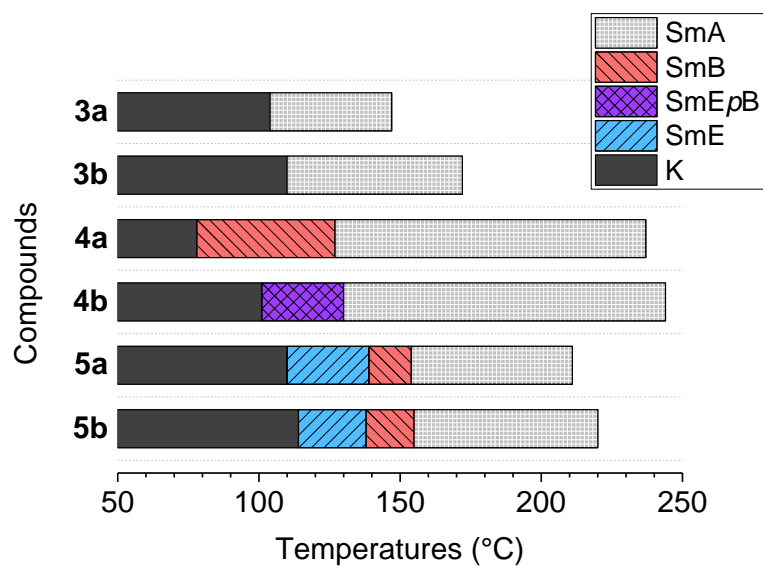


*Scheme 2.* Regioselective dehydroiodination of compounds **3a,b**. The reaction proceeds in *anti*-manner on the most stable conformations, where the perfluorinated chain and the mesogenic moieties are antiperiplanar.

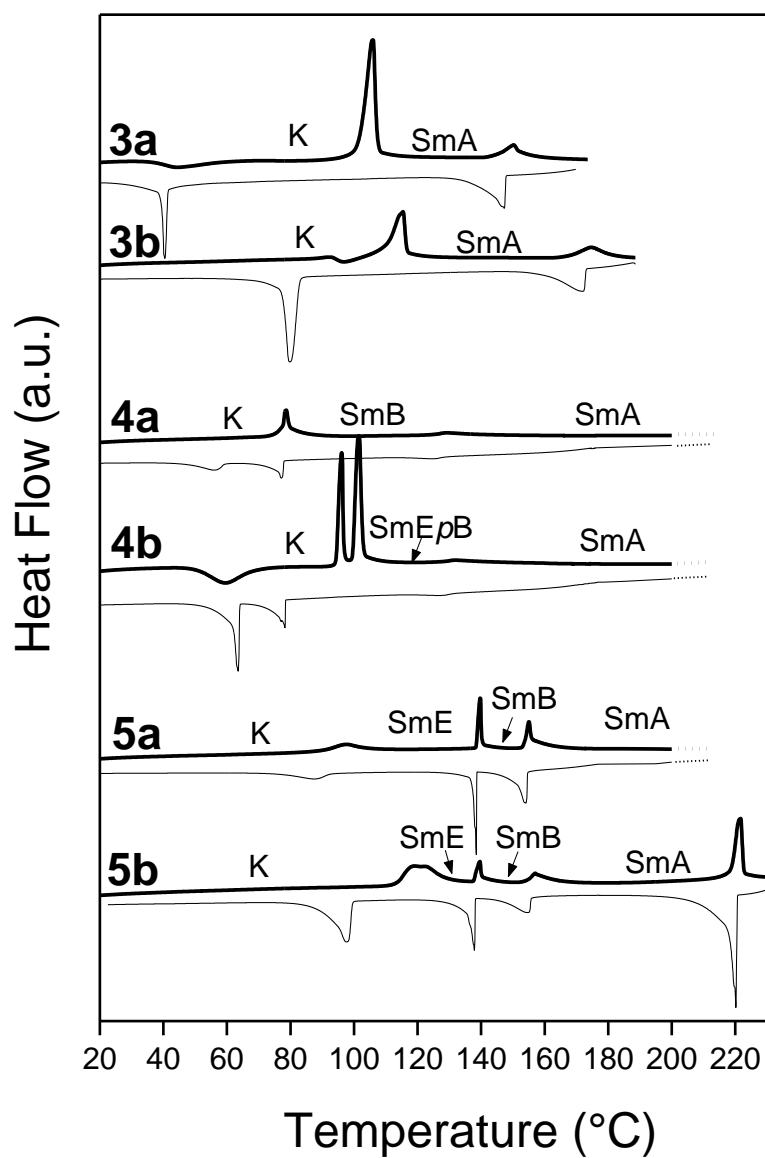
## 1.2. Liquid crystal properties

The mesomorphic properties of the final compounds **3a,b**, **4a,b** and **5a,b** have been investigated by means of polarized optical microscopy (POM), differential calorimetry (DSC) and powder small-angle X-ray diffraction (XRD). All materials are liquid crystalline and exhibit lamellar mesophases.

The transition temperatures of the fluorinated liquid crystals are presented in figure 2, while the DSC thermograms are given in figure 3. As evidenced by POM investigation, all mesophases show a molecular orientation director that is normal to the smectic layers (i.e. non-tilted phases). The textural defects and their changes at the transitions strongly indicate the presence of SmA, SmB and SmE phase types. In figure 4 are shown representative POM textures of these mesophases, including the singular SmE<sub>p</sub>B one, observed for compound **4b**, which will be commented in the following section.



*Figure 2.* Transition temperatures of the fluorinated liquid crystalline biphenyl benzoate series **3a,b**, **4a,b** and **5a,b**.



*Figure 3.* DSC thermograms of the fluorinated liquid crystals recorded at  $5^{\circ}\text{C}\cdot\text{min}^{-1}$  at heating (top traces) and cooling (down traces). DSC traces for compounds **4a**, **4b** and **5a** were not recorded beyond  $200^{\circ}\text{C}$  because of risk of decomposition.



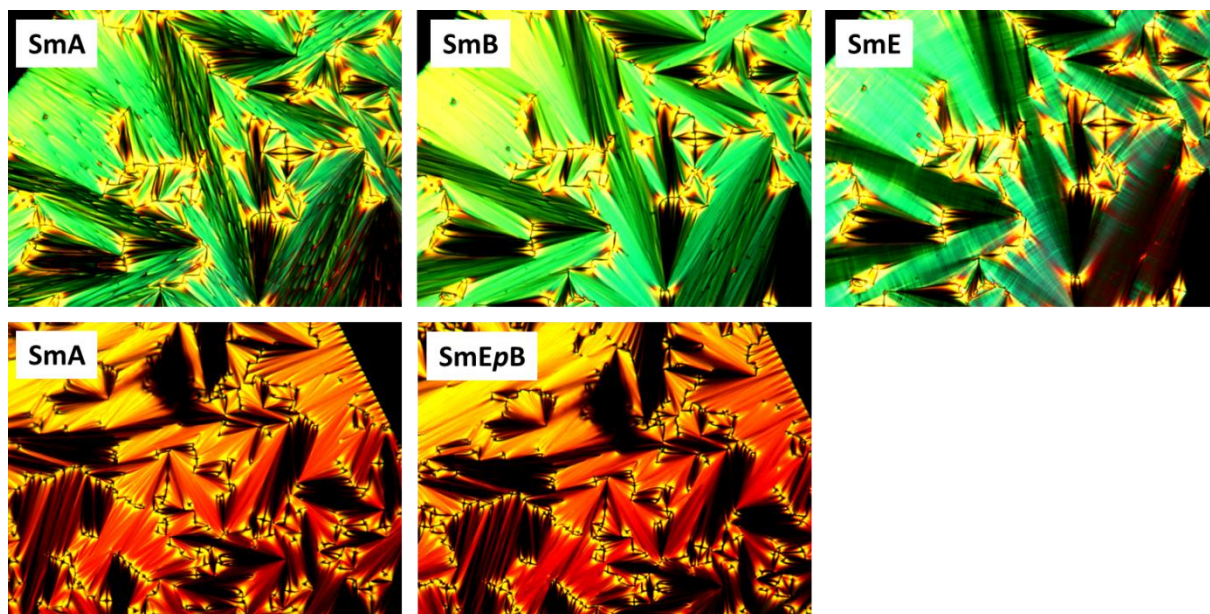


Figure 4. POM textures observed for the mesophases SmA (180°C), SmB (150°C) and SmE (120°C) of compound **5b** (top), and for the mesophases SmA (210°C) and SmEpB (100°C) of compound **4b** (down).

All compounds have been investigated by X-ray scattering at different temperatures to fully characterize the mesophases. In total, four different types of mesophases have been identified, namely the SmA, SmB, SmE phases and an unusual smectic E pseudo-B (SmEpB) phase, whose representative patterns are given in figure 5.

As a common feature, all X-ray patterns show the well-known diffuse bands  $h_H \approx 4.6 \text{ \AA}$  and  $h_F \approx 5.6 \text{ \AA}$ , corresponding to the average distance between disordered alkyl segments (spacer) and perfluorinated chains, respectively. All mesophases are lamellar in nature and their symmetry is determined by the molecular organization within the mesogenic sub-layer (see figure 6). Below are described the common characteristics of the four mesophases the present in the fluorinated compounds (see typical patterns in figure 5).

**SmA.** In this mesophase, the lateral molecular arrangement is of liquid-like, leading to a merging of the diffuse bands  $h_{mes}$  and  $h_H$  (average distance between closest mesogens and alkyl chains, respectively)

**SmB.** The lateral organization of the mesogens (assimilated to cylinders) gives a two-dimensional hexagonal array ( $Z = 1$  molecule per lattice) which develops to moderate distances. The main reflexion (100) is the only one observed, and its broadening corresponds to correlation length of about  $200 \text{ \AA}$ .

**SmE.** The mesogens are organized at long-range within the layers, into an array of rectangular symmetry  $p2gg$  ( $Z = 2$ ), with a ratio of the lattice parameters  $a/b \neq 3^{1/2}$  (see figure 6). The main reflexions (200) and (110) are distinct and narrow, while the higher order reflexion (210) indicates an alternated tilting of the mesogen rows.

**SmEpB.** In this SmE *pseudo-B* mesophase, the lateral organization of the mesogens is found to follow an hexagonal geometry, ranging at moderate distances (similar to the SmB phase), but for which the hexagonal symmetry is lost due to a non-cylindrical symmetry of the mesogens. It results in an array of rectangular symmetry  $p2gg$  ( $Z = 2$ ) due to the randomly tilted mesogen bundles within the layers. This structure is deduced from the presence of a unique and rather broad signal corresponding to the merging of the two main reflexions (200) and (110), along with the presence of the first higher reflexion peak (210) coming from the alternated tilting of the mesogen rows within the bundles of molecules.

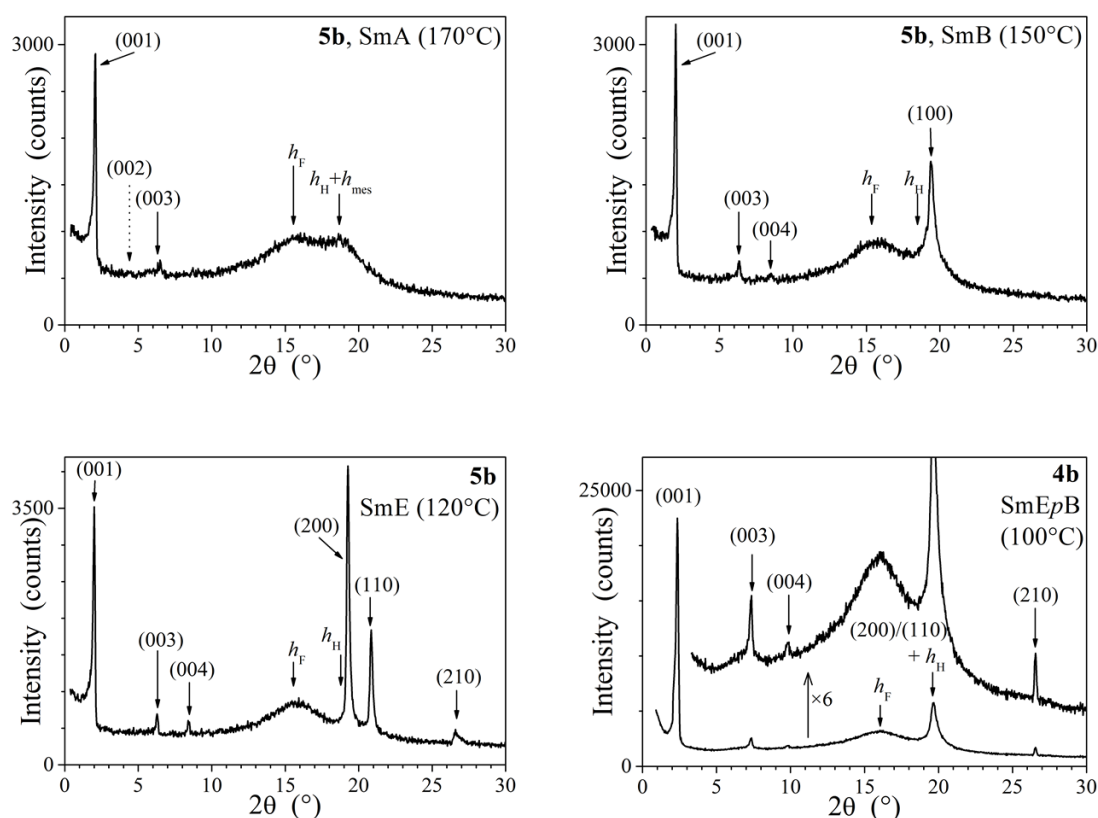


Figure 5. Powder X-ray patterns of representative SmA, SmB and SmE mesophases, recorded in compound **5b**, as well as the specific SmEpB mesophase recorded for compound **4b**.  $h_F$ ,  $h_H$  and  $h_{mes}$  stand for the average distance between fluorinated chains, alkyl segments (spacers) and mesogens, respectively.

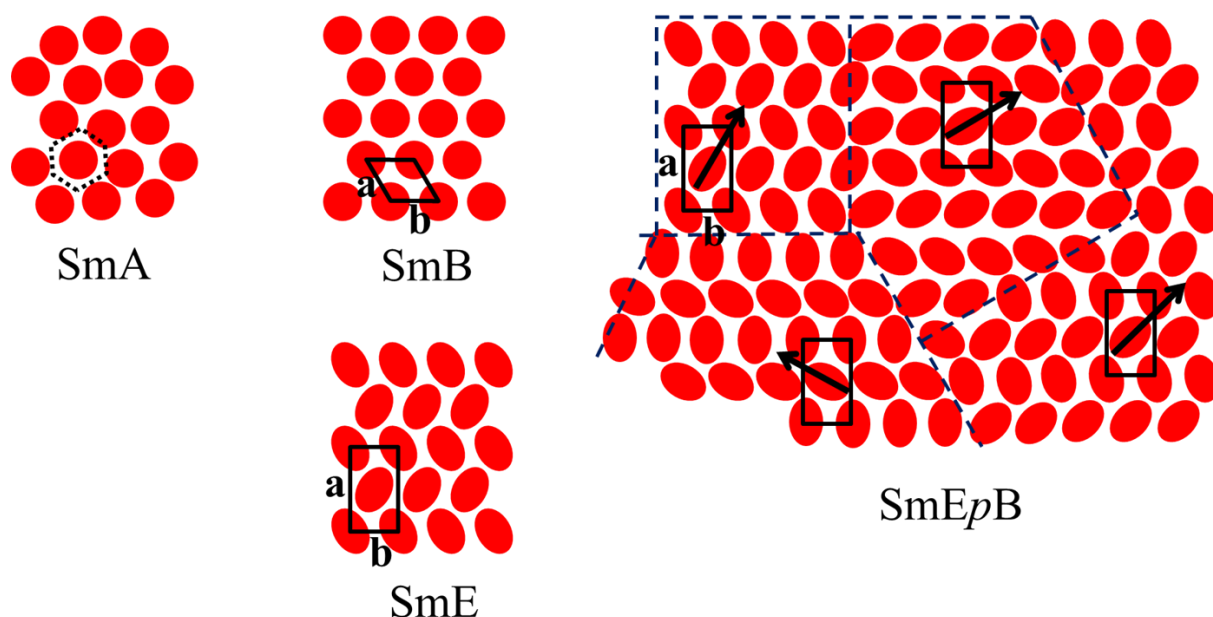
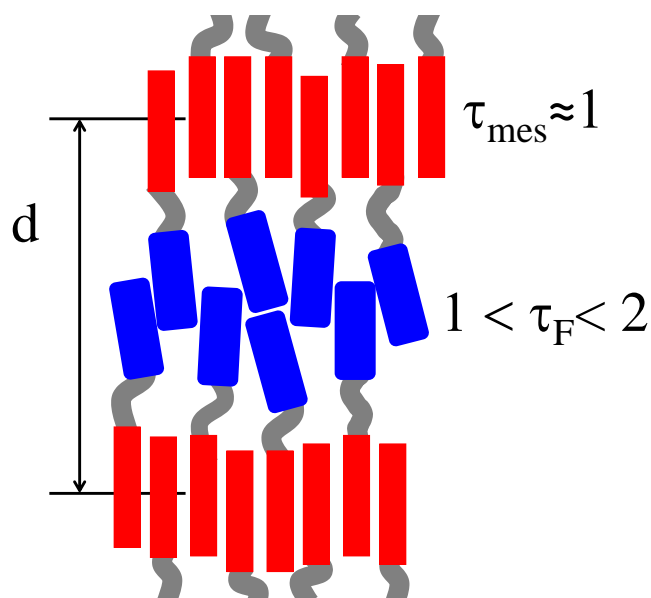


Figure 6. Illustration of the molecular organization within the smectic layers for the different mesophases observed in this work. The round and oblique shapes stand for the cylindrical-shaped molecule that can respectively be non-tilted or tilted, within the layers. The SmEpB phase is characterized by a hexagonal geometry analogous to that of SmE phase but with randomly tilted mesogen bundles within the layers.

The fine molecular packing of the fluorinated liquid crystal series could further be characterized. In particular, it was possible to determine how the different parts of the molecules were organized within the layers, *i.e.* the mesogens, the spacers and the fluorinated segments. The molecular packing could be deduced from geometrical calculations using our X-ray data and molecular volumes issued from dilatometry measurements (see supporting information).[29]

First of all, the molecular sections of the fluorinated segments was found to be about 50% larger than for the mesogenic moiety and the aliphatic spacers (compare  $\sigma_F \approx 35 \text{ \AA}$  with  $\sigma_{mes} \approx \sigma_H \approx 22\text{-}24 \text{ \AA}$ ). In perfect agreement with literature data,[9,10,29] this steric mismatch imposes a partial intercalation/interdigitation of the molecules. Actually, it turns out that the mesogens associate in a monolayer ( $\tau_{mes} \approx 1$ ), while the perfluorinated segments associate in a partial bi-layer with a intercalation ratio  $\tau_F$  from 1.48 to 1.68, depending of the compound and the type of mesophase. An illustration of the molecular packing of the series of fluorinated

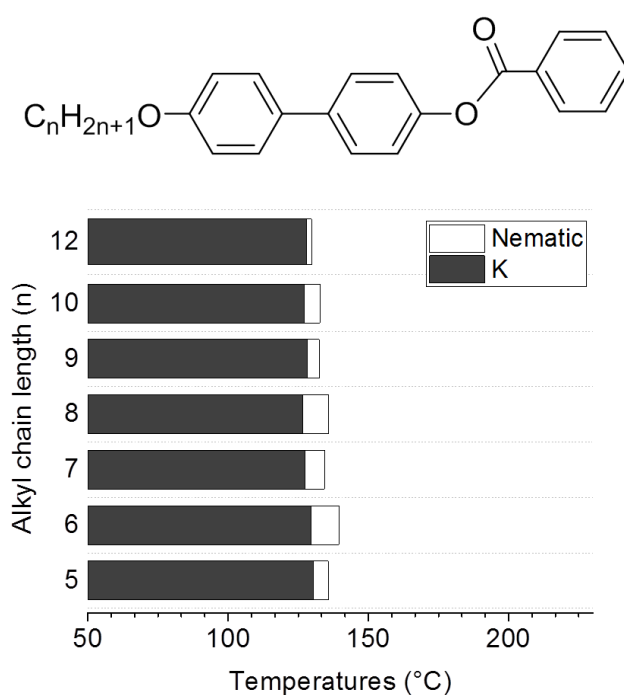
liquid crystal series is shown in figure 7. Note that such a partial molecular intercalation has already been observed in smectic phases made of calamitic mesogens linked to a single perfluorinated chain via a flexible spacer.[9]



*Figure 7.* Model of molecular packing of the smectic phases of the fluorinated liquid crystal series investigated herein. The molecular arrangement is described by three alternated sub-layers made of the mesogens (red segments) associated in a monolayer ( $\tau_{mes} \approx 1$ ), the aliphatic spacer highly shrunken (gray segments) and the perfluorinated chains (blue segments) arranged in a partial bi-layer ( $1 < \tau_F < 2$ ).

Let us now comment on the difference of mesomorphic properties in the biphenyl benzoate series (figure 2). First of all, all compounds show a moderate melting point (*ca* between 75 to 115°C). The SmA is systematically observed at highest temperature with possible additional SmB, SmE and/or SmEpB phases. Overall, the mesophases are quite stable and are present on a quite wide temperature range, over 140°C for instance in the case of propenyloxy series **4a,b**. Excepted for compound **5a**, the DSC thermograms were not recorded beyond 200°C because of the materials decomposition, starting between 200 to 250°C depending of the compounds (TGA measurements). Indeed, the strong stabilization of the mesomorphic character is due to the fluorophobic effect provided by the presence of the terminal perfluoroalkyl segment.[8,9] This effect is clearly evidenced by comparing their mesomorphic

behavior with the one of the fully hydrogenated analogous series of alkoxybiphenyl benzoates presented in figure 8.[18] This series only shows an enantiotropic nematic phase (for  $n = 5$  to 12) on a very narrow temperature range (less than  $10^\circ\text{C}$ ), above the melting point at about  $130^\circ\text{C}$ . The comparison of the two series (fluorinated *vs* alkylated) clearly demonstrates the role of the perfluorinated chains as a microphase separation promotor which results in the strong stabilization of the lamellar mesophases. As shown from figure 2, the thermal stabilization of the smectic phases is further slightly improved by lengthening of the perfluorinated segment from  $\text{C}_6\text{F}_{13}$ - to  $\text{C}_8\text{F}_{17}$ -.



*Figure 8.* Transition temperatures of the fully hydrogenated 4'-n-alkoxybiphenyl-4-yl-benzoate series, as a function of the alkylchain length ( $n$ ), from ref. [17]

As already commented by F. Guittard[8] and R. Zentel,[9] the mesomorphic properties of liquid crystals with a perfluorinated chain is highly favored when the perfluorinated segment is decoupled from the rigid aromatic moiety via a flexible spacer. This decoupling allows an adjustment of the intermolecular organization of the fluorinated parts and of the aromatic parts, taking into account a steric mismatch between these two parts, in particular (see figure 7). In the present work, three different type of flexible spacers have been used, namely 2-iodopropoxy, (*E*)-2-propenyloxy and ethyl-3-thiopropoxy, corresponding respectively to compounds **3a,b**, **4a,b** and **5a,b**. Except for (*E*)-2-propenyloxy[21] and to the best of our knowledge, these spacers have never been used in fluorinated-based liquid crystals, so far.

The 2-iodopropyl spacer leads to the narrowest mesomorphic range with only the presence of a SmA phase (compounds **3a,b**). This behavior is explained by the molecular packing disturbance provided by the bulky iodine atom laterally attached to the spacer.

The *trans*-2-propenyloxy spacer gives the most remarkable mesomorphic stabilization, with the presence at low temperatures of the SmB and SmEpB mesophases for **4a** and **4b**, respectively. The slight lengthening of the perfluorinated segment therefore induces a (non-correlated) tilting of the mesogens (figure 6). It is worthy to note that 2-propenyloxy spacer, essentially formed here as *trans* stereoisomer, is the most favorable configuration for the smectic phase stabilization. It is also interesting to note that such a short (*E*)-2-propenyloxy spacer is enough to decouple the two rigid perfluorinated and mesogenic moieties for leading to liquid crystal organization.

Finally, the ethyl-3-thiopropoxy spacer gives quite similar results for both perfluorinated chain length, *i.e* the presence of the phase sequence SmA, SmB and SmE at similar temperatures (compounds **5a,b**). The comparison of the mesomorphic properties of the two series **4a,b** and **5a,b** seems to indicates that a marked lengthening of the flexible spacer (2-propenyloxy to ethyl-3-thiopropoxy) tend to reduce the stability of the mesophase (more than 40°C temperature range reduction).

## 2. Conclusions

A series of liquid crystalline biphenyl benzoate derivatives carrying a perfluorinated segment via a flexible linker has been synthesized and characterized. The perfluorinated segment was of two different lengths (C<sub>6</sub>F<sub>13</sub>- and C<sub>8</sub>F<sub>17</sub>-) and three uncommon flexible linkers were used,

namely 2-iodopropoxy, ethyl-3-thiopropoxy and (*E*)-2-propenyloxy. The later was purely of *trans* isomer and issued from an unusual regioselective dehalogenation reaction.

As compared to the fully hydrogenated counterparts which only exhibit a nematic phase, the fluorinated derivatives show lamellar mesophases on a very wide temperature range (up to 140°C). This result confirms the remarkable microsegregation effect of the fluorinated segment, provided by the flexible linker. All molecules exhibit non-tilted lamellar SmA, SmB and/or SmE phases. An unusual SmE *pseudo*-B was evidenced that is characterized by a hexagonal geometry (analogous to that of SmE phase) but with randomly tilted mesogen bundles within the layers. The fine investigation of the mesomorphic properties by X-rays scattering and geometrical calculations allowed the detailed description of the molecular packing as a monolayer association of the mesogenic parts and a bilayer arrangement (intercalation) of the perfluorinated segments (interdigitation ratio comprise between 1.48 and 1.68 depending of the mesophase and temperature).

### 3. Experimental

#### *Techniques*

The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker AC 300 at 300, 75 and 282 MHz, respectively.  $\text{CFCl}_3$  was used as standard reference for  $^{19}\text{F}$  NMR. The IR spectra were recorded on a Bruker IFS 66V/S spectrometer. HRMS (EI) experiments were performed on Bruker spectrometers at the Mass Spectrometry Service from the “Institut de Chimie” of Strasbourg University. Optical textures were observed with a Leitz Orthoplan polarizing microscopy equipped with a Mettler FP82 hot stage and a FP80 unit. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments DSCQ1000 instrument operated at scanning rates of  $5^\circ\text{C}\cdot\text{min}^{-1}$  on heating and on cooling. The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  under air flow. Powder XRD patterns were obtained with a linear monochromatic Cu  $K\alpha_1$  beam ( $\lambda=1.5405 \text{ \AA}$ ) obtained using a sealed-tube generator equipped with a bent quartz monochromator and a curved Inel CPS 120 counter gasfilled detector; periodicities up to  $70 \text{ \AA}$  can be measured, and the sample temperature controlled to within  $\pm 0.01 \text{ }^\circ\text{C}$  from 20 to 200  $^\circ\text{C}$ . The sample was filled in Lindemann capillaries and exposure times were of 6 h.

## Materials and Synthesis

**4-allyloxy-4'-hydroxybiphenyl (1).**[30] A mixture of 4,4'-dihydroxybiphenyl (16.0 g, 86 mmol) and potassium hydroxide (2.41 g, 43 mmol) in dry methanol (250 mL) was heated at 65 °C and stirred until complete dissolution. Then, allyl bromide (5.20 g, 43 mmol) was slowly added and the mixture was refluxed for 24 hours. The resulting suspension was filtered off, and methanol was removed under reduced pressure. Diethyl ether (100 mL) and aqueous solution of 5% HCl (100 mL) were added to the crude residue. After phase separation and distillation of diethyl ether, the product was purified by column chromatography (cyclohexane/EtOAc : 70/30) to provide compound **1** as a white solid. Yield: 45 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.5 (d, 2ArH, J = 6.7 Hz), 7.4 (d, 2ArH, J = 6.7 Hz), 7.0 (m, 2ArH), 6.8 (m, 2ArH), 6.1 (m, 1H, CH=CH<sub>2</sub>), 5.3 (tdd, 2H, <sup>3</sup>J<sub>trans</sub> = 17.1 Hz, <sup>3</sup>J<sub>cis</sub> = 10.3 Hz, CH=CH<sub>2</sub>), 5.0 (s, OH), 4.60 (d, 2H, CH<sub>2</sub>O).

**4'-allyloxy-(1,1'-biphenyl)-4-yl benzoate (2).** To a vigorously stirred mixture of 4-allyloxy-4'-hydroxybiphenyl (**1**) (3.75 g, 15.5 mmol) and 5 mL of trimethylamine in dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL), was added dropwise a solution of 30 mL of dry CH<sub>2</sub>Cl<sub>2</sub> containing 3.6 mL (31.0 mmol) of benzoylchloride. The mixture was heated at 35 °C under stirring for 14 h, and then it was cooled to room temperature, washed twice with 100 mL of water with 4% Na<sub>2</sub>CO<sub>3</sub>, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum and the crude product (powder) was washed twice with distilled water. Compound **2** was finally recrystallized in EtOH (78% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.25 (d, 2H, J = 7.3 Hz), 7.6 (m, 7H), 7.25 (d, 2H, 7.0 Hz), 7.0 (8.6 Hz), 6.10 (m, 1H, CH=CH<sub>2</sub>), 5.4 (tdd, 2H, <sup>3</sup>J<sub>trans</sub> = 17.1 Hz, <sup>3</sup>J<sub>cis</sub> = 10.3 Hz, CH=CH<sub>2</sub>), 4.60 (d, 2H, CH<sub>2</sub>O). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 165.2 (C=O), 158.2 (ArO), 149.4 (ArO), 138.6, 133.6, 133.2 (CH<sub>2</sub>=CH), 130.3, 128.8, 128.4, 127.3, 126.9, 122.2, 117.7 (CH=CH), 115.0, 66.6 (OCH<sub>2</sub>).

## Synthesis of the fluorinated liquid crystals **3**

In a 25 mL round bottomed flask, was placed under N<sub>2</sub> atmosphere a mixture of **2** (0.66 g, 2.0 mmol), perfluoro 1-iodohexane or perfluoro 1-iodooctane (2.5 mmol), AIBN (13 mg, 0.08 mmol) and 2 mL of 1,2-dichloroethane. The mixture was then stirred at 75 °C for 18 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was subjected to a column chromatography on silica gel (ethyl acetate/hexane: 1/3) followed by a recrystallization in ethanol, to provide **3a** and **3b** as white solids.



**4'-{(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyloxy)-(1,1'-biphenyl)-4-yl benzoate (3a).** Yield: 89 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.25 (d, 2H, *J* = 7.5 Hz), 7.5-7.7 (m, 7H), 7.30 (d, 2H, *J* = 8.2 Hz), 7.0 (d, 2H, *J* = 8.5 Hz), 4.55 (quint., 1H, CHI), 4.21-4.38 (dd, 2H, <sup>2</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 4.8 Hz, CHI-CH<sub>2</sub>O), 2.85-3.23 (m, 2H, CF<sub>2</sub>-CH<sub>2</sub>-CHI). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 165.2 (C=O), 157.2 (ArO), 150.1 (ArO), 138.3, 134.2, 133.6, 130.2, 129.51, 128.5, 128.3, 127.8, 121.9, 115.2, 72.8 (CH<sub>2</sub>-O), 37.8 (t, <sup>2</sup>*J*<sub>CF</sub> = 21 Hz, CF<sub>2</sub>-CH<sub>2</sub>), 12.7 (C-I). <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ(ppm) -80.5 (t, CF<sub>3</sub>, <sup>3</sup>*J*<sub>FF</sub> = 10.0 Hz), -113.1 & -113.3 (dm & dm, 2×1F, *J*<sub>A-B</sub> = 295 Hz, 2 diastereoisomers of -CHI-CH<sub>2</sub>-CF<sub>2</sub>), -121.5 (m, 2F), -122.6 (m, 2F), -123.3 (m, 2F), -125.8 (m, 2F). HRMS (ESI) calculated for C<sub>28</sub>H<sub>18</sub>F<sub>13</sub>IO<sub>3</sub>Na<sup>+</sup>: 799.314 (found: 799.005).

**4'-{(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-iodoundecyloxy)-(1,1'-biphenyl)-4-yl benzoate (3b).** Yield: 82 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.24 (d, 2H, *J* = 7.2 Hz), 7.5-7.7 (m, 7H), 7.30 (d, 2H, *J* = 8.4 Hz), 7.0 (d, 2H, *J* = 8.7 Hz), 4.55 (quint., 1H, CHI), 4.21-4.38 (dd, 2H, <sup>2</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 4.8 Hz, CHI-CH<sub>2</sub>O), 2.85-3.23 (m, 2H, CF<sub>2</sub>-CH<sub>2</sub>-CHI). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 165.2 (C=O), 157.2 (ArO), 150.1 (ArO), 138.4, 134.2, 133.6, 130.2, 129.5, 128.6, 128.4, 127.8, 122.0, 115.3, 72.8 (CH<sub>2</sub>-O), 37.8 (t, <sup>2</sup>*J*<sub>CF</sub> = 21 Hz, CF<sub>2</sub>-CH<sub>2</sub>), 12.6 (C-I). <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ(ppm) -80.5 (t, CF<sub>3</sub>, <sup>3</sup>*J*<sub>FF</sub> = 10.0 Hz), -113.1 & -113.3 (dm & dm, 2×1F, *J*<sub>A-B</sub> = 300 Hz, 2 diastereoisomers of -CHI-CH<sub>2</sub>-CF<sub>2</sub>), -121.5 (m, 2F), -122.6 (m, 2F), -123.3 (m, 2F), -125.8 (m, 2F). HRMS (ESI) calculated for C<sub>30</sub>H<sub>18</sub>F<sub>17</sub>IO<sub>3</sub>Na<sup>+</sup>: 899.329 (found: 898.980).

#### Synthesis of the fluorinated liquid crystal 4.

DBU (0.300 g, 3.28 mmol) was added to a solution of compound **3** (0.5 mmol) in 20 mL CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The mixture was stirred for 6 h and was quenched with 5 mL of aqueous NH<sub>4</sub>Cl. The organic layer was extracted and washed with aqueous K<sub>2</sub>CO<sub>3</sub> then with water. After drying (Na<sub>2</sub>SO<sub>4</sub>), the solvent was removed under vacuum. The crude product was purified on a column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane: 1/3), followed by recrystallization in ethanol to provide **4a** and **4b** as white solids.

**(E)-4'-{(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoronon-2-enyloxy)-(1,1'-biphenyl)-4-yl benzoate (4a).** Yield: 86 %: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.24 (d, 2H, *J* = 6.9 Hz), 7.5-7.7 (m, 7H), 7.30 (d, 2H, *J* = 8.4 Hz), 7.0 (d, 2H, *J* = 8.7 Hz), 6.66 (dtt, 1H, <sup>3</sup>*J*<sub>trans</sub> = 15.6 Hz, <sup>3</sup>*J*<sub>H-F</sub> = 3.6 Hz, <sup>4</sup>*J*<sub>H-F</sub> = 2.4 Hz, CH=CH-CH<sub>2</sub>O, *E* enantiomer), 6.1 (dt, 1H, <sup>3</sup>*J*<sub>trans</sub> = 15.6 Hz, <sup>3</sup>*J*<sub>H-F</sub> = 12.3 Hz, CF<sub>2</sub>-CH=CH-, *E* enantiomer), 4.75 (dm, 2H, -CH<sub>2</sub>O-). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 165.2 (C=O), 157.4 (ArO), 150.0 (ArO), 138.4, 137.2 (t, <sup>3</sup>*J*<sub>C-F</sub> = 9.1 Hz, CF<sub>2</sub>-CH=CH), 133.9, 133.6,

130.2, 129.5, 128.6, 128.3, 127.8, 122.0, 118.0 (t,  $^2J_{CF} = 23.0$  Hz,  $CF_2-\underline{C}H=CH$ ), 115.0, 66.1 ( $CH_2-O$ ).  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$ (ppm) -80.5 (t,  $CF_3$ ,  $^3J_{FF} = 9.9$  Hz), 111.6 (m,  $CF_2-\underline{C}H=CH$ ,  $^3J = 12.9$  Hz), -121.4 (m, 2F), -122.6 (m, 2F), -123.0 (m, 2F), -125.9 (m, 2F). HRMS (ESI) calculated for  $C_{28}H_{17}F_{13}O_3Na^+$ : 671.401 (found: 671.068).

**(E)-4'-{(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoronon-2-enyl)oxy}-(1,1'-biphenyl)-4-yl benzoate (4b)**. Yield: 83%:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.25 (d, 2H,  $J = 7.2$  Hz), 7.5-7.7 (m, 7H), 7.25 (d, 2H,  $J = 8.7$  Hz), 7.0 (d, 2H,  $J = 8.7$  Hz), 6.66 (dt, 1H,  $^3J_{trans} = 15.6$  Hz,  $^4J_{H-F} = 2.1$  Hz,  $CH=\underline{C}H-CH_2O$ , *E* enantiomer), 6.15 (dt, 1H,  $^3J_{trans} = 15.6$  Hz,  $^3J_{H-F} = 12.6$  Hz,  $CF_2-\underline{C}H=CH-$ , *E* enantiomer), 4.75 (m, 2H,  $-CH_2O-$ ).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$ (ppm) 165.2 (C=O), 157.4, 150.0, 138.4, 137.2 (t,  $^3J_{C-F} = 9.0$  Hz,  $CF_2-\underline{C}H=CH$ ), 133.9, 133.6, 130.2, 129.5, 128.5, 128.3, 127.8, 121.9, 118.0 (t,  $^2J_{CF} = 23.3$  Hz,  $CF_2-\underline{C}H=CH$ ), 114.9, 66.9 ( $CH_2-O$ ).  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$ (ppm) -80.5 (t,  $CF_3$ ,  $^3J_{FF} = 9.7$  Hz), 111.6 (m,  $CF_2-\underline{C}H=CH$ ,  $^3J = 12.2$  Hz), -121.2 (m, 2F), -121.7 (m, 4F), -122.5 (m, 2F), -123.0 (m, 2F), -125.9 (m, 2F). HRMS (ESI) calculated for  $C_{30}H_{17}F_{17}O_3Na^+$ : 749.416 (found: 749.097).

### Synthesis of the fluorinated liquid crystal 5.

In a 25 mL round bottomed flask, was placed under  $N_2$  atmosphere a mixture of **2** (0.66 g, 2 mmol),  $C_6F_{13}-CH_2-CH_2-SH$  or  $C_8F_{17}-CH_2-CH_2-SH$ , AIBN (0.013 g, 0.08 mmol) and 2 mL of 1,2-dichloroethane. The mixture was then stirred at  $75^\circ C$  for 18. After cooling to room temperature, the solvent was removed under vacuum and the residue was subjected to a column chromatography on silica gel (ethyl acetate/hexane: 1/3) followed by a recrystallization in ethanol, to provide the liquid crystals **5a** and **5b** as white crystals.

**4'-[3-{(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio}propoxy]-(1,1'-biphenyl)-4-yl benzoate (5a)**. Yield: 88%:  $^1H$  NMR ( $CDCl_3$ ) 8.25 (d, 2H,  $J = 6.9$  Hz), 7.5-7.7 (m, 7H), (d, 2H, 6.9 Hz), 7.00 (d, 2H, 9.0 Hz), 4.13 (t, 2H,  $CH_2O$ ), 2.80 (m, 4H,  $CH_2-S-CH_2$ ), 2.41 (m, 2H,  $CF_2-CH_2$ ), 2,12 (quint., 2H,  $CH_2-\underline{C}H_2-CH_2$ ).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$ (ppm) 165.2 (C=O), 158.3 (ArO), 149.9 (ArO), 138.6, 133.5, 133.1, 130.1, 129.5, 128.5, 128.1, 127.7, 121.9, 114.8, 65.9, 32.0 (t,  $\underline{C}H_2-CF_2$ ,  $^3J_{C-F} = 22.1$  Hz), 29.0, 28.7, 22.7.  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$ (ppm) -80.8 (t,  $CF_3$ ,  $^3J_{FF} = 9.7$  Hz), -114.3 (m, 2F,  $CF_2-CH_2$ ), -121.9 (m, 2F), -122.8 (m, 2F), -123.4 (m, 2F), -126.1 (m, 2F). HRMS (ESI) calculated for  $C_{30}H_{23}F_{13}SO_3Na^+$ : 733.535 (found: 733.102).

**4'-[3-{(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio}propoxy]-(1,1'-biphenyl)-4-yl benzoate (5b)**. Yield: 86%.  $^1H$  NMR ( $CDCl_3$ ) 8.25 (d, 2H,  $J = 7.2$  Hz), 7.5-

7.7 (m, 7H), 7.28 (d, 4H,  $J = 8.7$  Hz), 7.0 (d, 2H,  $J = 8.7$  Hz), 4.15 (t, CH<sub>2</sub>O), 2.82 (m, 4H, CH<sub>2</sub>-S-CH<sub>2</sub>), 2.41 (m, 2H, CF<sub>2</sub>-CH<sub>2</sub>), 2,12 (quint., 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 165.2 (C=O), 158.3 (ArO), 149.9 (ArO), 138.6, 133.6, 133.1, 130.1, 129.5, 128.5, 128.1, 127.7, 121.9, 114.7, 65.9, 32.0 (t, CH<sub>2</sub>-CF<sub>2</sub>, <sup>3</sup>J<sub>C-F</sub> = 21.8 Hz), 29.0, 28.7, 22.7. <sup>19</sup>F NMR (CFCl<sub>3</sub>) δ(ppm) -80.7 (t, CF<sub>3</sub>, <sup>3</sup>J<sub>FF</sub> = 9.7 Hz), -114.3 (tm, 2F,  $J = 8.6$  Hz, CF<sub>2</sub>-CH<sub>2</sub>), 3F, CF<sub>3</sub>), -121.7 (m, 2F), -121.9 (m, 4F), -122.7 (m, 2F), -123.4 (m, 2F), -126.1 (m, 2F), HRMS calculated for C<sub>32</sub>H<sub>23</sub>F<sub>17</sub>S<sub>03</sub>Na<sup>+</sup>: 833.550 (found: 833.104).

**Appendix A. Supplementary data:** Supplementary data with this article (Transition temperatures, Xray diffraction data, molecular volumes, intercalation ratio data, along with <sup>1</sup>H-, <sup>13</sup>C- and <sup>19</sup>F-NMR spectra) can be found in the online version.

## References

- [1] G.W. Gray, *Mol. Cryst. Liq. Cryst.* 7 (1969) 127-151
- [2] M. Hird, K.J. Toyne, *Mol. Cryst. Liq. Cryst.* 323 (1998) 1-67
- [3] P. Kirsch, M. Bremer, *Angew. Chem. Int. Ed.* 39 (2000), 4216-4235
- [4] P. Kirsch, *F. Fluorine Chem.* 177 (2015) 29-36
- [5] F. Guittard, S. Geribaldi, *J. Fluorine Chem.* 107 (2001) 363-374
- [6] M. Hird, *Chem. Soc. Rev.* 26 (2007) 2070.
- [7] P. Kirsch, M. Lenges, A. Ruhl, F. Huber, R.D. Chambers, G. Sandford, *J. Fluorine Chem.* 128 (2007) 1221-1226.
- [8] F. Guittard, E. Taffin de Givenchy, S. Garibaldi, A. Cambon, *J. Fluorine Chem.* 100 (1999) 85-96.
- [9] C. Tschierske *Top. Curr. Chem.* 318 (2012) 1-108.
- [10] S. Pensec, F.G. Tournilhac, P. Bassoul, *J. Phys. II France* 6 (1996) 1597-1605.
- [11] R. Miethchen, M. Hein, *Carbohydrate Res.* 327 (2000) 169-183.
- [12] S. Hernández-Ainsa, J. Barberá, *J. Fluorine Chem.* 177 (2015) 37-45.
- [13] X. Cheng, M. Prehm, M. kumar Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske, *J. Am. Chem. Soc.* 125 (2003) 10977-10996
- [14] X.S. Cheng, S. Diele, C. Tschierske, *Angew. Chem. Int. Ed.* 39 (2000) 592-595
- [15] X. Li, L. Andruzzi, E. Chiellini, G. Galli, C.K. Ober, A. Hexemer, E.K. Kramer, D.A. Fischer, *Macromolecules*, 35 (2002) 8078-8087.
- [16] D. Lose, S. Diele, G. Pelzl, E. Dietzmann, W. Weissflog, *Liq; Cryst.* 24 (1998) 707-717.
- [17] F. Tournilhac, L.M. Blinov, J. Simon, S.V. Yablonsky, *Nature* 359 (1992) 621-623.
- [18] J.W. Brown, D.J. Byron, D.J. Harwood, R.C. Wilson, A.R. Tajbakhsh, *Mol. Cryst. Liq. Cryst.* 173 (1989), 121-140.
- [19] N.O. Brace, *J. Org Chem.* 27 (1962) 4491-4498.
- [20] N. Mekni, A. Hedhli, A. Baklouti, *J. Fluorine Chem.* 114 (2002) 43-46.
- [21] A. Khalfallah, N. Tounsi, A. Ayari, R. Oueslati, A. Hedhli, *J. Soc. Chim. Tunisie.* 13 (2011) 27-33.

- [22] H. Yoshino, S. Matzubara, K. Oshima, K. Matsumoto, R. Hagiwara, Y. Ito, *J. Fluorine Chem.* 125 (2004) 455-458.
- [23] N.O. Brace, J.E. van Elswyk, *J. Org. Chem.* 41 (1976) 766-771.
- [24] V. Círka, B. Améduri, B. Boutevin, O. Paleta, *J. Fluorine Chem.* 83 (1997) 151-158.
- [25] G. Foulard, T. Brigaud, C. Portella, *Tetrahedron* 52 (1996) 6187-6200.
- [26] B. Boutevin, Y. Hervaud, M. Nouri, *Eur. Polym. J.* 26 (1990) 877-882.
- [27] F. Moingeon, J. Roeser, P. Masson, F. Arnaud-Neu, S. Méry, *Chem Commun.* (2008) 1341-1343
- [28] A. Khalfallah, A. Ayari, B. Boughariou, A. Hedhli, *J. Incl. Phenom. Macrocycl. Chem.* 2010, 67, 1-6.
- [29] C de Gracia de Lux, B. Donnio, B. Heinrich, M.-P. Krafft, *Langmuir* 29 (2013) 5325-5336.
- [30] P.C. Hartmann, A. Collet, M. Viguiet, C. Blanc, *J. Fluorine Chem.* 125 (2004) 1909-1918.